

The Pt(II)-catalyzed Baeyer–Villiger oxidation of cyclohexanone with H₂O₂ in ionic liquids†

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The Pt(II)-catalyzed Baeyer–Villiger oxidation of cyclohexanone with H₂O₂ in a two-phase system, H₂O–IL, is a viable procedure, characterized by synthetically interesting yields, better than those of the same reaction in H₂O–halogenated solvents.

Introduction

The Baeyer–Villiger oxidation of ketones to esters has been largely used in organic synthesis, in that it can occur in the presence of a number of functional groups, is stereoselective, and shows a regiochemical preference for the migrating group.¹ The importance of the reaction is demonstrated by the large number of papers that, also recently, dealt with, *inter alia*, the mechanism,^{2,3} theoretical investigations,^{4–6} the synthesis of α -fluorinated esters,⁷ and the stereochemical output.^{8–10}

However, in the classical procedure, the Baeyer–Villiger oxidation suffered, from the environmental point of view, from two major drawbacks, because organic peracids and halogenated solvents had to be used. Thus, many attempts have been made to move towards greener procedures, as recently reviewed.¹¹ New oxidant systems were tested, among which enzymes and hydrogen peroxide were the green choice. Monooxygenases from different sources^{12–15} or whole cells^{16–19} were used, with interesting results,

especially with respect to enantioselective biocatalysis. As for H₂O₂, it needs to be activated. Several heterogeneous catalysts,^{20–24} selenium compounds,^{25,26} and metal complexes^{27–29} have been used. Also, the use of a fluorinated biphasic system³⁰ and a nanoflow system with fluorinated lanthanide catalyst³¹ were reported. Among metal catalysts, platinum(II) complexes with chelating diphosphines gave good results,³² although a chlorinated solvent was still necessary. To explore the possibility of moving towards a more sustainable process, we investigated the Baeyer–Villiger oxidation of cyclohexanone (a substrate that reacted with difficulty with the Pt(II) catalysts in 1,2-dichloroethane) with hydrogen peroxide, catalyzed by Pt(II) complexes, in ionic liquids (ILs). In fact, ILs have been proposed as novel and environmentally benign reaction media for several organic syntheses.^{33–36} *N*-alkylpyridium and *N,N'*-dialkyl imidazolium cations coupled with a variety of inorganic anions have been used as suitable solvents for several organic reactions as well as in catalytic processes: Friedel–Craft reactions,^{37,38} Diels–Alder cycloadditions,^{39–44} metal-catalyzed hydrogenations,^{45–49} epoxidation^{50–52} and bromination of double and triple bonds⁵³ are just a few examples in this quite new field. To the best of our knowledge, only three papers reported Baeyer–Villiger oxidation in commercial ionic liquids, but one⁵⁴ used the dangerous *m*-chloroperbenzoic acid as oxidant, while cyclohexanone was unreactive under the conditions of the second.⁵⁵ The third paper reports the heterogeneously catalyzed oxidation of arylketones.⁵⁶ In the present investigation ILs with differently substituted imidazolium cations and with different anions were tested, with the aim of comparing hydrophobic and hydrophilic ionic liquids.⁵⁷

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Front row from left 1: Floris; 2: Sordi; 4: Conte; 5: Mirruzzo.
Back row from left 1: Galloni.

Valeria Conte gained her Laurea degree in Chemistry in 1982 and a PhD in Chemical Sciences in 1987, both at Padova University, under the supervision of Prof. G. Modena. From 1985–86 she was also a PhD student with Prof. J. K. Stille, CSU Fort Collins Co., USA. A CNR Fellow from 1987–1988, she became a CNR researcher at “CNR Centro Meccanismi Reazioni Organiche” Padova University (1988–98), including a period as a NATO–CNR senior fellow at CSU Fort Collins Co., USA (1993). From 1998–2001 she was Associate Professor of Organic Chemistry at Foggia University and is currently Associate Professor of Organic Chemistry at Tor Vergata University, Rome (2001–present). Her main research interests include reaction mechanisms of metal-catalyzed oxidation with peroxides, vanadium dependent bromoperoxidases mimicking systems and oxidation reactions in ionic liquids.

