Catalytic intermolecular hydroamination of alkenes
Beneficial effect of ionic solvents

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Abstract

Rhodium(III) pre-catalysts exhibit a much higher catalytic activity in ionic solvents (phosphonium or imidazolium salts) than in THF for the hydroamination of norbornene with aniline. The nature of the anionic part of the ionic solvent seems to play an important part, bromides ions being the more efficient in increasing the catalytic activity. For the same reaction, the activity of platinum(II) pre-catalysts is evidenced for the first time, and is also increased when used in tetrabutylphosphonium bromide as solvent. The catalytic activity and selectivity also depend upon the nature of the ligands in the platinum precursor.
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1. Introduction

The hydroamination of unsaturated carbon–carbon bonds (an atom-economical process) is a subject of current interest both for basic research as well as for the chemical industry [1,2]. In recent years, great efforts have been made worldwide to develop efficient reaction procedures, but these have met with limited success. Indeed, although significant improvements have been reported for the hydroamination of alkynes, dienes and vinylarenes, as well as for the intramolecular hydroamination of alkenes [3–7], the *intermolecular* hydroamination of non-functionalized alkenes is still a challenge for chemists.

The main contributions in the area of homogeneously catalyzed *intermolecular* hydroamination of

alkenes started with the report by Coulson of the rhodium-catalyzed hydroamination of ethylene in aprotic solvents (THF, HMPA, etc.) [8,9]. This catalytic system, however, is limited to ethylene and to highly basic secondary amines.

From that time, most contributions deal with the hydroamination of norbornene with aniline, chosen as a test reaction. For this reaction, different homogeneous catalytic systems have shown some activity, e.g. $(PEt_3)_2Ir(C_2H_4)_2Cl/ZnCl_2$ [10], $(Ph_3P)_3RhCl_3/PhN-HLi$ [11–13], and more recently, $[IrCl(BINAP)]_2/P_2$-fluoride, in which the naked fluoride ion significantly increases the catalytic activity [14]. All these reactions were conducted in homogeneous THF solutions.

A few years ago, we reported that ionic solvents [15–19] such as imidazolium or tetraalkylphosphonium salts behave like classical dipolar aprotic solvents for the C/O alkylation of sodium naphtoate with benzyl halides [20]. This observation encouraged us to

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test such solvents for the intermolecular hydroamination of alkenes. Indeed, apart from the well recognized advantages of ionic solvents (low vapor pressure, thermal stability, easy isolation of reaction products, etc.), it could be anticipated that the anion associated with the onium part could play a beneficial role, depending on the strength of its interaction with transition metal species in either step of the catalytic cycle [21–23]. Recently, a liquid–liquid two phase system (1-ethyl-3-methylimidazolium trifluoromethane sulfonate/heptane) has been shown to be effective for the continuous, zinc-catalyzed *intramolecular* hydroamination of an activated aminoalkene, 3-aminopropylvinyl ether [24].

In this communication, we wish to report our first results about the use of ionic solvents for the test reaction, the catalytic hydroamination of norbornene with aniline.

2. Experimental

2.1. Materials and methods

n-Tetrabutylphosphonium bromide (Janssen), imidazolium salts (Acros), norbornene (Fluka), *N,N*-dibutylaniline (Acros), phosphanes (Acros), rhodium and platinum salts (Strem) were use as received. Aniline (Fluka) was distilled before use. All sample manipulations of transition metal complexes were carried out under argon using standard Schlenk tube and vacuum techniques.

2.2. Instumentation

GC analyses were performed on a Hewlett-Packard HP 4890 (FID) chromatograph (HP 3395 integrator) equipped with a 30 m HP1 capillary column and GC–MS analyses on a Hewlett-Packard HP 6890 apparatus equipped with a HP 5973 M ion detector.

Catalytic experiments were conducted in 80 ml glass-lined autoclaves equipped with a stirring bar. The temperature of the autoclave was maintained at the desired value by means of the lagging fluid from a constant temperature circulator.

