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# Biphasic hydroformylation catalysis in ionic liquid media

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Dedicated to Prof. M.L.H. Green on the occasion of his retirement from the position of Head of the Inorganic Chemistry Department at Oxford University

### Abstract

The ionic liquids 1-butyl-3-methyl-imidazolium tetrafluoroborate ([bmim][BF4]), 1-butyl-3-methyl-imidazolium hexafluorophosphate ( $[bmim][PF_6]$ ) and 1,2-dimethyl-3-butyl-imidazolium hexafluorophospate ( $[bdmim][PF_6]$ ) were investigated as potential media for hydroformylation catalysis in a liquid-liquid biphase reaction environment. The study used the known rhodium/tppti\* (tppti\* = tri(*m*-sulfonyl) triphenyl phosphine 1,2-dimethyl-3-butyl-imidazolium salt) system as the catalyst and hexene-1 as the substrate, which enabled the produced heptanal to be conveniently isolated from the ionic liquid by phase separation. All catalyst evaluations were carried out in high-purity ionic liquids to avoid any decomposition of the catalyst, substrate and/or ionic liquid. The activity of the biphasic ionic liquid system containing the Rh/tppti\* catalyst was approximately one order of magnitude lower than that observed for the conventional Rh/PPh3 catalyst in toluene. The Rh/tppti\* catalyst system showed a decrease of activity in the semicontinuous hydroformylation of hexene-1 due to catalyst deactivation and/or metal loss. The n/i ratio of the produced heptanal only slightly increased after changing the Rh/P ratio from 1:3 to 1:100 in [bmim][PF<sub>6</sub>]. The loss of rhodium metal from the ionic liquid phases appears to be correlated to the solubility characteristics of the ionic liquid and the concentration of the aldehyde in the organic phase. In support of this theory, the ionic liquid  $[bmim][PF_6]$  gave the best results due to its very low miscibility with polar substances. A high-pressure NMR (HP-NMR) study revealed that the solution structure of  $HRh(^{13}CO)(tppts)_3$  (tppts = tri(*m*sulfonyl)triphenyl phosphine sodium salt) in [bmim][BF4] was similar to that of HRh(<sup>13</sup>CO)(PPh<sub>3</sub>)<sub>3</sub> in toluene-d<sup>8</sup>. The HP-NMR investigation at elevated syngas pressures showed that HRh(13CO)(tppts)<sub>3</sub> lies in equilibrium with HRh(13CO)<sub>2</sub>(tppts)<sub>2</sub>. © 2004 Elsevier Ltd. All rights reserved.

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### 1. Introduction

The separation of homogeneous hydroformylation catalysts from reaction mixtures has been a tremendous challenge and continues to be the focus of intense research [1]. Over the last three decades, several elegant approaches have been explored to overcome this limitation including aqueous [2] and fluorous biphase catalysis [3], reactions in supercritical media [4] and catalyst immobilization onto solid support materials [5]. Although some of these novel concepts have successfully been developed into commercial processes, like the Ruhr Chemie Rhône Poulenc Process used in the production of butyraldehyde [2], catalyst recovery continues to be one of the key issues of homogeneous catalysis.

More recently, ionic liquids have been used as alternative reaction media for homogeneous catalysis [6]. Based on their highly charged nature, ionic liquids are

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well suited for biphasic reactions with organic substrates. While the first hydroformylation reaction in an ionic liquid (at that time referred to as a molten salt) was performed by Parshall [7] as earlier as 1972, it was not until 1995 that Chauvin et. al. [8] used water-soluble phosphine ligands like the tri(*m*-sulfonyl)triphenyl phosphine sodium salt (tppts) [9] to retain active rhodium complexes in the ionic liquid phases and used them successfully in biphasic hydroformylation catalysis. Since then, a variety of different metal complexes have been investigated for liquid–liquid biphasic hydroformylation reactions in ionic liquid media [10].

As the production of aldehyde is one of the largest volume processes [11] in the chemical industry we have recently attempted to ascertain the viability of ionic liquids for hydroformylation reactions [12]. In this paper, we report our findings on the biphasic hydroformylation catalysis using conventional rhodium catalysts in ionic liquid media, which was encouraged by the initial report of Chauvin et. al. [8]. In this study we have investigated the reactivity of the hydroformylation catalyst HRh(CO)(P)<sub>3</sub> (P = phosphine ligand) in imidazolium based ionic liquid derivatives of tetrafluoroborate and hexafluorophosphate. In addition, we have complimented our investigation with a high-pressure NMR (HP-NMR) study of the reaction mixture containing the active rhodium species.