Results and discussion

The oxidation reactions were carried out mostly at room temperature, under an inert atmosphere (argon). $[\text{Pt}(\text{dppd})(\mu\text{-OH})_2(\text{BF}_4)_2]$ (dppb = 1,4-bis(diphenylphosphino)butane) was used as catalyst (Fig. 1), since it was shown that, the larger the P–Pt–P angle, the more effective the catalyst.⁵⁸

Actually, the inert atmosphere is not strictly necessary as far as the Baeyer–Villiger oxidation is concerned, but is desirable for prolonging the catalyst life especially in view of a possible recycle. Cyclohexanone was chosen as the substrate, because its reaction in the organic solvent gave poor yields due to extensive formation of 1,1'-dihydroxy dicyclohexylperoxide,⁵⁹ as a parallel undesired reaction promoted by the acidity of commercial H_2O_2 solutions. Therefore any improvement is valuable. In this and similar BV reactions, the role of the Pt complex is crucial, since, in its absence, no oxidation occurs.²⁹

The reaction was carried out using the different hydrophilic and hydrophobic ILs in order to identify, first of all, which system, homogeneous *versus* a two-phase one, is superior. The two-phase option is obviously due, as in the case of the chlorinated solvents, to the use of aqueous solutions of hydrogen peroxide as primary oxidant. The ILs were chosen on the basis of their availability and stability in the presence of an oxidant and water. It is to be noted that in several cases irreproducible results were obtained by using different samples of commercial ILs. This fact is likely due to an insufficient purity of the samples used. Such an aspect has been already addressed on other occasions by several authors.⁵⁷ Therefore, in order to have ILs with appropriate purity we synthesized our solvents with a two step synthesis. The first was a quaternization reaction between an alkyl substituted imidazole and an alkyl bromide, to obtain a solid precursor. The second was a metathesis reaction in which the bromide ion was exchanged with an appropriate anion able to give a liquid product at room temperature. Both these steps were executed following literature procedures^{60–64} with appropriate modifications.⁶⁵ Characterization of ionic liquids was made by ^1H NMR and their identity was confirmed by comparison with literature data.⁵³ In the course of our study we used 1-butyl-3-methylimidazolium, [bmim⁺], 1-ethyl-3-methylimidazolium, [emim⁺], 1-hexyl-3-methylimidazolium,

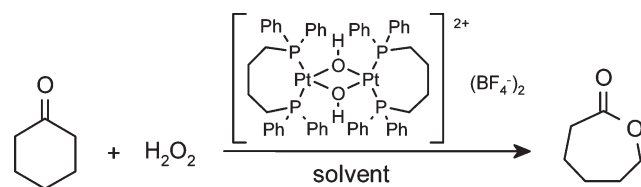


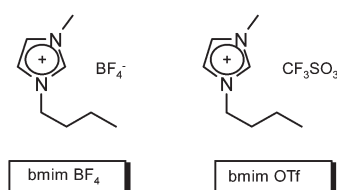
Fig. 1 The Pt(II)-catalyzed Baeyer–Villiger oxidation of cyclohexanone.

Table 1 Pt(II)-catalyzed Baeyer–Villiger oxidation of cyclohexanone with H_2O_2 in hydrophilic ionic liquids, at room temperature

Solvent	Reaction time/min	Yield of lactone (%)	Reactants ratio ^a substr. : H_2O_2 : cat.
bmim BF_4	300	5	200 : 100 : 1.5
bmim OTf	180	4	200 : 100 : 1.5
CHCl_3	450	10	200 : 100 : 1.0
CH_2Cl_2 ⁵⁹	250	ca. 10	200 : 100 : 1.0 ^b

^a [cyclohexanone] = 3 M, [H_2O_2] = 1.5 M, [cat] = 2.3×10^{-2} M. ^b [cyclohexanone] = 7.5 M, [H_2O_2] = 3.75 M, [cat] = 7.5×10^{-3} M, cat = (dppe)PtCF₃, dppe = diphenylphosphinoethane.