2.3. Reactions

The general procedure is exemplified in the case of RhCl$_3$: the autoclave was charged with RhCl$_3$·3H$_2$O (34 mg, 0.129 mmol) and n-Bu$_4$PBr (7.1 g), closed and submitted to argon-vacuum cycles. A degassed solution of norbornene (1.25 g, 12.9 mmol) in aniline (4.1 ml, 45 mmol), prepared independently, was then syringed into the autoclave and the temperature adjusted to 140 °C. After 6 days, the autoclave was allowed to cool to room temperature. The reaction mixture was dropped into 50 ml of diethylether, stirred, and then filtered. The solid phase was extracted again with diethylether (3 × 50 ml). The external standard (*N,N*-dibutylaniline) was added to the collected etheral phases and the solution analyzed by GC and GC–MS.

3. Results and discussion

We have first chosen to test the hydroamination of norbornene **1** with aniline **2** (pK_a = 9.42) using RhCl$_3$·3H$_2$O, a pre-catalyst which has been reported to be active only for the hydroamination of ethylene with highly basic amines such as piperidine (pK_a = 11.02) in THF at 200 °C. The main results have been gathered in Table 1. Reactions were performed in an autoclave at 140 °C for 6 days, using RhCl$_3$/norbornene/aniline ratios of 1/100/350. The ionic solvents used are commercially available and abbreviated as indicated in footnotes of Table 1. Reaction products were identified by comparison (GC and GC–MS) with authentic samples prepared as previously reported [12] and quantified with calibration curves using *N,N*-dibutylaniline as external standard.
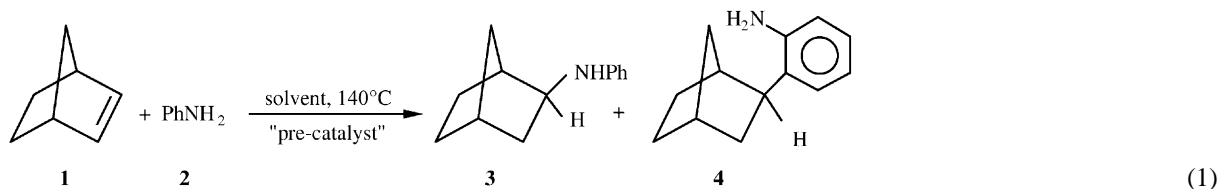

$$\text{(1)}$$

Table 1

Hydroamination of norbornene with $PhNH_2$ (rhodium catalysts)[a]

Run	Solvent[b]	Catalyst precursor	Reaction products (turnover numbers)	
			3	**4**
1	THF (7.5 ml)	$RhCl_3 \cdot 3H_2O$ (0.13 mmol)	0	0
2	[EMI][Cl] (3 g)	$RhCl_3 \cdot 3H_2O$ (0.13 mmol)	∼0	∼0
3	[BMI][Cl] (3.6 g)	$RhCl_3 \cdot 3H_2O$ (0.13 mmol)	∼0	∼0
4	[BMI][Cl] (7.2 g)	$RhCl_3 \cdot 3H_2O$ (0.13 mmol)	∼0	∼0
5	[BMI][PF_6] (6 g)	$RhCl_3 \cdot 3H_2O$ (0.13 mmol)	5.1	2.6
6	[BMI][Br] (5.7 g)	$RhCl_3 \cdot 3H_2O$ (0.13 mmol)	8.3	1.5
7	n-Bu_4PBr (7.1 g)	$RhCl_3 \cdot 3H_2O$ (0.13 mmol)	7.7	2.5
8	n-Bu_4PBr (7.1 g)	$(Ph_3P)_3RhCl$ (0.12 mol)	2.1	1.7

[a] Reactions conducted for 6 days at 140 °C using norbornene (13 mmol) and aniline (45 mmol).

[b] [BMI][Cl], 1-butyl-3-methyl imidazolium chloride; [BMI][PF_6], 1-butyl-3-methyl imidazolium hexafluorophosphate; [EMI][Cl], 1-ethyl-3-methyl imidazolium chloride; [BMI][Br], 1-butyl-3-methyl imidazolium bromide.