# 2. Experimental

### 2.1. General experimental details and materials

All operations were performed in a Vacuum Atmospheres or MBraun dry box under purified nitrogen or using Schlenk techniques under a nitrogen atmosphere. The following chemicals have been purchased from Aldrich and have been used as received: anhydrous heptane, anhydrous toluene, dichloromethane, hexene-1, 1-chlorobutane, 1-methyl-imidazol, 1,2-dimethyl-imidazol, Celite, alumina, activated carbon, sodium tetrafluoroborate, sodium hexafluorophosphate and potassium hexafluorophosphate. The following compounds have been purchased from Strem and have been used as received: tris(*m*-sulfonylphenyl)phosphine sodium salt (tppts) and  $Rh(CO)_2(acac)$  (acac = acetylacetonate). The gases CO/H<sub>2</sub> (1:1, UHP grade) and <sup>13</sup>CO (UHP grade) were purchased from BOC and MG industries, respectively. NMR spectra were recorded on a Varian Unity 400 spectrometer. Chemical shifts (ppm) were referenced to either an internal standard (e.g. tetramethylsilane) or an external standard (e.g. triphenylphoshite). HP-NMR experiments were performed using single-crystal sapphire NMR tubes [13]. Toluene-d<sub>8</sub> was purchased from Cambridge Isotopes and was degassed and dried over potassium metal. Gas chromatography samples were analyzed using a HP-5890 gas chromatograph with a 30 m Spb-1 capillary column, 0.25 mm i.d. and 0.25 mm film thickness and a HP-6890 GC/MS equipped with a 30 m HP-1 capillary column, 0.25 mm i.d. and 0.25 mm film thickness. Rhodium analyses were performed on an inductively coupled plasma–atomic emission spectrometer (ICP/AES), Jarrell-Ash Model 1100, with argon gas flow and torch alignment. The ICP/ AES instrument was calibrated with 10 ppm rhodium solution. Elemental analyses were performed by the Galbraith Laboratory.

### 2.2. Preparation of the ionic liquids

# 2.2.1. 1-Butyl-3-methyl-imidazolium tetrafluoroborate – [bmim][BF<sub>4</sub>]

A 500 ml round bottom flask was charged under N<sub>2</sub> with 95 g (0.54 mol) 1-butyl-3-methyl-imidazolium chloride [14] and 63 g (0.57 mol) sodium tetrafluoroborate in 250 ml of degassed water. After the reaction was stirred for 15 h at room temperature, the mixture was extracted with dichloromethane (3× 100 ml). The combined organic phases were dried over magnesium sulfate and filtered through a bed of activated carbon and alumina. After the removal of the volatile components under reduced pressure the ionic liquid [bmim][BF<sub>4</sub>] was obtained as a colorless liquid in 73% yield. Elemental analysis (%) calculated for C<sub>8</sub>H<sub>15</sub>N<sub>2</sub>BF<sub>4</sub>: C, 42.51; H, 6.69; N, 12.39. Found: C, 42.66; H, 7.12; N, 12.49%.

# 2.2.2. 1-Butyl-3-methyl-imidazolium hexafluorophosphate – [bmim][PF<sub>6</sub>]

A 1000 ml round bottom flask was charged under N<sub>2</sub> with 175 g (1.0 mol) 1-butyl-3-methyl-imidazolium chloride and 190 g (1.03 mol) potassium hexafluorophosphate in 400 ml degassed water. After the reaction was stirred for 15 h at room temperature, the mixture was extracted with dichloromethane (3× 200 ml). The combined organic phases were dried over magnesium sulfate and filtered through a bed of activated carbon and alumina. After the removal of the volatile components under reduced pressure the ionic liquid [bmim][PF<sub>6</sub>] was obtained as a colorless liquid in 80% yield. Elemental analysis (%) calculated for C<sub>8</sub>H<sub>15</sub>N<sub>2</sub>PF<sub>6</sub>: C, 33.81; H, 5.32; N, 9.86. Found: C, 33.92; H, 5.64; N, 9.72%.

# 2.2.3. 1,2-Dimethyl-3-butyl-imidazolium hexafluorophosphate – $[bdmim][PF_6]$

A 500 ml round bottom flask was charged under  $N_2$  with 56.6 g (0.3 mol) 1,2-dimethyl-3-butyl-imidazolium chloride and 55.4 g (0.33 mol) sodium hexafluorophosphate in 250 ml of degassed water. After the reaction was stirred for 15 h at 40 °C, the mixture was extracted with dichloromethane (3× 100 ml). The combined organic phases were dried over magnesium sulfate and filtered through a bed of activated carbon and alumina.

After the removal of the volatile components under reduced pressure the ionic liquid [bdmim][PF<sub>6</sub>] was obtained as a yellow-colored viscous liquid in 70% yield. Elemental analysis (%) calculated for  $C_9H_{17}N_2PF_6$ : C, 36.25; H, 5.75; N, 9.39. Found: C, 36.27; H, 5.83; N, 9.36%.

#### 2.3. HP-NMR investigation

A solution of 3 mg (0.013 mmol) Rh(CO)<sub>2</sub>(acac) and 43 mg (0.075 mmol) tppts in 2 ml of [bmim][BF<sub>4</sub>] containing 5 wt% of D<sub>2</sub>O was prepared under N<sub>2</sub> and charged into a sapphire NMR tube. The tube was placed into a safety shield container and pressurized to 60 psi with <sup>13</sup>CO/H<sub>2</sub> (1:1). To ensure the formation of HRh(CO)(tppts)<sub>3</sub> (**1a**), the tube was shaken at 60 °C for 1 h. After the pressure was released the <sup>31</sup>P{<sup>1</sup>H} and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded under 15 psi of <sup>13</sup>CO/H<sub>2</sub> (1:1), confirming the presence of **1a**. During the course of the HP-NMR investigation the tube was pressurize up to 2000 psi with <sup>13</sup>CO/H<sub>2</sub> (1:1) and further monitored by NMR spectroscopy.

