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Hydroformylation of 1-hexene with rhodium in non-aqueous ionic liquids : how to design the solvent and the ligand to the reaction

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A wide range of ionic liquids based on imidazolium and pyrrolidinium cations and weakly coordinating anions proved to be efficient solvents for the biphasic rhodium catalyzed hydroformylation of 1-hexene; the reaction rate and regioselectivity, and the retention of the rhodium can be optimized by fitting the nature of the anions and cations of the ionic liquid and the modified phosphite or phosphine ligands.

Ionic liquids are good solvents for transition-metal complexes in many homogeneously catalyzed reactions, *e.g.* olefin hydrogenation, hydroformylation, oligomerization and Pd mediated carbon–carbon coupling reactions.[1] In many cases the reaction products are very weakly soluble in the ionic phase so that the catalyst can be separated by simple decantation and recycled. The aqueous two-phase catalysis concept, which has been already applied industrially for propene hydroformylation,[2] can then be extended to substrates and ligands that are poorly soluble or non stable in water. Higher olefin Rh-hydroformylation has been performed using different 1-butyl-3-methylimidazolium room-temperature liquid salts as solvents, in the presence of phosphine ligands. The main difficulty is to immobilize the rhodium catalyst in the ionic liquid phase while maintaining its activity and selectivity. A solution is to modify the neutral phosphine ligands with ionic groups.[3] Thanks to their chemical and physical versatility,[4] ionic liquids can be specially designed to fit with the ligand and the operating conditions that provide the best performances in catalysis.

In this communication, for the first time we report the effect of the nature of the cations and anions of the ionic liquids on the Rh-catalyzed hydroformylation of 1-hexene. We also provide our preliminary study on the performances of different phosphorus ligand–ionic liquid systems.

We have prepared a wide range of ionic liquids by varying the nature of the cation *e.g.* 1,3-dialkylimidazolium, 1,2,3-trialkylimidazolium and *N,N*-dialkylpyrrolidinium and the nature of the anion *e.g.* BF_4^-, PF_6^-, $CF_3CO_2^-$, $CF_3SO_3^-$ (OTf^-) and $N(CF_3SO_2)_2^-$ (NTf_2^-). The BF_4^-, NTf_2^- and PF_6^- ionic liquids were prepared by anion exchange starting from imidazolium or pyrrolidinium chloride. The $CF_3SO_3^-$ and $CF_3CO_2^-$ salts were prepared by direct methylation of 1-alkylimidazole or 1-alkylpyrrolidine with the corresponding methyl esters.[5] We have measured the solubility of 1-hexene in these ionic liquids (Fig. 1). For a given anion, *e.g.* $CF_3CO_2^-$, the solubility of 1-hexene increases upon increasing the length of the alkyl chain of the 1,3-dialkylimidazolium *e.g.* 1-butyl-3-methylimidazolium (BMI^+) *vs.* 1-hexyl-3-methylimidazolium (HMI^+). Methylation of the C(2) atom of the imidazolium ring tends to decrease the solubility of 1-hexene *e.g.* 1-butyl-2,3-dimethylimidazolium $BDMI^+NTf_2^-$ *vs.* $BMI^+NTf_2^-$. No significant differences are observed by changing the 1-butyl-3-methylimidazolium cation for *N,N*-butylmethylpyrrolidinium (BMP^+). For a same cation, *e.g.* BMI^+, the solubility of 1-hexene increases as follows: $BF_4^- < PF_6^- < OTf^- < CF_3CO_2^- < NTf_2^-$.

In a first series of experiments, we performed 1-hexene hydroformylation using these different ionic liquids as solvents for the $Rh(CO)_2(acac)$ precursor associated with the sodium salt of monosulfonated triphenylphosphine (TPPMS) (Fig. 1). The results reveal that there is a correlation between the reaction rates (TOF min^{-1}) and the solubility of 1-hexene in ionic

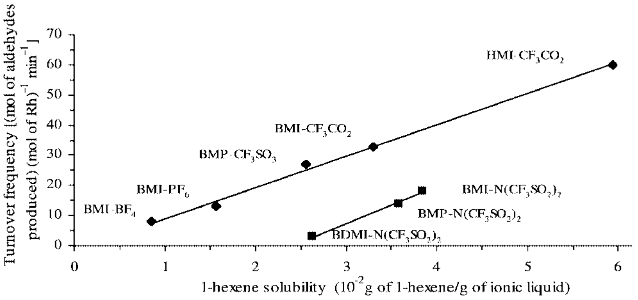
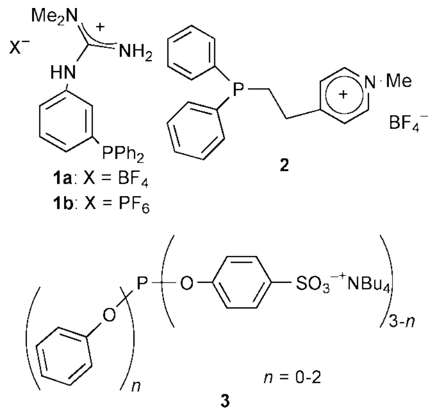
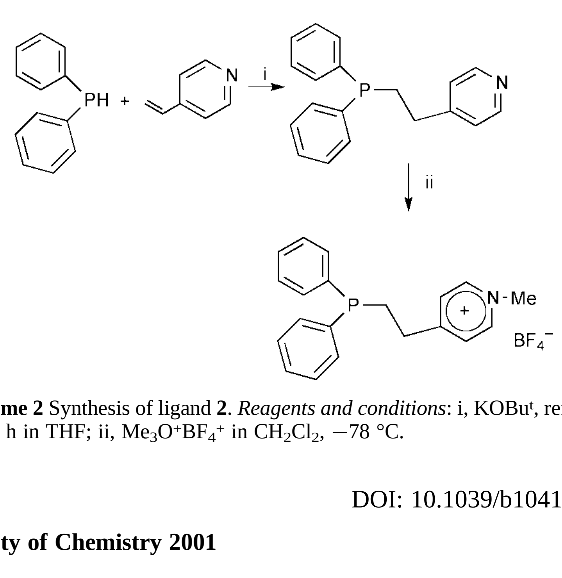