Hydrophilic Ionic Liquids



Hydrophobic Ionic Liquids

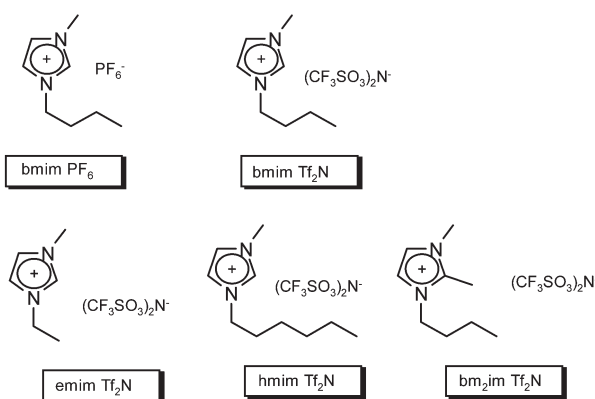


Fig. 2 Ionic liquids used as solvents for the Pt(II)-catalyzed Baeyer–Villiger oxidation of cyclohexanone.

[hmim⁺], and 1-butyl-2,3-dimethylimidazolium, [bm₂im⁺], cations and tetrafluoroborate, [BF_4^-], hexafluorophosphate, [PF_6^-], triflate, [CF_3SO_3^-], and bis(trifluoromethanesulfonyl)imide anions, [$(\text{CF}_3\text{SO}_2)_2\text{N}^-$]. The structures of ILs tested for performing the title reaction are collected in Fig. 2.

First, the reaction was performed in homogeneous phase, using butylmethylimidazolium tetrafluoroborate and triflate. The results are in Table 1, together with the reference reaction in chloroform and the literature for comparison.

The reaction in hydrophilic ILs was faster than that in chloroform, but gave poor results, likely due to a deactivation of the catalyst. Thus, hydrophobic ILs were tested, with the same cation and different anions (Table 2). In this case, the reaction time was even shorter, yields increased, and Tf_2N was the counterion with best results, with a lactone yield twice that in chlorinated solvents. Preliminarily, a $^{31}\text{P}\{^1\text{H}\}$ NMR experiment was carried out in order to determine the actual presence of $[\text{Pt}(\text{dppd})(\mu\text{-OH})_2(\text{BF}_4)_2]$ catalyst in the IL. The complex (22 mg) was mixed with bmim Tf_2N (1 ml) followed by 0.31 ml of cyclohexanone. Under these conditions the complex is only sparingly soluble in the IL phase. The NMR spectrum of the IL

Table 2 Pt(II)-catalyzed Baeyer–Villiger oxidation of cyclohexanone with H₂O₂ in hydrophobic ionic liquids, at room temperature

Solvent	Reaction time/min	Yield of lactone (%)	Reactants ratio ^a substr. : H ₂ O ₂ : cat.
bmim PF ₆	60	8	200 : 100 : 1.0
bmim Tf ₂ N	60	24	200 : 100 : 1.0
CHCl ₃	450	10	200 : 100 : 1.0

^a [cyclohexanone] = 3 M, [H₂O₂] = 1.5 M, [cat] = 1.5 × 10⁻² M.

phase showed the presence of the complex (δ 4.7 ppm, ¹J P–Pt 3550 Hz).⁵⁸ After addition of 35% H₂O₂ (0.13 ml) the mixture was stirred for 18 h. A new sample of the IL phase was dissolved in CDCl₃. The new spectrum showed, in addition to the starting complex, the presence of dppb dioxide (δ 34.9 ppm) in approximately a 1 : 1 ratio.