### 2.4. Catalyst evaluation

# 2.4.1. General experimental details for hydroformylation reactions

In a typical experiment carried out in a 300 ml autoclave, catalyst solution was prepared from the ionic liquid, the rhodium precursor Rh(CO)<sub>2</sub>(acac) and the phosphine (tppti\*) stock solution. The mixture was charged into the reactor under nitrogen and the volatile components removed under reduced pressure  $(10^{-2})$ Torr). The reactor was then flushed and pressurized with  $CO/H_2$  (1:1) to ca. 150 psi. The run olefin was charged in a glovebox into a 100 ml injection bomb, which was then mounted into the feed line of the reactor. After the reactor was heated to the run temperature, the reaction was initiated by injecting the olefin into the reactor and the pressure adjusted up to 600 psi CO/H<sub>2</sub> (1:1). The pressure in the reactor was maintained constant by making up the consumed  $CO/H_2$  (1:1) from the PVT tank. The conversion was followed by recording the pressure drop in the PVT tank.

The apparent turnover frequency (TOF) used in the kinetic analysis is defined as the rate of olefin conversion by 1 mol of rhodium and is expressed as the moles of olefin converted to aldehyde per moles of rhodium per minute:  $TOF = \{(dn_{olefin}/dt)_t\}/n_{Rh}$ . The rate of olefin conversion is calculated from the PVT pressure versus time data. The values for the TOF were determined during the initial 30 min of the gas consumption which corresponds to an approximate olefin conversion of between 10% and 20%.

For the semicontinuous hydroformylation of hexene-1, the autoclave was fitted with a dip leg that reached ca. 5 mm above the heavier ionic liquid phase. At the end of each run, the reactor was cooled to 15 °C, the stirrer was then stopped and the supernatant product phase was removed from the reactor. For metal balance, the concentration of Rh in each product was determined by ICP-AES. For each consecutive run, the catalyst phase was rapidly heated to the reaction temperature and a fresh charge of hexene-1 was injected to initiate the reaction.

For the rhodium analysis, aliquots of the product were ashed with 1 ml of concentrated  $H_2SO_4$  and left in a furnace at 530 °C for at least 8 h. The remaining residue was fused with 0.5 g  $K_2S_2O_7$ . The resulting mixture was solubilized in a 20%  $H_2SO_4$  solution. The rhodium analysis was performed using ICP/AES instrumentation with matrix-matched standards (3.35 RSD).

# 2.4.2. Preparation of the tri(m-sulfonyl)triphenylphosphine 1,2-dimethyl-3-butyl-imidazolium salt (tppti\*)

A 50 ml round bottom flask was charged under  $N_2$  with 10.1 g (0.017 mol) tri(*m*-sulfonyl)triphenyl phosphine sodium salt (tppts) and 10.0 g (0.053 mol) 1,2-dimethyl-3-butyl-imidazolium chloride in acetonitrile (25 ml). After the reaction was stirred for 3 days at room temperature, the mixture was filtered through a bed of Celite. The filter aid was further washed with acetonitrile (30 ml). The resulting filtrates were combined and used as a stock solution for the tppti\* ligand.

# 2.4.3. Biphasic Hydroformylation using $Rh(CO)_2(acac)$ / tppti\* in [bmim][BF<sub>4</sub>] (Table 2|Entries 1–10)

A mixture of 26 mg (0.1 mmol) Rh(CO)<sub>2</sub>(acac) and 3.2 ml (1.0 mmol) tppti<sup>\*</sup> (stock solution) in 60 ml [bmim][BF<sub>4</sub>] was stirred at room temperature. After 1 h the yellow solution was charged into a 300 ml autoclave and the volatile components removed under reduced pressure ( $10^{-2}$  Torr). The reactor was pressurized with CO/H<sub>2</sub> (1:1) to ca. 150 psi. After the reactor was heated to 100 °C, the reaction was initiated by injecting 61 g (720 mmol) hexene-1 with 300 psi of CO/H<sub>2</sub> (1:1) into the reactor. Due to the extended induction period after the first recycle run the reactor pressure was increased to 600 psi. All further runs were conducted at this run pressure.

# 2.4.4. Reaction of $Rh(CO)_2(acac)$ | tppti\* in [bmim] [PF<sub>6</sub>] (Table 2|Entries 11–20)

A mixture of 26 mg (0.1 mmol) Rh(CO)<sub>2</sub>(acac) and 3.2 ml (1.0 mmol) tppti\* stock solution in 60 ml [bmim][PF<sub>6</sub>] was stirred at room temperature. After 1 h the yellow solution was charged into a 300 ml autoclave and the volatile components removed under reduced pressure ( $10^{-2}$  Torr). The reactor was pressurized with CO/H<sub>2</sub> (1:1) to ca. 300 psi. After the reactor was heated to 100 °C, the reaction was initiated by injecting 26 g (307 mmol) hexene-1 in 38 ml of heptane with 600 psi of CO/H<sub>2</sub> (1:1) into the reactor. The autoclave studies using Rh/P ratios of 1:3 and 1:100 (Table 1/Entries 28, 29) were carried out under the identical conditions.

# 2.4.5. Reaction of $Rh(CO)_2(acac)/tppti^*$ in $[bdmim][PF_6]$ (Table 2/Entries 21–27)

A mixture of 26 mg (0.1 mmol) Rh(CO)<sub>2</sub>(acac) and 3.2 ml (1.0 mmol) tppti\* stock solution in 60 ml [bdmim][PF<sub>6</sub>] was stirred at room temperature. After 1 h the yellow solution was charged into a 300 ml autoclave and the volatile components removed under reduced pressure ( $10^{-2}$  Torr). The reactor was pressurized with CO/H<sub>2</sub> (1:1) to ca. 300 psi. After the reactor was heated to 100 °C, the reaction was initiated by injecting 25 g (295 mmol) hexene-1 in 38 ml of heptane with 600 psi of CO/H<sub>2</sub> (1:1) into the reactor.

