Ionic Liquids, 3‡. Synthesis and Utilisation of Protic Imidazolium Salts in Homogeneous Catalysis

Michel Picquet,[a] Igor Tkatchenko,[a,*] Immacolata Tommasi,[b] Peter Wasserscheid,[c] Jörg Zimmermann[c]

[a] Laboratoire de Synthèse et Electrosynthèse Organométalliques, FRE 2595 du CNRS, Faculté des Sciences Mirande, 9 ave A. Savary, BP 47870, 21078 Dijon Cedex, France
Fax: (+33)-380-393-772, e-mail: tkatchen@u-bourgogne.fr
[b] Department of Chemistry, University of Bari, Campus Universitario, via Orabona 4, 70126 Bari, Italy
[c] Institut für Technische und Makromolekulare Chemie der RWTH Aachen, Sammelbau Chemie, Worringer Weg 1, 52074 Aachen, Germany

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Abstract: Protonation of 1-alkylimidazoles provides halogen-free salts which act as ionic liquids and proton reservoir in proton- and metal-assisted catalytic processes like dimerisation of methyl acrylate and ring closing metathesis, and lead to significant improvements both in activity and selectivity.

Keywords: ionic liquids; protonation; imidazoles; dimerisation; ring closing metathesis

Owing to their unique properties, ionic liquids (ILs) have received considerable attention for applications as alternative solvents,[1] especially in homogeneous catalysis.[2] As demonstrated recently,[3] they are particularly suitable for activating and running catalytic reactions involving ionic complexes. In fact, ionic liquids are ideal solvents for sequestering ionic complexes (*similia similibus solventur*) and facilitating their recovery and recycling from the reaction products.

Although the pioneering work of Chauvin has demonstrated the beneficial use of Lewis acids,[4] little attention as been paid to the utilisation of *protic* ionic liquids (ILs) in catalysis. In addition to their easy access and the *de facto* lack of halide ions which may interfere with the cationic metal centre, it is expected that protic ionic liquids may have a dual function, as a proton source[5] and as a medium sequestering the ionic transition metal catalyst.[2] Different series of liquid crystalline 1-alkylimidazolium salts (alkyl = $C_{10}-C_{18}$) were isolated from the reaction of nitric, hydrochloric and tetrafluoroboric acids with the corresponding 1-alkylimidazoles; they induce a specific stereoselectivity for the catalysed Diels–Alder condensation reaction of cyclopentadiene and diethyl maleate.[6] The protonated Hünig base, $[HNEt(i\text{-}Pr)_2][CF_3COO]$ is reported to be an efficient medium for the nitration of arenes by NH_4NO_3/TFA.[7]

There are few reports on protic ILs based on 1-alkylimidazoles in the literature. In addition to the liquid crystalline 1-alkylimidazolium salts already mentioned,[6] 1-methylimidazolium tetrafluoroborate has been prepared by reacting aqueous tetrafluoroboric acid in ethanol or water with 1-methylimidazole.[8] The recent publication of Ohno and Yoshiwaza on ion conductive characteristics of ILs prepared by neutralisation of 1-alkylimidazoles[9] prompted us to report here on the synergic effect between protonated alkylimidazoles and palladium, rhodium or ruthenium catalysts observed in, respectively, methyl acrylate dimerisation (Pd, Rh) or RCM of *N,N*-diallyltosylamide (Ru), reactions where the presence of proton is essential for good performances.

The reaction of 1-methyl- (MIM) and 1-butylimidazole (BIM) with strong acids is quantitative in diethyl ether. The salts [HMIM]Y and [HBIM]Y (Y = BF_4, OTf, OTs) are free of water as evidenced by the lack of OH stretching absorbances in the 3500 – 3800 cm^{-1} region of the IR spectra. The NMR chemical shift of the NH proton ranges from $\delta = 12.15$ to 13.58 ppm in acetone-d_6 and is partially related to the concentration of the sample. It is noteworthy that IR spectroscopy reveals a strong dependence of the N–H stretching vibration upon the counter anion of the imidazolium salt: the average ν_{NH} decreases in the order $BF_4^- > TfO^- > TsO^-$, together with a broadening of the band, thus suggesting a stronger hydrogen bonding in the tosylate salts. Although these compounds melt between 30 and 109 °C, they are liquid under the reaction conditions used for catalysis.

