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Aerobic and Electrochemical Oxidative Cross-Dehydrogenative-Coupling (CDC) Reaction in an Imidazolium-Based Ionic Liquid

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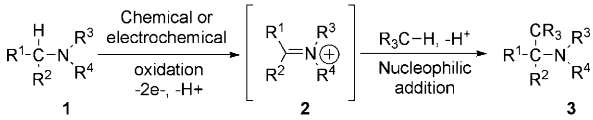
Abstract: The ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate [BMIm][BF$_4$] has demonstrated high efficiency when applied as a solvent in the oxidative nitro-Mannich carbon–carbon bond formation. The copper-catalyzed cross-dehydrogenative coupling (CDC) between *N*-phenyltetrahydroisoquinoline and nitromethane in [BMIm][BF$_4$] occurred with high yield under the described reaction conditions. Both the ionic liquid and copper catalyst were recycled nine times with almost no lost of activity. The electrochemical behavior of the tertiary amine substrate and β-nitroamine product was investigated employing [BMIm]-[BF$_4$] as electrolyte solvent. The potentiostatic electrolysis in ionic liquid afforded the desired product with a high yield. This result and the cyclic voltammetric investigation provide a better understanding of the reaction mechanism, which involves radical and iminium cation intermediates.

Keywords: cations · C–C coupling · C–H activation · ionic liquids · oxidation

Introduction

The generation of carbocation intermediates followed by their reaction with carbon nucleophiles is one of the most powerful strategies for the formation of C–C bonds. Different methods have been developed for the generation of these reactive intermediates.[1] We recently reported the use of a cheap copper salt as an efficient catalyst for the oxidative cross-dehydrogenative coupling (CDC) reaction between the Csp^3–H bond adjacent to a nitrogen atom (see **1**, Scheme 1) and different Nu–H nucleophiles (represented as C–H). This method resides in the in situ generation of a highly reactive electrophilic iminium intermediate **2** in the presence of peroxides or oxygen as oxidant.[2] This new methodology offers formation and ready access to products **3** with a variety of new C–C bonds (Csp^3–Csp^3, Csp^3–Csp^2, Csp^3–Csp bonds).



Scheme 1. Cross-dehydrogenative-coupling reaction.

Electrochemical oxidation has been largely investigated for the generation of carbocation intermediates; the electrochemical cyanation of tertiary amines constitutes a representative example of C–C bonds formation employing this method.[3] More recently Yoshida et al. developed a general two-step method, referred to as the “cation-pool method,” providing an easy access to α-functionalized tertiary amines.[4]

Room temperature ionic liquids (IL) are composed entirely of ions and exist in the liquid state at and around room temperature. They have several archetypal properties[5] such as intrinsic conductivity, high thermal stability, low-volatility, high polarity, and potentially wide electrochemical windows.[6] As a result, they are being increasingly used in many electrochemical experiments.[7] Combining all the above principles, we envisaged an oxidative carbon–

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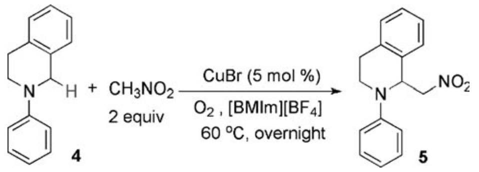
carbon bond formation in an IL via the anodic oxidation of an amine **1**, *N*-phenyltetrahydroisoquinoline (**4**) (see Table 1), to generate the corresponding iminium intermediate **2**, which would subsequently react with a carbon nucleophile (Scheme 1).

Results and Discussion

The chemical CDC reaction thus far has been performed in water or in an organic solvent. For our investigation in ionic liquids, it was necessary to determine the feasibility of the chemical CDC reaction in this medium. We therefore selected a well established coupling reaction between *N*-phenyltetrahydroisoquinoline (**4**) and nitromethane, to yield β-nitroamine **5** (see Table 1 for the structures), which had been carried out in water under an atmosphere of oxygen using CuBr as catalyst.[2e] β-Nitroamines such as **5** can be readily reduced to 1,2-diamines,[8] which are important molecules in medicinal chemistry and are useful ligands for catalysis.[9]

Table 1. Recycling of both catalyst and ionic liquid,[a] NMR yields based on the tertiary amine **4**, using an internal standard.