# 2.4.6. Reaction of $Rh(CO)_2(acac)/PPh_3$ in toluene (Table 2/Entries 30)

A mixture of 6.5 mg (0.025 mmol) Rh(CO)<sub>2</sub>(acac) and 66 mg (0.25 mmol) PPh<sub>3</sub> was dissolved in 60 ml toluene and stirred at room temperature. The yellow solution was charged into a 300 ml autoclave and pressurized with CO/H<sub>2</sub> (1:1) to ca. 300 psi. After the reactor was heated to 100 °C, the reaction was initiated by injecting 61 g (720 mmol) hexene-1 at 600 psi of CO/ H<sub>2</sub> (1:1) into the reactor.

# 3. Results and discussion

### 3.1. Catalyst screening in HP-NMR tubes

We started our study by investigating hydroformylation reactions in ionic liquids under different reaction environments. This initial study was conveniently carried out in sapphire NMR tubes which enabled us to visually follow phase separations and determine solubility limitations. In this investigation the well-established catalyst precursor Rh(CO)<sub>2</sub>(acac) (acac = acetylacetonate) was dissolved in the ionic liquid [bmim][PF<sub>6</sub>] with (a) no phosphine, (b) triphenylphoshine (PPh<sub>3</sub>) and (c) the tri(*m*-sulfonyl)triphenyl phosphine 1,2-dimethyl-3-butyl-imidazolium salt (tppti\*). The resulting solutions were loaded into HP-NMR tubes and treated with the substrate hexene-1. The organic phases showed a lower density and therefore generated the top layers while the ionic liquids were confirmed as the bottom phases. After the reaction mixtures were pressurized with CO/  $H_2$  (1:1) to 600 psi the tubes were shaken at 100 °C. The reaction was stopped after 3 h and the tubes were cooled to room temperature. During this time the organic components separated from the ionic liquid phases. While the reaction without a ligand and with the ligand tppti\* gave colorless organic phases (upper layer), the experiment using the ligand PPh<sub>3</sub> showed a strong yellow coloration of the organic phase. As the complex HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> has a yellow coloration in solution, it is a good indication that a substantial amount of the catalyst migrated during the reaction from the ionic liquid into the organic layer. After the pressure was released from the sapphire NMR tubes the organic products were analyzed for their composition and rhodium metal content. In all three cases a significant amount of aldehyde was produced. Concerning the issue of metal leaching, only the reaction mixture using tppti\* exhibited a negligible amount of rhodium loss from the ionic liquid, while the other ionic liquid phases suffered from a significant amount of metal loss. On the basis of these initial experiments, the approach of using highly charged ligands like for example tppti\* seemed to be a viable method for retaining a rhodium catalyst in an ionic liquid.

One interesting result was that although the organic phase in the reaction using no ligand was colorless, a large amount of rhodium metal was found in this phase. Furthermore, a significant amount of aldehyde was produced in this reaction which indicates that species other than HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> are active for the hydroformylation of the olefin. Most likely the aldehyde was produced by rhodium-hydrido-carbonyl complexes which tend to form under hydroformylation reaction conditions in the absence of suitable ligands and have been observed in other areas of oxo-catalysis [15]. For this reason, all of our produced aldehyde samples were analyzed for their rhodium content.

Another potentially complicating factor in the evaluation of these ionic liquid media for hydroformylation catalysis are the solubility limitations of the highly charged phosphine ligand. In an early HP-NMR study

Table 1

Selected  ${}^{31}P{}^{1}H{}$  and  ${}^{13}C{}^{1}H{}$  NMR data for the Rh/P catalyst system (P = PPh<sub>3</sub>, tppts) in [bmim][BF<sub>4</sub>], toluene-d<sup>8</sup> and water under varying pressure conditions

Solvent	Pressure <sup>a</sup> (psi)	Complex	$\delta(^{13}CO)$ (ppm)	$J_{\rm C-Rh}$ (Hz)	$\delta(^{31}PR_3)$ (ppm)	$J_{\rm P-Rh}$ (Hz)	
[bmim][BF <sub>4</sub> ]	15	HRh( <sup>13</sup> CO)(tppts) <sub>3</sub>	195.2	62	32.2	126	
[bmim][BF <sub>4</sub> ]	2000	HRh( <sup>13</sup> CO) <sub>2</sub> (tppts) <sub>2</sub>	199.2	61	39.1	137	
Toluene-d <sup>8</sup>	15	$HRh(^{13}CO)(PPh_3)_3$	206.6	62	37.8	156	
Toluene-d <sup>8</sup>	1000	HRh( <sup>13</sup> CO) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	199.9	63	33.8	139	
H <sub>2</sub> O	15/3000	HRh( <sup>13</sup> CO)(tppts) <sub>3</sub>	204.9	55	42.8	156	

<sup>a</sup> Syngas <sup>13</sup>CO/H<sub>2</sub> (1:1).

we realized that not all the water-soluble phosphine ligands like the tri(*m*-sulfonyl)triphenyl phosphine sodium salt (tppts) are also automatically soluble in ionic liquid phases. Although the ligand showed excellent solubility in water, it only dissolved in [bmim][BF<sub>4</sub>] after the addition of small amounts of water. Even more surprising was the fact that it has negligible solubility in [bmim][PF<sub>6</sub>]. To verify this low solubility we charged  $[bmim][PF_6]$  together with  $Rh(CO)_2(acac)$  and tppts (Rh/P ratio 1:10) into a HP-NMR tube. The resulting mixture was stepwise pressurized with  $CO/H_2$  (1:1) to 2000 psi and heated up to 150 °C. During this process we recorded the  ${}^{31}P{}^{1}H{}$  NMR spectra of the solution and were unable to detect neither coordinated nor free tppts. On the basis of this investigation we synthesized a more soluble derivative of the phoshine ligand. After exchanging the sodium cation of tppts with 1,2-dimethyl-3-butyl-imidazolium we prepared the tri(m-sulfonvl)triphenvl phosphine 1,2-dimethyl-3-butylimidazolium salt (tppti\*) which showed good solubility characteristics in [bmim][PF<sub>6</sub>] and was used in all the following catalyst evaluations.