Subsequently, the importance of the cation was checked, keeping Tf₂N as the anion and varying the length and the number of imidazolium alkyl chains. As can be seen from the results in Table 3, the different cations affected the reaction time more than the yield of lactone.

The output of the oxidation was then investigated as a function of the reactants concentration, while keeping their ratio constant (Table 4). Also here, the variation of initial concentrations affected the reaction time more than the caprolactone formation. It should be pointed out that, under the conditions reported in Tables 1–4, blank experiments carried out in the absence of catalyst gave no conversion. Additionally, when in selected experiments carried out at room temperature conversion of the substrate has been quantitatively calculated, it has been found that it never exceeds 35% which compares well with literature data.⁵⁸

Finally, the effect of the catalyst amount, other conditions being equal, was investigated. The results are collected in Table 5. Of course, higher percents of the catalyst sped up the reaction. However, the yields of lactone remained the same, within experimental error.

To summarize the results, it is possible to say that the Pt(II)-catalyzed Baeyer–Villiger oxidation of cyclohexanone with hydrogen peroxide improves when performed in ionic liquids, not only in terms of avoiding halogenated solvents, but also in terms of reduced reaction times and increased yields. The specific imidazolium cation seems relatively important and the anion plays a major role, bis(trifluoromethanesulfonyl)imide being the counterion that consistently gives higher yields.

In order to verify, still at a preliminary stage, the performance of our methodology with other cyclic ketones, 2-methyl-cyclohexanone has been reacted under the conditions described in Table 4, second entry. The results are promising considering that 50% yield was obtained using [bmim⁺][(CF₃SO₂)₂N⁻] at room temperature. Further studies with this and other substrates are warranted.

To complete the investigation of the parameters potentially affecting the reactivity, an experiment was performed at 40 °C,

Table 3 Pt(II)-catalyzed Baeyer–Villiger oxidation of cyclohexanone with H₂O₂ in different bis(trifluoromethanesulfonyl)imides, at room temperature

Solvent	Reaction time/min	Yield of lactone (%)	Reactants ratio ^a substr. : H ₂ O ₂ : cat.
emim Tf ₂ N	215	16	200 : 100 : 1.0
bmim Tf ₂ N	60	24	200 : 100 : 1.0
hmim Tf ₂ N	60	19	200 : 100 : 1.0
bm ₂ im Tf ₂ N	75	17	200 : 100 : 1.0

^a [cyclohexanone] = 3 M, [H₂O₂] = 1.5 M, [cat] = 1.5 × 10⁻² M.

Table 4 Pt(II)-catalyzed Baeyer–Villiger oxidation of cyclohexanone with H₂O₂ bmim Tf₂N, with different concentrations,^a at room temperature

[ketone]/M	[H ₂ O ₂]/M	10 ² × [cat.]/M	Reaction time/min	Yield of lactone (%)
3.0	1.5	1.50	60	24
0.85	0.5	0.50	120	23
0.48	0.3	0.26	210	18

^a Substrate : H₂O₂ : catalyst = 200 : 100 : 1.0.

Table 5 Pt(II)-catalyzed Baeyer–Villiger oxidation of cyclohexanone with H₂O₂ in different ILs, with different amount of catalyst, at room temperature

Solvent	Reactants ratio ^a	10 ² × [cat.]/M	React. time/min	Yield of lactone (%)
bmim PF ₆	(A)	1.5	60	8
	(B)	2.3	30	9
emim Tf ₂ N	(A)	1.5	215	16
	(B)	2.3	120	15
bmim Tf ₂ N	(A)	1.5	60	24
	(B)	2.3	30	25

^a [cyclohexanone] = 3 M, [H₂O₂] = 1.5 M; (A), substrate : H₂O₂ : catalyst = 200 : 100 : 1.0; (B), substr. : H₂O₂ : cat. = 200 : 100 : 1.5.