The tail-to-tail dimerisation of methyl acrylate (Scheme 1) with the system {$Pd(acac)_2$, $[HPBu_3][BF_4]$, $[HOEt_2][BF_4]$}[10] is very sensitive to the presence of

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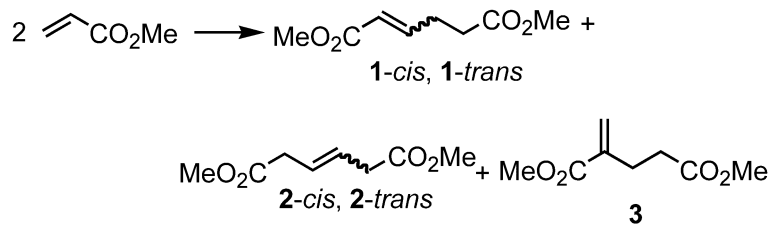


Scheme 1.

Table 1. Dimerisation of methyl acrylate catalysed by ionic palladium and rhodium species.

Entry	Solvent	Catalytic system	TOF (h^{-1})
1	Methyl acrylate[a]	$Pd(acac)_2$/$[HPBu_3][BF_4]$/$[Et_2OH][BF_4]$	110
2	$[BMIM][BF_4]$[a, b]	$Pd(acac)_2$/$[HPBu_3][BF_4]$/$[Et_2OH][BF_4]$	72
3	$[BMIM][BF_4]$[a, c]	$Pd(acac)_2$/$[HPBu_3][BF_4]$/$[Et_2OH][BF_4]$	100
4	$[HMIM][BF_4]$[d]	$Pd(acac)_2$/$[HPBu_3][BF_4]$/$[Et_2OH][BF_4]$	35
5	$[HBIM][BF_4]$[a]	$Pd(acac)_2$/$[HPBu_3][BF_4]$/$[Et_2OH][BF_4]$	220
6	Methyl acrylate[a]	$[Cp^*Rh(C_2H_4)]$/$[Et_2OH][BF_4]$	429
7	$[BMIM][BF_4]$[a, e]	$[Cp^*Rh(C_2H_4)]$/$[Et_2OH][BF_4]$	616
8	$[HBIM][BF_4]$[a, e]	$[Cp^*Rh(C_2H_4)]$/$[Et_2OH][BF_4]$	3
9	$[HBIM][BF_4]$[a, f]	$[Cp^*Rh(C_2H_4)]$/$[Et_2OH][BF_4]$	168
10	$[HMIM][BF_4]$[d, f]	$[Cp^*Rh(C_2H_4)]$/$[Et_2OH][BF_4]$	9

Reaction conditions for palladium: $[Pd(acac)_2]$ (1 equiv.), $[HPBu_3][BF_4]$ (10 equiv.), methyl acrylate (300 equiv.), imidazolium salt (50 weight % of the amount of methyl acrylate), $[HOEt_2][BF_4]$ (8 equiv.); 1 h, 80 °C, agitation: 500 rpm. *Reaction conditions for rhodium*: $[RhCp^*(C_2H_4)_2]$ (1 equiv.), $[HOEt_2][BF_4]$ (1.2 or 300 equiv.), methyl acrylate (1000 equiv.), imidazolium salt (50 weight % of the amount of methyl acrylate); 1 h, 80 °C, agitation: 500 rpm.
[a] Monophasic.
[b] $[Cl^-] = 3.6\%$.
[c] $[Cl^-] = 0.5\%$.
[d] Biphasic.
[e] 1.2 equiv. $[Et_2OH][BF_4]$.
[f] 300 equiv. $[Et_2OH][BF_4]$, *in situ* preparation.

chloride ion. In fact, adding one equivalent of Cl^- (as [BMIM]Cl) to the palladium catalyst inhibits the reaction.[11] By using different batches of $[BMIM][BF_4]$, prepared by metathetical exchange of Cl and BF_4,[12] we observed activities which depend on the Cl^- content of the IL and are lower than that observed for neat methyl acrylate (Table 1).