Scheme 1. Initial steps of the hydroformylation mechanism.



Despite the fact that the mechanism for hydroformylation catalysis is well established in organic [16] and aqueous [17] solvents, we wanted to study the active rhodium species in an ionic liquid environment (Scheme 1). To build upon a recent study focused on the in situ investigation of the rhodium-sulfoxantphos hydroformylation catalyst [18] in ionic liquids, we set out to investigate the rhodium-tppts catalyst system using HP-NMR techniques. In these experiments a mixture consisting of Rh(CO)<sub>2</sub>(acac), tppts (Rh/P ratio 1:6) and [bmim][BF<sub>4</sub>] was pressurized with 60 psi of <sup>13</sup>CO/  $H_2$  (1:1) in a sapphire NMR tube. To ensure the formation of the catalyst species  $HRh(^{13}CO)(tppts)_3$  (1a) the solution was shaken at 60 °C for 1 h. After the pressure was released the  ${}^{31}P{}^{1}H{}$  and  ${}^{13}C{}^{1}H{}$  NMR spectra were recorded (Fig. 1). The  ${}^{31}P{}^{1}H$  NMR spectrum of the catalyst solution showed a doublet at 32.2 ppm for the rhodium bound tppts ligand and a minor resonance at 29.1 ppm for the uncoordinated phosphine oxide species tri(m-sulfonyl)triphenylphosphine oxide trisodium (tppts-oxide) (Table 1). A strong signal at -3.7 ppm was apparent for uncoordinated tppts. The corresponding  ${}^{13}C{}^{1}H$  NMR spectrum of the catalyst solution showed a doublet at 195.2 ppm for the metal coordinated carbon monoxide. For a better comparison we also investigated  $HRh(^{13}CO)(PPh_3)_3$  **1b** in toluene-d<sup>8</sup> under  ${}^{13}$ CO/H<sub>2</sub> (1:1) pressure. Furthermore, we used the HP-NMR study by Horváth et. al. [17] for hydroformylation catalysis in aqueous phases as a reference. Thus, similar to the results of our catalyst investigation in  $[bmim][BF_4]$ , the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **1b** in tolu-



Fig. 1. High-pressure NMR investigation of a rhodium hydroformylation catalyst in the ionic liquid [bmim][BF<sub>4</sub>] at 15 and 2000 psi <sup>13</sup>CO/H<sub>2</sub> (1:1).

#### <sup>31</sup>P{<sup>1</sup>H}-HP-NMR

ene-d<sup>8</sup> showed a doublet at 37.8 ppm for the rhodium bound PPh<sub>3</sub> (Table 1). The corresponding <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of the solution exhibited a doublet at 206.6 ppm for the coordinated carbon monoxide ligand. On the basis of these spectroscopic results it can be assumed that the structure of  $HRh(^{13}CO)(tppts)_3$  in [bmim][BF<sub>4</sub>] is very similar to that of  $HRh(^{13}CO)(PPh_3)_3$  in toluene-d<sup>8</sup>.

Following this we studied the rhodium catalyst in ionic liquids under elevated syngas pressure. Mechanistic of  $HRh(^{13}CO)(PPh_3)_3$ studies [16] (1b)and  $HRh(^{13}CO)_2(PPh_3)_2$  (2b) in toluene have suggested the presence of two coordinatively unsaturated catalyst  $\{HRh(^{13}CO)(PPh_3)_2\}$ intermediates (3b)and  $\{HRh(^{13}CO)_2(PPh_3)\}$  (4b). While both of these species are responsible for the production of aldehyde, it is believed that the normal to iso ratio (n/i) of the aldehyde is largely controlled by the competitive reactions of the olefin with the species 3b and 4b resulting in high or low n/i ratios, respectively. Although we are not able to record the NMR spectra of the reactive intermediates 3b and 4b, we can observe the resting state of the catalyst in form of complexes 1b and 2b. As the equilibrium between these two complexes is strongly pressure dependent, complex 1b can readily be converted into complex **2b** at a  ${}^{13}$ CO/H<sub>2</sub> (1:1) pressure of less than 300 psi in a toluene-d<sup>8</sup> solution. In contrast, the investigation of HRh(<sup>13</sup>CO)(tppts)<sub>3</sub> 1a in an aqueous solution showed that applied pressures of  ${}^{13}CO/H_2$  (1:1) as high as 3000 psi did not lead to the formation of HRh(<sup>13</sup>CO)<sub>2</sub>(tppts)<sub>2</sub> (2a) [17]. Based on this information, we pressurised the complex 1a in [bmim][BF<sub>4</sub>] stepwise with <sup>13</sup>CO/H<sub>2</sub> and recorded the corresponding NMR spectra. The increasing pressure resulted in the formation of new doublets in both the  ${}^{31}P{}^{1}H$  NMR spectrum (39.1 ppm) and the  ${}^{13}C{}^{1}H{}$  NMR spectrum (199.2 ppm). By going to higher syngas pressures, the intensities of the NMR resonances for 1a continued to decrease. Finally, at a <sup>13</sup>CO/H<sub>2</sub> pressure of 2000 psi the NMR signals for 1a disappeared. We believe that the newly formed species in [bmim][BF4] has the solution structure of HRh(<sup>13</sup>CO)<sub>2</sub>(tppts)<sub>2</sub> (2a) and corresponds to **2b** which has been observed in toluene- $d^8$ under elevated pressure. After the ionic liquid sample was depressurized the NMR resonances of 1a were detected again. It is interesting to note that the NMR signal of the high-pressure species 2a in [bmim][BF<sub>4</sub>] exhibited a down field shift, while the related complex **2b** in toluene-d<sup>8</sup> showed an upfield shift for the corresponding resonances. Although the ionic liquid and toluene samples showed the formation of the high-pressure rhodium species 2a and 2b, the chemical environment on the metal center in  $[bmim][BF_4]$  seems to be different to that in the toluene-d<sup>8</sup>. Finally, it should be noted that the in situ formation of 1a in [bmim][BF<sub>4</sub>] can be accompanied by a series of side reactions. Although it was possible to suppress most of the side reactions through the use of high-purity ionic liquids, we did sometimes observe the formation of unknown species during the investigation of 1a in ionic liquids.