Run	1	2	3	4	5	6	7	8	9
Yield[a]	80	90	>99	>99	>99	95	90	85	80

The above reaction was performed in [BMIm][BF$_4$] as solvent. Such 1,3-dialkyl imidazolium based ILs have considerable interest in both catalysis and electrochemistry.[7] [BMIm][BF$_4$] was synthesized according to the reported method and was obtained as a colorless liquid.[10] The IL [BMIm][BF$_4$] appeared as an effective solvent for the CDC reaction between tertiary amine **4** and nitromethane and the desired product **5** was obtained in a 80% NMR yield (Table 1, run 1) compared to a 90% NMR yield in water.[2e] Interestingly, the IL and the catalyst could be recycled nine times with almost no lost of activity (Table 1). It is also important to note that an increase of yield was observed after the first recycling. In fact, a better yield of the desired coupling product **5** was obtained in runs 2 to 6, suggesting a possible activation of the copper catalyst by the IL solvent. Imidazolium-based ILs can dramatically accelerate the electron transfer from metal complexes to oxygen molecule.[11] Moreover, the in situ generation of a carbene intermediate in an ionic liquid, which can play the role of ligand for metal centers, has also been clearly demonstrated.[12]

The results summarized in Table 1 clearly show that the chemical CDC reaction between a tertiary amine and nitromethane is also efficient in an IL. The next step was to verify if such an oxidative coupling could be carried out electrochemically. ILs as electrolytes are known to have a potentially wide electrochemical window.[6] Indeed, the electrochemical window of [BMIm][BF$_4$] covers about 4 V (from −2.5 to 2.2 V vs Ag/AgNO$_3$ 0.01 M at a glassy carbon (GC) electrode and between −1.8 and 1.8 V at a Pt electrode (voltammograms not shown)). In both cases, the oxidation limit occurs at a potential significantly more positive than those of the oxidation of tertiary *N*-phenylamine **4** and of β-nitroamine **5** (see Figures 1 and 2). As seen in Figure 1, the cyclic voltammogram (CV) of amine **4** in [BMIm][BF$_4$] at a GC electrode reveals a non-reversible oxidation peak at a potential of 0.55 V vs Ag/AgNO$_3$, which corresponds to the oxidation of a tertiary *N*-phenylamine. The CV of the β-nitroamine **5** (Figure 2) shows a similar oxidation peak but at a more positive potential of 0.75 V. The tertiary *N*-phenylnitroamine **5** is more difficult to oxidize due to the inductive effect of the nitro group. In the CVs of Figure 1 and Figure 2, on the first negative scan after reversal of the potential, a reduction peak appears around 0.2 V (Figure 1) and 0.3 V (Figure 2) to which corresponds an oxidation peak at 0.2 and 0.4 V respectively in the second positive scan. The increase of current of these redox couples upon cycling indicates that the species giving rise to these reversible systems do accumulate on the electrode. This is most probably due to the formation of conducting polymers or oligomers on the electrode surface. Such polymerization/oligomerization would be responsible for the partial passivation of the electrode seen in these CVs by the decrease of the oxidation peak current, upon repetitive scanning, for the oxidation of amines **4** and **5** (at 0.55 V in Figure 1 and 0.75 V in Figure 2) and the decrease of the reduction current of the nitro group of **5** at −1.7–1.8 V in Figure 2.