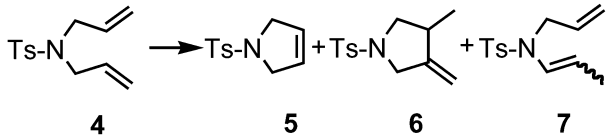
The use of $[HBIM][BF_4]$, (50 weight %) leads to a monophasic system and provides TOF in the range of 170 – 220 h^{-1}, therefore demonstrating the beneficial use of protic ILs (Table 1). The reaction products (selectivity for linear dimers > 98%) can be extracted with toluene, which opens the route to catalyst recovery and recycling.[11,13] However, the use of $[HMIM][BF_4]$, induces the formation of a biphasic system which, under the same conditions, leads to lower TOF (25 – 30 h^{-1}), presumably indicating mass transfer control. It is worthy to note that the reaction of $Pd(acac)_2$ with $[HBIM][BF_4]$ gives rise to a mixture of $[Pd(acac)(bim)_2][BF_4]$ and $[Pd(bim)_4][BF_4]_2$, which suggests that the [HBIM] cation acts as a proton reservoir for the protonation of $Pd(acac)_2$. This process is known to be the first step towards the formation of the active species for the dimerisation of methyl acrylate.[14] Moreover, ^{13}C NMR monitoring of the reactions mixtures indicates no evidence for the formation of *N*-heterocarbene complexes *via* oxidative addition of the metal centre at C-2.[15,16] Nevertheless, the beneficial use of this proton reservoir cannot be generalised: for example, the use of $[Rh(C_5Me_5)(C_2H_4)_2]$, which is reported to be very efficient upon protonation for this reaction,[17] provides, in comparison, much lower results (Table 1). An explanation for these poorer results may be a strong coordination of the imidazole to the rhodium centre, which is partly overcome by higher concentration of acid.

The RCM and ROMP of functionalised diolefins have been reported to be tuned with the use of Lewis or Brønsted acids. For example, ruthenium(II) tris(pyrazolyl)borate alkylidenes are activated for RCM by the addition of $AlCl_3$, CuCl and HCl,[18] and living ROMP in aqueous solution employing Grubbs' carbene with cationically functionalised phosphine ligands only occurs in the presence of small amounts of DCl.[19] The

Table 2. Ring closing metathesis of *N,N*-diallyltosylamide **4** catalysed by [Ru(=C=C=CPh$_2$)(*p*-cymene) (PCy$_3$)Cl][OTf]

Entry	Catalyst carrier	T [°C]	Conversion [%]	Selectivity [%]		
				(**5**)	(**6**)	(**7**)
11	[HBIM][BF$_4$]	50[a]	81	81	0	0
12	[HBIM][OTf]	50[a]	100	100	0	0
13	[HBIM][OTf]	34[a]	100	100	0	0
14	[HBIM][OTf]	80[b]	100 (97[c])	100	0	0
15	[BMIM][BF$_4$]	80[d]	29	10	7	12
16	Toluene	80[e]	98.5 (99[f])	99	0	0

Conditions: Imidazolium salt (400 equiv.), *N,N*-diallyltosylamide (50 equiv.), [Ru(=C=C=CPh$_2$)(*p*-cymene)(PCy$_3$)Cl][OTf] (1 equiv., 2 mol %).
[a] For 15 min.
[b] For 1 h.
[c] Isolated yield.
[d] For 5 h.
[e] For 1 h.
[f] Literature data, see ref.[20]



Scheme 2.

positive effect of Brønsted acids is also observed with cationic ruthenium allenylidene complexes.[20] The best results reported in RCM of *N,N*-diallyltosylamide (Scheme 2) correspond to the use of [Ru(=C=C=CPh$_2$)(*p*-cymene)(PCy$_3$)Cl][PF$_6$] with 0.5 equiv. of [HOEt$_2$][BF$_4$]. Moreover, ionic liquids have been recently reported for catalyst recycling and improvement.[21,22]