Table 6 Pt(II)-catalyzed Baeyer–Villiger oxidation of cyclohexanone with H₂O₂ in bmim Tf₂N at different temperatures^a

Temperature/°C	Reaction time/min	Yield of lactone (%)
20	120	23
40	120	47
40	120	31 ^b

^a [cyclohexanone] = 0.85 M, [H₂O₂] = 0.5 M, [catalyst] = 5 × 10⁻³ M. ^b Second run with the same IL–catalyst sample.

where the yield in lactone increased up to 47%, within 120 min (Table 6). The reaction reported in the second entry of Table 6 was replicated three more times with fresh reagents and identical results within experimental error. The data so obtained are not reported in the Table.

Moreover, we attempted a recycle of the IL–catalyst system. After 2 hours at 40 °C, the reaction mixture was extracted with diethyl ether, dried under vacuum, added to the same amount of cyclohexanone and H₂O₂. From the second run, 31% lactone was still recovered (see Table 6, second run with the same IL–catalyst sample).

In conclusion, the Pt(II)-catalyzed oxidation of cyclohexanone by hydrogen peroxide significantly improved when performed in ionic liquids, resulting in a reaction that was faster and more efficient than in organic solvents. It is difficult to attribute such an improvement to a particular macroscopic property of the ILs used, because the different imidazolium cations used behaved similarly. The yield of lactone increased with temperature and, despite the sensitivity of the catalyst to prolonged exposure to hydrogen peroxide, recycling of the IL–catalyst system was practicable. It is reasonable to expect even better results with more reactive ketones.

Experimental

The ionic liquids, synthesized *ad hoc*, were dried under vacuum (0.5 mm Hg) at 80 °C for 2–4 h and fluxed with argon before use. The reaction was followed by gas chromatography, using decane as the external standard. Response factors for cyclohexanone and caprolactone were obtained as the slope of the straight line obtained plotting Area_{ketone}/Area_{decane} (or Area_{lactone}/Area_{decane}) values vs. [ketone]/[decane] (or [lactone]/[decane]) values, obtained from a number of solutions of known concentration. All measures were repeated at least three times.

In a typical experiment, the Pt catalyst was weighed in a Schlenk tube, under argon atmosphere, and was added to 1 mL IL and a known volume of cyclohexanone, previously fluxed with argon. A 100 μL sample was taken and added to a 1 mL flask containing a known amount of decane, dissolved with chloroform, and examined by GC, in order to obtain the initial concentration of the substrate. A known volume of titrated 35% H₂O₂ was added and the reaction was followed by GC, monitoring the decrease of ketone and the increase of lactone, until the concentration of the latter reached a plateau. All the reactions were repeated at least three times and were reproducible within experimental error.