An important feature of the CVs of amines **4** and **5** is the reduction peak at −1.2 V in the reverse scans which, as will be seen below, corresponds to the reduction of the iminium

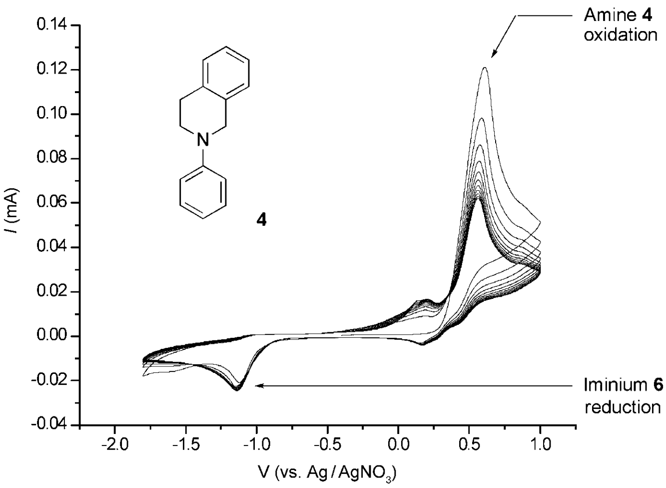


Figure 1. Cyclic voltammogram of N-phenyltetrahydroisoquinoline **4**, ([**4**]=5.10^{-2} M) in [BMIm][BF$_4$] at a GC electrode and a scan rate of 0.1 V s^{-1}.

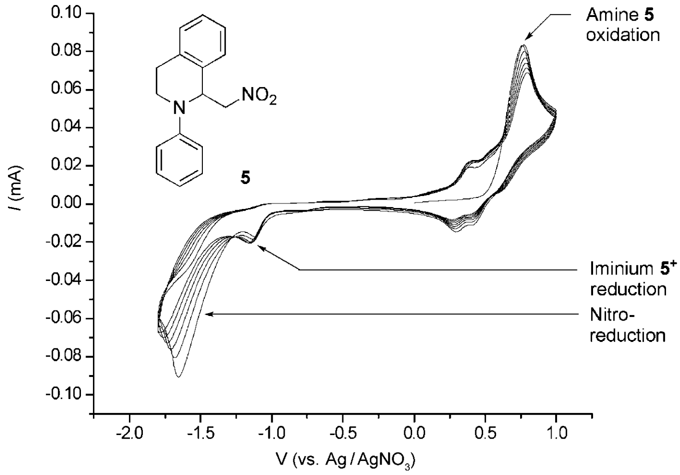
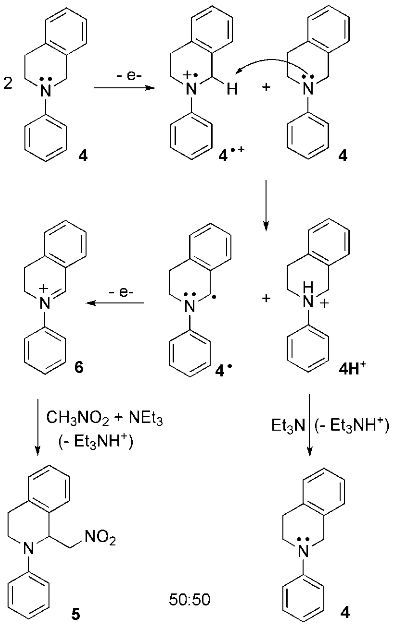


Figure 2. Cyclic voltammogram of the β-nitroamine **5**, ([**5**] = 5.10^{-2} M) in [BMIm][BF$_4$] at a GC electrode and a scan rate of 0.1 V s^{-1}.

cation generated by oxidation of the amine: iminium cation **6** from the oxidation of **4** (see Scheme 2) and iminium cation **5**$^+$ generated by oxidation of β-nitroamine **5**.



Scheme 2. Postulated mechanism for the formation of β-nitroamine **5** by oxidation of amine **4**.