The use of [HBIM][BF$_4$] in association with the triflate salt instead of the hexafluorophosphate one affords a dramatic increase in activity and selectivity (Table 2), better than that recently reported with the use of toluene or of [BMIM] salts.[20,22a] Changing the IL counteranion to triflate leads to a further increase in activity with no loss of selectivity. Moreover, the reaction product could be removed by simple extraction with diethyl ether, therefore opening the route to a continuous process.[22] The specific effect of the protic cation is further supported by the observation of a sluggish and non-selective reaction if [BMIM][BF$_4$] is used as the catalyst carrier (Table 2, entry 15).

In conclusion, protic 1-alkylimidazolium salts, which are liquid under the reaction conditions used are an attractive alternative to solvents for catalysis with ionic complexes. There are many obvious advantages comprising easy preparation, the facility of product isolation, the potential for recycling, and the prevention of deprotonation at C-2 which is well documented for 1,3-dialkylimidazolium salts.[23] Moreover, there are not entirely innocent and may provide new routes for the activation of catalyst precursors (see for example ref.[24]).

Experimental Section

For analytical and spectroscopic data, see supporting information.

General Procedure: Preparation of 1-Hydrogeno-3-butylimidazolium Tetrafluoroborate, [HBIM][BF$_4$]

In a Schlenk tube is placed under argon freshly distilled *N*-butylimidazole (20.218 g, 162.8 mmol). Under agitation (magnetic bar), [HOEt$_2$][BF$_4$] (22 mL, 163.08 mmol; Fluka, 54% wt) is slowly added (***Caution!*** the solution becomes warm and diethyl ether may boil). After completion of the addition and further agitation under argon for 10 min, Et$_2$O is added (50 mL) and the solution cooled to $-80\,^{\circ}C$ for 15 min. The white crystalline precipitate formed is recovered by inverse filtration. The solid is washed with Et$_2$O (3×10 mL) and dried under vacuum. The ether solution contains no [HBIM][BF$_4$].

General Procedure: Dimerisation of Methyl Acrylate (Table 1)

In a Schlenk tube are successively placed under argon and agitation (magnetic bar) [HPBu$_3$][BF$_4$] (10 equiv.), Pd(acac)$_2$ (1 equiv.), methyl acrylate (300 equiv.), the imidazolium salt (50 weight % of the amount of methyl acrylate). The mixture is stirred for 30 min at room temperature, then [HOEt$_2$][BF$_4$] (8 equiv.) is added and the solution stirred for 10 additional min. The Schlenk tube is heated at 80 °C for 1 h, then rapidly cooled to $-80\,^{\circ}C$. GC analysis (Megabore Carbowax/BTR, external diameter: 0.53 mm, length: 15 m; carrier gas: He (7.2 mL/min); splitless injector (injector temperature: 200 °C); FID detection (detector temperature: 220 °C); oven program: 45 °C (3 min), 12 °C/min up to 120 °C, 3 °C/min up to 200 °C, and 20 min at

200 °C) with methyl benzoate as internal standard is performed in duplicate.

General Procedure: RCM of *N,N*-Diallyltosylamide (Table 2)

In a Schlenk tube are successively placed under argon and agitation (magnetic bar) the imidazolium salt (4 mmol, 400 equiv.) and *N,N*-diallyltosylamide (0.5 mmol, 50 equiv.). The mixture is stirred 10 min at room temperature to obtain a colourless homogeneous liquid then [Ru(=C=C=CPh_2)-(*p*-cymene)(PCy_3)Cl][OTf] (0.01 mmol, 1 equiv., 2 mol %) is added. The red to violet solution is placed at 34 to 50 °C for 15 min then cooled to room temperature. The conversion is determined by ^{1}H NMR of the crude reaction mixture. The product is isolated by simple extraction with Et_2O (3 × 10 mL).

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References and Notes

[‡] Part 2: See *Chem. Commun.* **2003**, 28 – 29.
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