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Room-temperature ionic liquids as new solvents for organic electrosynthesis. The first examples of direct or nickel-catalysed electroreductive coupling involving organic halides

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Direct or Ni-catalysed electroreductive homocouplings of organic halides and couplings of organic halides with activated olefins are efficiently conducted by constant current electrolyses in an undivided cell in room-temperature ionic liquids as the solvent–electrolyte media.

Environmental considerations now constrain chemists to integrate the control of risks (and costs) into their procedures and the recent literature reflects various approaches aiming at eco-friendly processes.

In this context, electrosynthesis remains an attractive method since the use of electrons as a reagent does not involve the formation of any side-products. Another approach aspiring to "green chemistry" is the use of eco-friendly solvents in organic syntheses. This explains the rapidly growing interest in the properties of room-temperature ionic liquids (RTILs) in recent years. Indeed, it has already been demonstrated that a wide range of organic syntheses, including catalysed reactions, can be carried out in these alternative non-flammable solvents, which are attractive for their easy access, thermal stability, low vapour pressure but also because they allow simple product recovery and solvent recycling.[1–3]

Regarding electrochemical processes, RTILs are also promising solvents owing to their inherent conductivity which avoids the addition of a supporting electrolyte. Moreover, provided that both cation and anion are chosen appropriately, a non-protic medium with a large electrochemical window can be obtained. Many investigations have already been devoted to identifying RTILs as suitable media notably in batteries, fuel cells, photovoltaic cells or electroplating processes. However, to our knowledge, only one organic reaction combining RTILs and electrochemistry has been reported. Moreover, this synthesis is a non-faradaïc reaction in which a small amount of electricity engaged in the electroreduction of CO_2 generates catalytic species responsible for the addition of CO_2 to epoxides to yield cyclic carbonates.[4]

We want to exemplify in this paper that organic electrosyntheses can be efficiently achieved in RTILs and we report herein our preliminary results. As a first example we performed the electroreductive homocoupling of some alkyl- or benzyl-halides RX (eqn. (1)).

$$2RX + 2e^- \rightarrow R\text{–}R + 2X^- \qquad (1)$$

The electrochemical cell is identical to the one previously used with common organic solvents:[5] electroreduction occurs at a metallic grid cathode while the anode is a sacrificial metallic bar (*e.g.* Mg, Al, Fe) which is electrooxidized, without any diffusion limit, into the corresponding cation (Mg^{2+}, Al^{3+}, Fe^{2+}). In addition, the use of sacrificial anodes makes electroreductive synthesis a cheap process which can be easily conducted in undivided cells. We selected as the solvent–electrolyte media, salts of the type [R-mim][BF_4], where R is a linear alkyl chain and, in particular, we used octyl-methylimidazolinium tetrafluoroborate [octyl-mim][BF_4]. These salts are easily prepared by conventional methods[6] and they dissolve organic halides while being immiscible water, saturated hydrocarbons and EtO_2. These features allow easy product separation and solvent recycling. Thus, following electrolysis, the organic products are extracted by treating the electrolytic solution with pentane or EtO_2, and then the solvent is washed with an aqueous solution of $NaBF_4$† in order to eliminate metallic salts arising from the anodic reaction. After drying in a vacuum oven the RTIL is used again in further experiments.

In a typical experiment, 20 mmol of RX were added to 40 mL of [octyl-mim][BF_4]. The electrolysis was conducted by setting a constant current intensity between the nickel grid cathode and a magnesium or aluminium bar anode until GC analysis of samples indicated the consumption of RX. We noticed that, in spite of its ionic structure, the RTIL was not efficient enough as an electric conductor, very likely on account of its high viscosity, which would limit the ion mobility. This results in an important ohmic drop, and, therefore a high cell voltage when the current intensity is increased. This drawback can be easily overcome either by heating the solution to 40–50 °C or by adding a small amount of an organic co-solvent (*e.g.* DMF, 5–10% v/v) or even better, when necessary, by combining these two ways. In these reaction conditions, the electrolyses were conducted under a cathodic current density up to 5 mA cm^{-2} with a moderate cell voltage (1.5–10 V), which are usual values for electrosynthetic processes in organic media. Results are given in Table 1.