Next, the cyclic voltammogram of a solution of amine **4** plus two equivalents of nitromethane in [BMIm][BF$_4$] was recorded in order to see if the β-nitroamine **5** could be formed in situ upon oxidation of amine **4**. This CV did not show any peak corresponding to the β-nitroamine **5** (voltammogram not shown). The latter was not formed under these conditions. These voltammetric results will be discussed below together with the potentiostatic electrolysis results.

Electrolysis of amine **4** was then performed under controlled potential (potentiostatic electrolysis) in a standard two-compartment electrochemical H-cell with a glass frit as separator. A large area Pt electrode was used as working electrode instead of a GC electrode for practical reasons (see Experimental Section). The CV behavior on a Pt microelectrode was identical to that on a GC electrode. The anodic potential was fixed at 0.7 V, 150 mV more positive than the oxidation peak potential of amine **4** (see the Experimental Section and Supporting Information for details). The electrochemical reduction of the 1,3-dialkyl imidazolium cation (C2-hydrogen) was responsible for the massive hydrogen evolution observed at the cathode during the electrolysis.[13] The number of Coulombs consumed corresponded to the exchange of one electron per molecule of **4**. After the electrolysis, two equivalents of nitromethane were added to the cathodic compartment and the resulting mixture was stirred for 2 h. No organic compound (other than nitromethane) was detected after extraction with diethyl ether, suggesting that only charged species insoluble in diethyl ether and stabilized in the ionic liquid were present in the final electrolytic solution. On the other hand, when two equivalents of both triethylamine and nitromethane were added to the solution after electrolysis, the CV of Figure 3 was obtained showing the presence of an equimolar ratio of the desired β-nitroamine **5** and starting amine **4** (oxidation peaks of amine **4** at 0.55 V and β-nitroamine **5** at 0.75 V of equal intensity). Other features of the CV of Figure 3 are: the cathodic peak at −1.2 V corresponding to the reduction of both the iminium cation **6**, generated by the oxidation of **4** and the iminium cation **5**$^+$, generated by the oxidation of **5**; the peak corresponding to the reduction of the nitro group of **5**; and the nitromethane reduction peak. Note that there is no iminium cation present in the solution since the first scan of Figure 3 recorded towards the negative potentials does not show any reduction peak at −1.2 V. The iminium reduction peak is generated only after the first cycle in oxidation. The formation of an equimolar amount of β-ni-

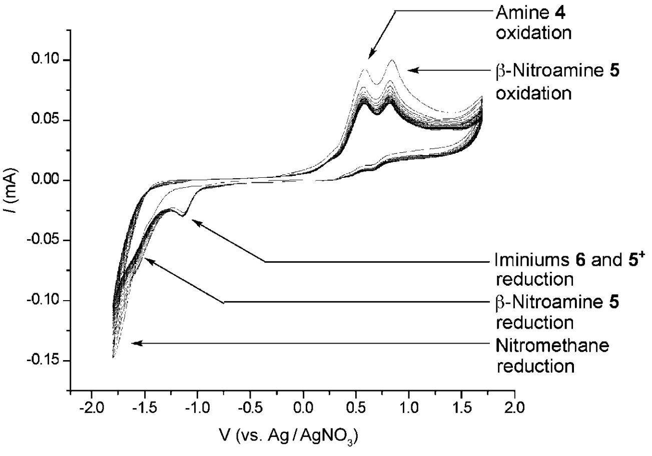


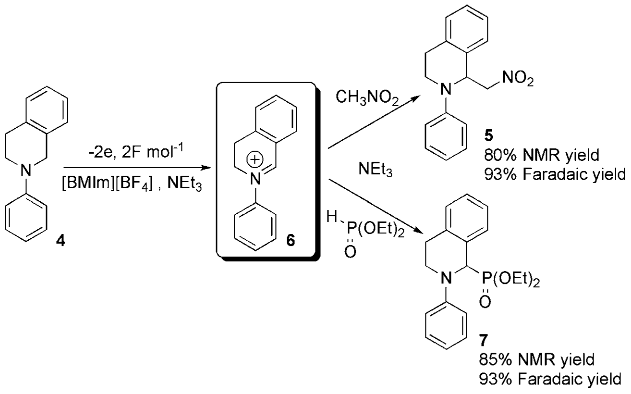
Figure 3. Cyclic voltammogram of the electrolysis solution after addition of 2 equiv of triethylamine and 2 equiv of nitromethane at a GC electrode and a scan rate of 0.1 V s^{-1}.

troamine **5** and starting amine **4** was confirmed by ether extraction of the final solution and NMR analysis of the crude product.