### 3.3. Preparation of high-purity ionic liquids

In addition to being important for catalyst lifetime, we also discovered that the purity of the ionic liquid is critical for the stability of the ionic liquid phase itself. In several biphasic hydroformylation experiments we observed the partial decomposition of [bmim][BF<sub>4</sub>] and [bmim][PF<sub>6</sub>]. After carefully analyzing the purity of these ionic liquids we found that trace amounts of acid were responsible for their decomposition. For this reason, we have used a synthesis procedure which produces high-purity ionic liquids [14]. In our synthesis 1-butyl-3-methyl-imidazolium chloride and 1,2-dimethyl-3-butyl-imidazolium chloride were either treated with NaBF<sub>4</sub> or KPF<sub>6</sub> giving [bmim][BF<sub>4</sub>], [bmim][PF<sub>6</sub>] and [bdmim][PF<sub>6</sub>], respectively. The reactions were carried out in water followed by extraction with dichloromethane. The work-up procedure involved the filtration of the extract through a bed of activated carbon and alumina which produced high-purity ionic liquids after the removal of the solvent. The ionic liquids prepared via this route showed a neutral pH value and did not suffer from any substantial decomposition during hydroformylation reactions.

# 3.4. Evaluation of biphasic hydroformylation catalysis using ionic liquid phases

As a control experiment in the beginning of our study we investigated the reactivity of Rh(CO)<sub>2</sub>(acac) in [bmim][PF<sub>6</sub>] without a ligand for the hydroformylation of hexene-1. The formed catalyst species produced C7aldehyde with a TOF between 21 and  $2 \text{ min}^{-1}$  and showed an n/i ratio for the aldehyde of 0.5–1.5 in the five respective runs. The low *n/i* ratio between 0.5 and 1.0 for the produced aldehyde is typically observed for rhodium catalysts in the absence of any coordinating ligand [15]. Typically under these reaction conditions, as mentioned earlier, rhodium forms an active rhodium-hydrido-carbonyl complex which readily converts olefin to aldehyde. The active species has no charge and dissolves preferentially in the organic phase. As a result, a substantial amount of the rhodium metal leaches from the ionic liquid into the organic layer. The loss of metal in our control experiment was also confirmed by rhodium metal analysis of the isolated product phases. After the first catalyst run an amount of 119 ppm of rhodium metal was found in the product phase. This amount corresponded to almost 75% of the initial rhodium charge to the reactor. Further runs showed continuous leaching of the metal until >90% of the initial rhodium charge was removed with the product phase. Corresponding to the loss of active metal species, the conversion of olefin was significantly reduced after every consecutive run. It is therefore not viable to run hydroformylation reactions in ionic liquids with rhodium catalysts which cannot be sufficiently retained in the ionic layer.

Our next investigation focused on the evaluation of Rh(CO)<sub>2</sub>(acac) with tppti\* in [bmim][BF<sub>4</sub>] (Fig. 2/Table 2/Entries 1-10). The initial two runs (Entries 1 and 2) were carried out at a  $CO/H_2$  (1:1) pressure of 300 psi. After we observed an extended induction period of 450 minutes in the first recycle we increased the reactor pressure to 600 psi  $CO/H_2$  (1:1) for all of the consecutive runs. The activity of the catalyst decreased in the following eight runs (Entries 3-10) with their TOF values decreasing from 14 to  $4 \text{ min}^{-1}$ . The *n/i* ratio of the aldehyde remained between 2.6 and 2.1. This ratio is typically observed for a rhodium based hydroformylation catalyst in the presence of a coordinating phosphine ligand (Rh/P ratio 1:10). The analysis of the resulting organic products revealed the presence of low amounts of soluble rhodium species. During the 10 runs almost 10% of the total rhodium charged was removed from the reactor with the product phase. Although the rhodium leaching contributed towards the drop in activity, other catalyst deactivation processes like the formation of rhodium carbonyl clusters are most likely the reason