As may be seen from Table 1, the control experiment (run 1) confirmed that no hydroamination product is formed using $RhCl_3 \cdot 3H_2O$ in THF. In ionic solvents, the reaction generates two products, the expected hydroamination product **3** and a product **4**, resulting from alkylation of aniline in the *ortho* position (Eq. (1)). The latter has already been observed and characterized in the hydroamination of **1** with **2** using $(Ph_3P)_3RhCl_3$/PhNHLi as catalytic system [11,12]. Among imidazolium salts, it clearly appears that those associated with the chloride ion (runs 2–4) gave only traces of reaction products. A control experiment indicated that [EMI][Cl] could be recovered unchanged (^{1}H NMR analysis in CD_3OD) after heating for 6 days at 140 °C in the presence of the catalyst [25].[1] In contrast, when the chloride ion is replaced by PF_6^- (run 5) or, better by a bromide ion (run 6), the reaction *reproducibly* affords **3** and **4** with significant turnover numbers. The beneficial effect of bromide ions is confirmed by the reaction conducted in n-Bu_4PBr (run 7). Last, the Wilkinson catalyst (run 8) appeared essentially inactive. Indeed, under the same conditions but without the rhodium complex, compounds **3** and **4** were formed in nearly the same amounts (calculated 3% overall yield), indicating that the phosphonium salt itself promotes some activation of the hydroamination reaction.

The **3**/**4** ratio (Table 1) varies with the nature of the ionic solvent. This variation is difficult to comment on since the reaction mechanism(s) is (are) not known at present time. Interestingly, however, it must be noted that the most active system (run 6) is also the most selective for the formation of the hydroamination product, **3** (84%).

In order to confirm the advantage of ionic solvents versus THF, some platinum complexes were considered for the first time as catalyst precursors for the hydroamination of **1** with **2** under the same conditions as for the experiments reported in Table 1. The main results are summarized in Table 2.

The first observation is that platinum salts or complexes exhibits at least some activity for the reaction, even in THF as solvent (run 14). However, as with rhodium-based pre-catalysts (vide supra), platinum complexes exhibit a much higher catalytic activity in n-Bu_4PBr (compare runs 12 and 14). Control experiments indicated that the phosphonium salt can be recovered unchanged (no trace of n-Bu_3P, ^{31}P and ^{1}H NMR analysis) after heating for 6 days at 140 °C in the presence of $PtCl_2$. Last, careful examination of the reaction medium of run 9 in a Schlenk tube heated at 100 °C indicated a single-phase, homogeneous system (dark clear solution).

Moreover, it appears from these exploratory experiments that the nature of the phosphorus ligand plays a role on the catalytic activity (runs 11–13): the catalytic activity seems to increase mainly with the basicity (pK_a) of the phosphorus ligand ($P(OMe)_3$: 2.60; PPh_3: 2.73; PPh_2Me: 4.65), but also depends on the bulkiness of the ligand. Last, as with rhodium precursors, the most active system (run 12) is also

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[1] Reported thermal decomposition temperatures of [EMI][Cl] and [BMI][Cl] are 285 °C and 254 °C, respectively.

Table 2
Hydroamination of norbornene with $PhNH_2$ (platinum catalysts)[a]

Run	Solvent	Catalyst precursor (mmol)	Reaction products (turnover numbers)	
			3	**4**
9	n-Bu$_4$PBr (7.1 g)	PtCl$_2$ (0.13)	8.1	2.1
10	n-Bu$_4$PBr (7.1 g)	(Ph$_3$P)$_2$Pt^{2+}(Tf)$_2^{-}$[b] (0.13)	1.6	1.2
11	n-Bu$_4$PBr (7.1 g)	[P(OMe)$_3$]$_2$PtBr$_2$ (0.13)	6	2.4
12	n-Bu$_4$PBr (7.1 g)	(PPh$_2$Me)$_2$PtBr$_2$ (0.05)	30	5.6
13	n-Bu$_4$PBr (7.1 g)	(PPh$_3$)$_2$PtBr$_2$ (0.14)	12.8	5.3
14	THF (7.5 ml)	(PPh$_2$Me)$_2$PtBr$_2$ (0.13)	2.7	0.5

[a] As shown in footnotes of Table 1.

[b] Tf: trifluoromethane sulfonate.

the most selective for the formation of **3** (84%). It may be noted that the selectivity **3/4** also depends on the nature of the phosphorus ligand. Indeed, using (PPh$_2$Me)$_2$PtBr$_2$, which leads to the highest activity and selectivity in n-Bu$_4$PBr, leads to the same selectivity when used in THF where the activity is much lower.

Work is in progress to develop the use of ionic solvents for the hydroamination of various alkenes and to try to determine the origin of the observed activation of the catalytic activity.[2]

Acknowledgements

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[2] Acceleration of reaction rates by the use of ionic liquids as solvents has already been observed in different cases. See for example [26–30].