According to the electrolysis and voltammetric results, and literature precedent,[3] a reaction mechanism can be postulated as shown in Scheme 2. It involves the generation of the radical cation $\mathbf{4}^{+\bullet}$ by a one-electron oxidation of amine **4** which would be deprotonated to the radical intermediate ($\mathbf{4}^{\bullet}$) by the amine **4**. Thus, one equivalent each of radical $\mathbf{4}^{\bullet}$ and protonated amine $\mathbf{4H}^+$ would be formed. The neutral radical $\mathbf{4}^{\bullet}$ would be further oxidized to the iminium cation **6**. In the absence of Et_3N, there is no nucleophile present in the solution to react with the iminium cation **6** and the charged species $\mathbf{4H}^+$ and **6** are much more soluble in the ionic liquid than in diethyl ether. The protonated amine $\mathbf{4H}^+$ is not oxidized in the potential region studied as evidenced by the absence of an oxidation peak in the CV of $\mathbf{4H}^+$ BF_4^- in [BMIm][BF_4] (voltammogram not shown). In the presence of two equivalents of Et_3N, $\mathbf{4H}^+$ and nitromethane would be deprotonated to regenerate the starting amine **4** and form the nucleophilic nitronate anion. The latter then would react with the iminium cation **6** to generate the desired β-nitroamine **5**. Hence a total of one electron per molecule of amine **4** is consumed to produce an equimolar amount of β-nitroamine **5** and starting amine **4**.

A similar mechanism involving the radical cation $\mathbf{4}^{+\bullet}$ and the radical $\mathbf{4}^{\bullet}$ might also take place in the copper-catalyzed aerobic chemical cross-dehydrogenative-coupling reaction. In fact, the addition of radical scavengers such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and 4-methyl-2,6-di-*tert*-butylphenol (BHT) to the standard conditions of copper-catalyzed nitro-Mannich reaction decreased significantly the yield of the coupling product in both ionic liquid and water. There would be a competition between oxidation of the radical $\mathbf{4}^{\bullet}$ to the iminium cation **6** and its reaction with the scavengers (coupling with TEMPO and H-abstraction from BHT).

Taking the proposed mechanism in consideration, we postulated the possibility of generating and accumulating carbocations electrochemically in [BMIm][BF_4] in the absence of nucleophiles ("cation pool").[4] Since the conditions described above were producing 50% of unreactive protonated amine $\mathbf{4H}^+$, we envisaged the addition of triethylamine in the electrolysis solution. The addition of such a base to the iminium cation **6** would be reversible and the base would then deprotonate $\mathbf{4H}^+$ to regenerate the starting amine **4** which would allow the complete anodic oxidation of amine **4** to the iminium cation **6**. Cyclic voltammetric studies demonstrated that triethylamine was not oxidized at the selected potential. Consequently, triethylamine was added to the [BMIm][BF_4] ionic liquid containing the amine **4** and the reaction mixture was subjected to potentiostatic anodic oxidation. The coulometric measurements corresponded to the expected consumption of two electrons per molecule of **4**. The starting amine **4** and the protonated amine $\mathbf{4H}^+$ were not detected and only the iminium cation **6** reduction peak could be observed in the CV, thus showing clearly that the cation **6** has been preformed in [BMIm][BF_4] (cation pool) by complete oxidation of **4**. Then, the addition of two equivalents of nitromethane and triethylamine to the ionic liquid cation pool produced the β-nitroamine **5** in an 80% NMR yield with high current efficiency (Scheme 3).