Fig. 2. TOF for biphasic hydroformylation reactions in different ionic liquid phases and rhodium metal content in the reactor during recycle runs.

for the loss in activity. The rhodium leaching from the ionic liquid phase into the organic layer may be associated with the solubility characteristics of [bmim][BF<sub>4</sub>]. The ionic liquid has the ability to readily dissolve in water and other polar solvents. Depending on the aldehyde content in the product phase, small amounts of ionic liquid and rhodium complex can become soluble and leach into the organic layer. In one of our investigations (Entry 3) 2.7 ppm rhodium metal was detected in the organic phase at an aldehyde content of 61%. However, when the aldehyde level in the product phase was only 21% the amount of rhodium leaching was reduced to only 0.3 ppm (Entry 10). This trend indicated that the increasing polarity of the organic phase is partially responsible for the metal loss from the ionic liquid phase.

The next investigation focused on the evaluation of  $[\text{bmim}][\text{PF}_6]$ . All reactions were carried out at 600 psi CO/H<sub>2</sub> (1:1) and 100 °C using Rh(CO)<sub>2</sub>(acac) and tppti\* (Rh/P ratio of 1:10) (Entries 11–20). The TOF values of the catalyst system decreased over the course of the investigation from 70 to 23 min<sup>-1</sup>. Again the *n/i* ratios of the produced aldehydes were observed from 2.6 to 1.8, supporting a phosphine-stabilized rhodium center as the catalytically active species. Although the initial rhodium retention was better than in [bmim][BF<sub>4</sub>], after the 6th recycle run the metal leaching became more prominent and surpassed the values obtained for the [bmim][BF<sub>4</sub>] system.

To investigate the impact of a changing metal to phosphine ratio we also investigated the [bmim][PF<sub>6</sub>] ionic liquid system with a Rh/P ratio of 1:3 and 1:100. As expected the TOF for the reaction carried out with a lower amount of phosphine ligand (1:3) was slightly increased to 75 min<sup>-1</sup> (Entry 28), while the TOF for the catalysis with the higher loading (1:100) was reduced to 30 min<sup>-1</sup> (Entry 29). Under both sets of reaction conditions the *n/i* ratios remained unchanged at 2.5 and 2.6. However, the higher amount of phosphine ligand helped to better retain the rhodium catalyst and reduced the metal loss to levels below the detection limit.

To broaden the scope of the studied ionic liquids we also investigated [bdmim][PF<sub>6</sub>] (Entries 21–27). Although the TOF values were slightly higher than those obtained for [bmim][BF<sub>4</sub>], ranging from 37 to 3 min<sup>-1</sup>, the rhodium leaching was significantly increased. This may indicate that the less polar cation is partially responsible for the higher rhodium loss. Furthermore, the catalyst system showed a drastically reduced activity after the 5th recycle run and we concluded the campaign after the 7th run due to low activity.

In our final study we investigated the conventional homogeneous rhodium catalyst under similar reaction conditions. The reaction was carried out in toluene using  $Rh(CO)_2(acac)$  together with PPh<sub>3</sub> (Rh/P ratio of 1:10). The homogeneous catalyst in a monophasic system

Table 2	
Evaluation of hydroformylation reactions in io	nic liquid media

Entry	Cycle <sup>a</sup>	Ionic liquid <sup>b</sup>	P <sup>c</sup> /Rh ratio	Rh reactor (µmol)	Rh product (ppm)	Time <sup>d</sup> (min)	Induct. (min)	TOF <sup>e</sup> (min <sup>-1</sup> )	n/i	Selectivity (%)		
										$1 - C_{6}^{=}$	Ald.	Iso. <sup>f</sup>
1	1 <sup>g</sup>	[bmim][BF <sub>4</sub> ]	10	100.00	4.1	230	40	23	2.2	5	58	37
2	$2^{g}$	[bmim][BF <sub>4</sub> ]	10	97.79	1.9	700	450	9	1.9	9	54	37
3	3	[bmim][BF <sub>4</sub> ]	10	96.51	2.7	330	35	14	2.2	4	61	34
4	4	[bmim][BF <sub>4</sub> ]	10	94.62	1.3	255	0	14	2.4	29	46	25
5	5	[bmim][BF <sub>4</sub> ]	10	93.75	1.0	265	0	13	2.1	28	47	25
6	6	[bmim][BF <sub>4</sub> ]	10	93.07	0.8	360	0	11	2.5	32	44	24
7	7	[bmim][BF <sub>4</sub> ]	10	92.54	0.3	410	0	9	2.5	39	39	22
8	8	[bmim][BF <sub>4</sub> ]	10	92.34	0.5	365	0	8	2.5	47	34	19
9	9	[bmim][BF <sub>4</sub> ]	10	92.03	0.4	310	0	7	2.6	55	30	15
10	10	[bmim][BF <sub>4</sub> ]	10	91.79	0.3	275	0	4	2.6	66	21	13
11	1	[bmim][PF <sub>6</sub> ]	10	100.00	0.7	100	12	70	2.6	32	63	5
12	2	[bmim][PF <sub>6</sub> ]	10	99.59	1.4	120	26	68	2.5	10	73	17
13	3	[bmim][PF <sub>6</sub> ]	10	98.69	1.8	100	13	68	2.4	8	67	25
14	4	[bmim][PF <sub>6</sub> ]	10	97.77	1.7	100	19	61	2.3	5	62	33
15	5	[bmim][PF <sub>6</sub> ]	10	96.57	3.9	120	18	52	2.3	8	55	37
16	6	[bmim][PF <sub>6</sub> ]	10	93.87	1.9	265	25	44	1.9	1	59	40
17	7	[bmim][PF <sub>6</sub> ]	10	92.57	2.2	240	28	35	1.9	1	54	45
18	8	[bmim][PF <sub>6</sub> ]	10	91.07	2.9	300	41	32	1.8	1	52	47
19	9	[bmim][PF <sub>6</sub> ]	10	89.17	3.9	300	50	26	1.8	1	49	50
20	10	[bmim][PF <sub>6</sub> ]	10	86.57	3.7	300	75	23	1.9	2	44	54
21	1	[bdmim][PF <sub>6</sub> ]	10	100.00	2.3	180	20	37	2.3	4	37	59
22	2	[bdmim][PF <sub>6</sub> ]	10	98.5	2.2	180	20	37	2.2	5	57	38
23	3	[bdmim][PF <sub>6</sub> ]	10	97.1	2.5	210	50	33	2.2	8	53	40
24	4	[bdmim][PF <sub>6</sub> ]	10	95.4	2.7	180	35	28	2.3	13	45	42
25	5	[bdmim][PF <sub>6</sub> ]	10	93.6	2.9	250	50	20	2.3	9	41	50
26	6	[bdmim][PF <sub>6</sub> ]	10	91.7	3.2	360	105	12	2.4	14	39	47
27	7	[bdmim][PF <sub>6</sub> ]	10	89.6	2.1	500	250	3	2.6	49	17	34
28	1	[bmim][PF <sub>6</sub> ]	3	100	0.68	150	60	75	2.5	2	81	17
29	1	[bmim][PF <sub>6</sub> ]	100	100	0.02	200	13	30	2.6	9	87	4
30 <sup>i</sup>	1	Toluene	10	25.0	_	120	0	400	2.6	2	95	3