Fig. 1 Turnover frequency as a function of 1-hexene solubility in the ionic liquids. *Reaction conditions*: $Rh(CO)_2(acac)$ 0.075 mmol, 1-hexene/Rh = 800, TPPMS/Rh = 4 , heptane was used as internal standard, CO/H_2 (molar ratio) = 1, $P(CO/H_2)$ = 2 MPa, T = 80 °C, TOF determined at 25% conversion of 1-hexene.



1a: X = BF_4
1b: X = PF_6
2
3

Scheme 1



Scheme 2 Synthesis of ligand **2**. *Reagents and conditions*: i, $KOBu^t$, reflux for 3 h in THF; ii, $Me_3O^+BF_4^+$ in CH_2Cl_2, −78 °C.

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Table 1 Hydroformylation with different ligand–ionic liquid systems[a]

Entry	Ligand L	L/Rh	Ionic liquid	Reaction time/min	Conversion[b] (%)	Aldehydes[c] (mol %)	n/i[d]	TOF[e]/min^{-1}
1	**1a**	10	$BMI^+BF_4^-$	180	77	74	3.7	3
2	**1b**	7		210	83	78	4	3
3	**2**	4		180	87	96	2.6	4
4	**3**	9.5	$BMI^+PF_6^-$	180	96	88	12.6	4
5[f]	**3**			240	85	89	11.2	2
6[g]	**3**			330	42	88	11.7	1

[a] *Reaction conditions*: $Rh(CO)_2(acac)$ 0.075 mmol, 1-hexene/Rh = 800, CO/H_2 (molar ratio) = 1 ; $P(CO/H_2)$ = 2 MPa, T = 80 °C, heptane (internal standard) = 2 mL, 1-hexene = 7.5 mL, ionic liquid = 4 mL. [b] Conversion = [(initial 1-hexene) − (1-hexene after reaction)]/(initial 1-hexene). [c] The other products are 2- and 3-hexenes. [d] Linear to branched aldehyde ratio. [e] Mol of aldehydes per mol Rh per minute at 25% conversion. [f] Recycling of 4. [g] Recycling of 5.

liquids. In all cases, the selectivity in aldehydes is > 97%, the remainder being isomerized hexenes. Surprisingly, in the NTf_2^- based ionic liquids, lower TOF are obtained despite the relatively good solubility of 1-hexene in these media. As suggested by the determination of ionic liquid relative polarity,[6] the NTf_2^- based salts could be more coordinating than the PF_6^- salts. In all cases, the n/i ratio is not affected by the nature of the solvent.

In a second series of experiments, we have synthesized the monosubstituted guanidinium triphenylphosphine ligands **1a** and **1b**,[7] and the pyridinium diphenylethylphosphine ligand **2** (Scheme 1). Ligand **2** was prepared in two steps according to Scheme 2. Ligands **1a** and **1b** show good solubility in the ionic liquid $BMI^+BF_4^-$. They give good selectivities towards the linear aldehydes. Similar catalytic performances were obtained by using **1a** or **1b** (Table 1, entries 1 and 2). However, the retention of the Rh in the $BMI^+BF_4^-$ phase was more efficient with **1a** (the Rh content in the organic phase was lower than the detection limit according to ICP analysis for **1a**, while the level was 0.8% of the initial Rh for **1b**). Ligand **2** (entry 3) presents higher reaction rates and higher selectivity towards aldehydes than **1a** and **1b**. However, the leaching of the Rh in the organic phase was found to be higher for **2** (2% of the initial Rh).

Phosphites and bisphosphites are well known ligands for Rh-hydroformylation to afford higher reaction rates.[8] Because of their instability toward hydrolysis, examples of their use in aqueous two-phase hydroformylations are rare.[9] Ionic liquids offer suitable alternative solvents. We describe here the first use of phosphite based ligands for the biphasic hydroformylation of 1-hexene in ionic liquids. Ligand **3**, a mixture of tetrabutylammonium salt of the mono- di- and tri-sulfonated triphenylphosphites, has been prepared by transesterification of triphenylphosphite with the tetrabutylammonium salt of *p*-hydroxyphenylsulfonic acid.[9] In the reaction with the ligand **3**, using $BMI^+PF_6^-$ as the solvent, good catalytic activity is observed (entry 4). The selectivity for the linear aldehyde is much higher than the selectivity obtained with phosphine ligands (enties 1–3). The use of the modified phosphite **3** limits the loss of the Rh in the organic phase (leaching is 2% of the initial Rh used). At the end of the run, the organic phase is decanted and separated from the ionic liquid which is reused (entry 5 and 6). Despite a loss of activity which could be ascribed to a partial degradation of the Rh active catalyst during the separation, the n/i ratio remains high after two recyclings.

In conclusion, it is shown that thanks to the great versatility of ionic liquids, it is possible to optimize Rh-hydroformylation performances by adjusting the nature of the anions and cations present in the solvent and the nature of the ligands. Phosphite ligands, which are unstable in an aqueous two-phase system, can be used. The problem of Rh leaching can be minimized by the modification of phosphorus ligands with cationic (guanidinium or pyridinium) or anionic (sufonate) groups. By adjusting the ligand and the ions of the solvent, excellent Rh retention has been achieved.

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