Scheme 3. Results of the cation pool method in an ionic liquid.

To evaluate further the potential of this new cation-pool method, we investigated the formation of a C–P bond using diethylphosphite as nucleophile in place of the conjugate base of nitromethane using the same conditions and procedure described above.[14] The biologically important α-aminophosphonate **7** was synthesized in 85% yield with high current efficiency (Scheme 3). This result demonstrates the efficiency of the cation-pool method in ionic liquid. In fact, when Geniès et al. reported the electrochemical oxidative phosphonation of ring-substituted *N*,*N*-dimethyl anilines in acetonitriles,[3h,i] the desired α-aminophosphonates were obtained only in moderate yields (<30%) with moderate current efficiencies. It is important to note that the addition of nitromethane or diethylphosphite with the chemically preformed iminum salt **6** generated also the desired coupling products with high efficiency (see Supporting Information).

Conclusion

To conclude, we have demonstrated that ionic liquids and in particular [BMIm][BF_4] are highly effective solvents for copper-catalyzed cross-dehydrogenative coupling (CDC) with oxygen as terminal oxidant. By using ionic liquids as such, both the solvent and the copper catalyst can be recycled nine times without significant lost of activity. Furthermore, we have also demonstrated the possibility of using an electrochemical method rather than a metal catalyst to carry out CDC in ionic liquids as solvent and electrolyte. Finally, a detailed mechanism of the anodic nitro-Mannich carbon–carbon bond formation process was described. Further studies for the detection and the characterization of proposed intermediates along with the extension of the scope of the CDC reaction in ionic liquids are being pursued.

Experimental Section

General: ^{1}H NMR spectra were recorded on a Varian 400 MHz spectrometer in $CDCl_3$. Thin-layer chromatography was performed using Sorbent Silica Gel 60 F254 TLC plates and visualized with ultraviolet light. All reagents were purchased from Aldrich and Acros, deoxygenated and back filled with Argon before used. 2-Phenyl-1,2,3,4-tetrahydroisoquinoline (**4**) was prepared by the literature method.[2h]

General procedure for the aerobic CDC nitro-Mannich reaction in ionic liquids: To a mixture of CuBr (1.4 mg, 0.01 mmol), **4** (42 mg, 0.2 mmol), $[BMIm][BF_4]$ (0.4 mL) and nitromethane (21.5 μL, 0.4 mmol) was added. Then the 20 mL test-tube was filled up with molecular oxygen and sealed. The reaction was stirred using a magnetic stirrer at 60 °C for 16 h. The resulting mixture was extracted with diethyl ether. The solvent was evaporated and the residue was purified by column chromatography on silica gel (hexane/ethyl acetate 5:1), and the fraction with an $R_f = 0.5$ was collected and concentrated to give the desired product **5**.

Recycling: Residues of solvents in the ionic liquid were removed under vaccum and the $[BMIm][BF_4]$ containing the copper bromide catalyst was recharged with **4** and nitromethane. The test tube was sealed and the reaction was stirred under an atmosphere of oxygen at 60 °C for 16 h. The extraction and purification procedures were the same as those described above.

General procedure for the anodic nitro-Mannich reaction in ionic liquids: In a two-compartment electrochemical cell with a glass frit as separator, the ionic liquid $[BMIm][BF_4]$ (3 mL) was added to the three-neck anodic compartment containing **4** (31 mg, 0.15 mmol). Amine **1** was carefully dissolved upon heating by stirring using a magnetic stirrer under an Argon atmosphere. The cathodic compartment was filled with $[BMIm][BF_4]$ (3 mL). The platinum mesh wire-netting working electrode (area = 1.3 cm^2) was positioned in the anodic compartment and the platinum auxiliary electrode in the cathodic compartment (see Figure 1 of the Supporting Information). The oxidation potential was fixed at 0.7 V (vs. Ag/$AgNO_3$) and the colorless solution was stirred at room temperature until the current reached less than 1 % of its initial intensity. To the orange product mixture, nitromethane (16 μL, 0.3 mmol) and triethylamine (44 μL, 0.315 mmol) were added and the solution was stirred for 12 h at room temperature. The resulting mixture was extracted with diethyl ether and filtered through a short layer of silica gel and eluted with diethyl ether. The solvent was evaporated and the residue was analyzed by thin layer chromatography and ^{1}H NMR spectroscopy.