<sup>a</sup> All reactions were carried out in a 300 ml autoclave (2200 rpms) at 100 °C and 600 psi (CO/H<sub>2</sub> ratio 1:1). <sup>b</sup> Ionic liquid [bmim][BF<sub>4</sub>] 1-butyl-3-methyl-imidazolium tetrafluoroborate, [bmim][PF<sub>6</sub>] 1-butyl-3-methyl-imidazolium hexafluorophosphate and [bdmim][PF<sub>6</sub>] 1,2-dimethyl-3-butyl-imidazolium hexafluorophosphate.

<sup>c</sup> Phosphine ligand tri(*m*-sulfonyl)triphenylphosphine tris(1,2-dimethyl-3-butyl-imidazolium) salt (tppti\*). <sup>d</sup> Full reaction time (including induction period).

<sup>e</sup> TOF defined as mol(aldehyde) per mol(rhodium) per minute (determined during the initial 30 min of gas consumption).

<sup>f</sup> Isomerized  $1 - C_6^=$  to  $2 - C_6^=$  and  $3 - C_6^=$ .

<sup>g</sup> Reactor pressure at 300 psi.

<sup>i</sup> Run ligand – triphenylphosphine.

exhibited a significantly higher TOF value of 400 min<sup>-1</sup> with an n/i ratio of 2.6 for the produced aldehyde. For comparison the best TOF values obtained for any of the biphasic hydroformylation runs in ionic liquids ranged between 70 and 75 min<sup>-1</sup> under comparable reaction conditions. Finally the homogeneous catalyst system showed a significantly higher reactivity, however, the biphasic ionic liquid catalyst systems offer the possibility of convenient product separation and easy catalyst recovery.

#### 4. Conclusion

The ionic liquids  $[bmim][BF_4]$ ,  $[bmim][PF_6]$  and  $[bdmim][PF_6]$  were successfully used for the immobilization of rhodium based hydroformylation catalysts and have been evaluated for the production of aldehyde in a liquid-liquid biphase environment. The purity of the ionic liquids was strictly monitored to avoid any decomposition of the catalyst, substrate and/or ionic liquid. A complimentary HP-NMR study confirmed that the solution structure of HRh(<sup>13</sup>CO)(tppts)<sub>3</sub> (1a) in [bmim][BF<sub>4</sub>] is similar to that of HRh(<sup>13</sup>CO)(PPh<sub>3</sub>)<sub>3</sub> (1b) in toluened<sup>8</sup>. Furthermore, the NMR investigation at elevated syngas pressures showed that 1a lies in equilibrium with the high-pressure species HRh(<sup>13</sup>CO)<sub>2</sub>(tppts)<sub>2</sub> (2a). As expected the activity of the biphasic ionic liquid system containing the Rh/tppti\* catalyst is approximately one order of magnitude lower than the conventional Rh/ PPh<sub>3</sub> catalyst in toluene. The Rh/tppti\* catalyst system showed a decrease of activity in the semicontinuous hydroformylation of hexene-1 due to catalyst deactivation and/or metal loss. The *n/i* ratio of the produced heptanal only slightly increased after changing the Rh/P ratio from 1:3 to 1:100 in [bmim][PF<sub>6</sub>]. The loss of rhodium metal from the ionic liquid phases seemed to be dependent on the solubility characteristics of the ionic liquid and on the concentration of the aldehyde in the organic phase. In this respect, the ionic liquid  $[bmim][PF_6]$  was preferred due to its very low miscibility with polar substances. Although ionic liquids offer tremendous opportunities for the development of novel separation technologies, further progress will be necessary to fully establish their potential as a large-volume reaction medium.

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