Bibenzyl was obtained in good yields from benzyl bromide or benzyl chloride after a reaction time involving an electric charge of 1.1 Faraday per mol of organic halide, which means a current efficiency close to 100%. The yield is also good in the case of dichlorodiphenylmethane, which leads to an olefinic coupling product after a four-electron reduction (2 F per mole of starting halide). For an alkyl bromide, R–R is formed with a moderate yield, the alkane RH and the alkene R(–H) were detected as by-products.

We have also developed in the past many C–C bond forming reactions involving electrochemistry and the use of transition metal complexes as homogeneous catalysts.[7] Thus we started to investigated electroreductive nickel-catalysed couplings in a RTIL with the homocoupling of an aryl halide into a biaryl (eqn. (2)).

$$2ArX + 2e^- \xrightarrow[\text{Anode Fe or stainless steel}]{\text{RTIL, cata NiBr}_2\text{bpy}} Ar - Ar + 2X^- \qquad (2)$$

Table 1 Direct electroreductive coupling of organic halides in [octyl-mim][BF_4][a]

R–X	Isolated R–R	Yield (%)
$C_8H_{17}Br$[b]	$C_{16}H_{34}$	48
Ph–CH_2Br	Ph–CH_2–CH_2–Ph	75
Ph–CH_2Cl	Ph–CH_2–CH_2–Ph	78
Ph–CCl_2–Ph	$Ph_2C{=}CPh_2$	68

[a] General conditions: [octyl-mim][BF_4] (40 mL) + DMF (4 mL), RX (20 mmol), nickel grid cathode (20 cm^2), Mg or Al bar anode, RT, I = 0.1 A unless otherwise stated. [b] I = 0.05 A.

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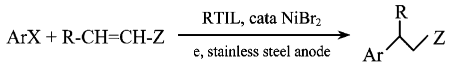
This reaction has been previously carried out in aprotic as well as in protic solvents.[8] The catalytic species is generated by the electroreduction of the divalent $Ni(bpy)^{2+}$ complex into the zerovalent $Ni^0(bpy)$ complex which reacts by oxidative addition to the aromatic halide. More details on the catalytic cycle have been described elsewhere.[9]

For these experiments, the solvent–electrolyte medium [octyl-mim][BF_4]–DMF (90 : 10 v/v) was added to ArX and $NiBr_2bpy$ (5% *vs.* ArX) as the catalyst precursor. The electrosyntheses conducted in the undivided cell under a constant current (5 mA cm^{-2}) were efficient in these conditions. Fig. 1 shows that ArX (*e.g.* PhBr) was almost fully consumed within the theoretical time (one mol of electron engaged per mol of PhBr), corresponding to a faradaïc yield close to 100%. As expected, biphenyl is the major product formed in 80% isolated yield.

The results were very similar with either a nickel, a stainless steel or an iron bar as the sacrificial anode.

Such excellent current efficiencies and good chemical yields were observed with various other aryl halides as indicated in Table 2. These results are as good as those previously obtained in classical organic solvents.[8a]

A second example of a Ni-catalysed electroreductive coupling in a RTIL is the arylation of an activated olefin (eqn. (3)).



$$ArX + R\text{-}CH{=}CH\text{-}Z \xrightarrow[\text{e, stainless steel anode}]{\text{RTIL, cata NiBr}_2} Ar\text{-}CH(R)\text{-}CH_2\text{-}Z \qquad (3)$$

This reaction has been previously reported, using $NiBr_2$ as catalyst precursor in mixed solvents DMF–pyridine (9 : 1) or DMF–MeCN (1 : 1).[10] Although the mechanism of the reaction remains to be clarified, it should be pointed out that pyridine or acetonitrile probably interact with the electrogenerated low valent Ni-species, thus preventing precipitation of nickel metal. The addition of a nitrogeneous co-solvent is no longer required since the RTIL [octyl-mim][BF_4] can act similarly owing to the presence of one nitrogen atom bearing a free electron-pair.