General procedure for the cation pool method in ionic liquids: In The electrochemical cell, the electrodes and the procedure were the same as those described above except that triethylamine (28 μL, 0.3 mmol) was added to the anodic compartment. After completion of the electrolysis, nitromethane (16 μL, 0.3 mmol) or diethylphosphite (26 μL, 0.3 mmol) and triethylamine (44 μL, 0.315 mmol) were added and the solution was stirred for 12 h at room temperature. The resulting mixture was extracted with diethyl ether and filtered through a short layer of silica gel and eluted with diethyl ether. The solvent was evaporated and the residue was analyzed by thin-layer chromatography and ^{1}H NMR spectroscopy.

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[1] a) G. A. Olah, *Angew. Chem.* **1995**, *107*, 1519–1532; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1393–1405; b) B. E Maryanoff, H.-C. Zhang, J. H. Cohen, I. J Turchi, C. A. Maryanoff, *Chem. Rev.* **2004**, *104*, 1431–1628; c) J.-i. Yoshida, K. Kataoka, R. Horcajada, A. Nagaki, *Chem. Rev.* **2008**, *108*, 2265–2299; d) M. Speranza, *Chem. Rev.* **1993**, *93*, 2933–2980; e) A. D. Dilman, S. L. Ioffe, *Chem. Rev.* **2003**, *103*, 733–772.

[2] a) L. Zhao, O. Baslé, C.-J. Li, *Proc. Natl. Acad. Sci. USA* **2009**, *106*, 4106–4111; b) C.-J. Li, *Acc. Chem. Res.* **2009**, *42*, 335–344; c) W.-J. Yoo, C. A. Correia, Y. Zhang, C.-J. Li, *Synlett* **2009**, 138–142; d) O. Baslé, C.-J. Li, *Org. Lett.* **2008**, *10*, 3661–3663; e) O. Baslé, C.-J. Li, *Green Chem.* **2007**, *9*, 1047–1050; f) Z. Li, D. S. Bohle, C.-J. Li, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 8928–8933; g) Z. Li, C.-J. Li, *Eur. J. Org. Chem.* **2005**, 3173–3176; h) Z. Li, C.-J. Li, *J. Am. Chem. Soc.* **2005**, *127*, 6968–6969; i) Z. Li, C.-J. Li, *J. Am. Chem. Soc.* **2005**, *127*, 3672–3673; j) Z. Li, C.-J. Li, *Org. Lett.* **2004**, *6*, 4997–4999; k) Z. Li, C.-J. Li, *J. Am. Chem. Soc.* **2004**, *126*, 11810–11811.

[3] a) S. S. Libendi, Y. Demizu, O. Onomura, *Org. Biomol. Chem.* **2009**, *7*, 351–356; b) N. Shankaraiah, R. A. Pilli, L. S. Santos, *Tetrahedron Lett.* **2008**, *49*, 5098–5100; c) T. Tajima, A. Nakajima, *J. Am. Chem. Soc.* **2008**, *130*, 10496–10497; d) N. Girard, J.-P. Hurvois, *Tetrahedron Lett.* **2007**, *48*, 4097–4099; e) E. Le Gall, J. P. Hurvois, T. Renaud, C. Moinet, A. Tallec, P. Uriac, S. Sinbandhit, L. Toupet, *Liebigs Ann.* **1997**, 2089–2101; f) S. Michel, E. Le Gall, J. P. Hurvois, C. Moinet, A. Tallec, P. Uriac, L. Toupet, *Liebigs Ann.* **1997**, 259–267; g) F. Effenberger, H. Kottmann, *Tetrahedron* **1985**, *41*, 4171–4182; h) G. Bidan, M. Geniès, R. Renaud, *Electrochim. Acta* **1981**, *26*, 275–282; i) G. Bidan, M. Geniès, *Tetrahedron* **1981**, *37*, 2297–2301.

[4] a) J. Yoshida, S. Suga, S. Suzuki, N. Kinomura, A. Yamamoto, K. Fujiwara, *J. Am. Chem. Soc.* **1999**, *121*, 9546–9549; b) S. Suga, S. Suzuki, A. Yamamoto, J. Yoshida, *J. Am. Chem. Soc.* **2000**, *122*, 10244–10245; c) J. Yoshida, S. Suga, *Chem. Eur. J.* **2002**, *8*, 2650–2658.

[5] a) P. Wasserscheid, T. Welton, *Ionic Liquids in Synthesis Vol. 1*, 1st ed., Wiley-VCH, Weinheim, **2003**; b) T. Welton, *Chem. Rev.* **1999**, *99*, 2071–2083; c) K. J. Fraser, I. E. Izgorodina, M. Forsyth, J. L. Scott, D. R. MacFarlane, *Chem. Commun.* **2007**, 3817–3819; d) D. R. MacFarlane, M. Forsyth, E. I. Izgorodina, A. P. Abbott, G. Annat, K. Frasera, *Phys. Chem. Chem. Phys.* **2009**, *11*, 4962–4967, and references therein.

[6] a) F. A. Uribe, R. A. Osteryoung, *J. Electrochem. Soc.* **1988**, *135*, 378–381; b) Z. J. Karpinski, S. Song, R. A. Osteryoung, *Inorg. Chim. Acta* **1994**, *225*, 9–14; c) M. A. M. Noël, R. D. Allendoerfer, R. A. Osteryoung, *J. Phys. Chem.* **1992**, *96*, 2391–2494; d) H. Matsumoto, M. Yanagida, K. Tanimoto, M. Nomura, *Chem. Lett.* **2000**, 922–923.

[7] For a recent reviews, see: a) P. Hapiot, C. Lagrost, *Chem. Rev.* **2008**, *108*, 2238–2264; b) R. G. Evans, G. Compton, *ChemPhysChem* **2006**, *7*, 488–496.

[8] a) L. Bernardi, B. F. Bonini, E. Capito, G. Dessole, M. Comes-Franchini, M. Fochi, A. Ricci, *J. Org. Chem.* **2004**, *69*, 8168–8171, and references therein; b) H. Adams, J. C. Anderson, S. Peace, A. M. K. Pennell, *J. Org. Chem.* **1998**, *63*, 9932–9934.

[9] D. Lucet, T. Le Gall, C. Mioskowski, *Angew. Chem.* **1998**, *110*, 2724–2772; *Angew. Chem. Int. Ed.* **1998**, *37*, 2580–2627.

[10] V. Farmer, T. Welton, *Green Chem.* **2002**, *4*, 97–102.

[11] D. S. Choi, D. H. Kim, U. S. Shin, R. R. Deshmukh, S.-g. Lee, C. E. Song, *Chem. Commun.* **2007**, 3467–3469.

[12] L. Xu, W. Chen, J. Xiao, *Organometallics* **2000**, *19*, 1123–1127.

[13] a) M. Feroci, I. Chiarotto, M. Orsini, G. Sotgiu, A. Inesia, *Adv. Synth. Catal.* **2008**, *350*, 1355–1359, and reference therein.

[14] a) O. Baslé, C.-J. Li, *Chem. Commun.* **2009**, 4124–4126; b) W. Han, A. R. Ofial, *Chem. Commun.* **2009**, 6023–6025.

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