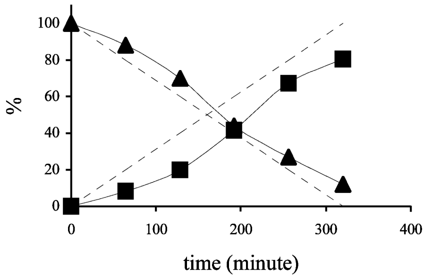


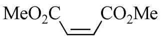
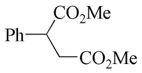
Fig. 1 Progress *vs.* time of the Ni(bpy) catalysed conversion of PhBr into Ph–Ph in [C_8H_{17}-mim][BF_4]. (Experimental conditions are as indicated in Table 1.) —▲—▲— residual PhBr, —■—■— yield of Ph–Ph, - - - - - theoretical curves.

Table 2 Ni(bpy) catalysed electrosynthesis of biaryls from aryl halides in [octyl-mim][BF_4][a]

ArX	Ar–Ar and isolated yield (%)
Ph–Br	Ph–Ph 80
4-CF_3–C_6H_4Cl	4-CF_3–C_6H_4–C_6H_4–4′-CF_3 86
3-CF_3–C_6H_4Br	3-CF_3–C_6H_4–C_6H_4–3′-CF_3 72

[a] General conditions: [octyl-mim][BF_4] (40 mL) + DMF (2 mL), ArX (20 mmol), $NiBr_2$(bpy) (1 mmol), nickel grid cathode (20 cm^2), iron bar anode, $T \approx 40$ °C, I = 0.1 A, electric charge = 1.1 F mol^{-1}.

Table 3 Ni-catalysed electroreductive arylation of activated olefins in [octyl-mim][BF_4][a]

ArBr	Activated olefin	Product and isolated yield (%)
Ph–Br	CH_2=CH–CO–Me	Ph–CH_2–CH_2–CO–Me, 58
Ph–Br	CH_2=CH–CO_2–Bu	Ph–CH_2–CH_2–CO_2–Bu, 61
Ph–Br		 , 41
3-MeO–C_6H_4Br	CH_2=CH–CO–Me	3-MeO–C_6H_4–$(CH_2)_2$–CO–Me, 42

[a] General conditions: [octyl-mim][BF_4] (40 mL) + DMF (4 mL), ArX (20 mmol), activated olefin (30 mmol), $NiBr_2$ (1 mmol), nickel grid cathode (20 cm^2), stainless steel bar anode, $T \approx 40$ °C, I = 0.1 A, electric charge = 2.8–3 F per mol of ArBr.

Using the experimental device and electrolysis conditions identical to those described above, the conjugate additions were carried out in solutions containing a mixture of an aromatic bromide, an activated olefin in slight excess and a catalytic amount of $NiBr_2{\cdot}3H_2O$. The results presented in Table 3 show that the reaction is also possible in [octyl-mim][BF_4] since the arylated olefins are obtained in moderate yields, ArH being the major side-product. Yields and current efficiencies (60–70%) are however slightly lower than those obtained at 70–100 °C in DMF–pyridine mixtures[10] but experimental conditions in RTILs have not been optimized.

This reaction can also be conducted in RTILs other than [octyl-mim][BF_4], *e.g.* Ni-catalysed electrocoupling between bromobenzene and butyl acrylate in octylpyridinium tetrafluoroborate gave butyl 3-phenylpropionate in 52% yield.

In conclusion, we have demonstrated with these preliminary experiments that direct or Ni-mediated electrosyntheses by reductive coupling can successfully achieve C–C bond formation in simple and mild conditions by using RTILs as solvent–electrolyte media. This shows that three approaches, electrochemistry, homogeneous catalysis and eco-friendly solvents, aimed at “green chemistry” can be advantageously combined.

Notes and references

† The use of $NaBF_4$ (0.1 mol L^{-1}) in the aqueous washing solutions allows good separation of [octyl-mim][BF_4] which is immiscible in water while [octyl-mim]Br is partially miscible.

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