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References

- 1 G. R. Krow, in *Comprehensive Organic Synthesis*, ed. B. M. Trost and I. Fleming, Pergamon Press, Oxford, 1991, Vol. 7, pp. 671–688.
- 2 C. M. Crudden, A. C. Chen and L. A. Calhoun, *Angew. Chem., Int. Ed.*, 2000, **39**, 2851–2855.
- 3 A. Berkessel, M. R. M. Andreae, H. Schmickler and J. Lex, *Angew. Chem., Int. Ed.*, 2002, **41**, 4481–4484.
- 4 Y. Itoh, M. Yamanaka and K. Mikami, *Org. Lett.*, 2003, **5**, 4803–4806.
- 5 R. R. Sever and T. W. Root, *J. Phys. Chem. B*, 2003, **107**, 10521–10530.
- 6 R. R. Sever and T. W. Root, *J. Phys. Chem. B*, 2003, **107**, 10848–10862.
- 7 S. Kobayashi, H. Tanaka, H. Amii and K. Uneyama, *Tetrahedron*, 2003, **59**, 1547–1552.
- 8 S. Stončius, U. Berg and E. Butkus, *Tetrahedron: Asymmetry*, 2004, **15**, 2405–2413.
- 9 K. Ito, A. Ishii, T. Kuroda and T. Katsuki, *Synlett.*, 2003, 643–646.
- 10 S.-I. Murahashi, S. Ono and Y. Imada, *Angew. Chem., Int. Ed.*, 2002, **41**, 2366–2368.
- 11 G.-J. Ten Brink, I. W. C. E. Arends and R. A. Sheldon, *Chem. Rev.*, 2004, **104**, 4105–4123.
- 12 M. T. Reetz, B. Brunner, T. Schneider, F. Schulz, C. M. Clouthier and M. M. Kayser, *Angew. Chem., Int. Ed.*, 2004, **43**, 4075–4078 and references therein.
- 13 M. T. Reetz, F. Daligault, B. Brunner, H. Hinrichs and A. Deege, *Angew. Chem., Int. Ed.*, 2004, **43**, 4078–4081.
- 14 S. Wang, M. M. Kayser, H. Iwaki and P. C. K. Lau, *J. Mol. Catal. B: Enzym.*, 2003, **22**, 211–218.
- 15 B. G. Kyte, P. Rouvière, Q. Cheng and J. D. Stewart, *J. Org. Chem.*, 2004, **69**, 12–17.
- 16 J. D. Carballeira, E. Álvarez and J. V. Sinisterra, *J. Mol. Catal. B: Enzym.*, 2004, **28**, 25–32.
- 17 M. D. Mihovilovic, F. Rudroff, W. Kandioller, B. Grötzl, P. Stanetty and H. Spreitzer, *Synlett.*, 2003, 1973–1976.
- 18 M. C. Gutiérrez, V. Alphand and R. Furstoss, *J. Mol. Catal. B: Enzym.*, 2003, **21**, 231–238.
- 19 P. L. A. Overbeeke, P. Schenkels, F. Secundo and J. A. Jongejan, *J. Mol. Catal. B: Enzym.*, 2003, **21**, 51–53.
- 20 R. Duchateau, T. W. Dijkstra, J. R. Severn, R. A. van Santen and I. V. Korobkov, *Dalton Trans.*, 2004, 2677–2682.
- 21 U. R. Pillai and E. Shale-Demessie, *J. Mol. Catal. A: Chem.*, 2003, **191**, 93–100.
- 22 A. Corma, M. T. Navarro and M. Renz, *J. Catal.*, 2003, **219**, 242–246.
- 23 M. Renz, T. Blasco, A. Corma, V. Fornés, R. Jensen and L. Nemeth, *Chem. Eur. J.*, 2002, **8**, 4708–4717.
- 24 C. Palazzi, F. Pinna and G. Strukul, *J. Mol. Catal. A: Chem.*, 2000, **151**, 245–252.
- 25 Y. Miyake, Y. Nishibayashi and S. Uemura, *Bull. Chem. Soc. Jpn.*, 2002, **75**, 2233–2237.
- 26 G.-J. Ten Brink, J.-H. Vis, I. W. C. E. Arends and R. A. Sheldon, *J. Org. Chem.*, 2001, **66**, 2429–2433.
- 27 C.-M. Che and J.-S. Huang, *Coord. Chem. Rev.*, 2003, **242**, 97–113 and references therein.
- 28 G. Strukul, *Top. Catal.*, 2002, **19**, 33–42.
- 29 G. Strukul, *Angew. Chem., Int. Ed.*, 1998, **37**, 1198–1209.
- 30 X. Hao, O. Yamazaki, A. Yoshida and J. Nishikido, *Tetrahedron Lett.*, 2003, **44**, 4977–4980.
- 31 K. Mikami, Md. N. Islam, M. Yamanaka, Y. Itoh, M. Shinoda and K. Kudo, *Tetrahedron Lett.*, 2004, **45**, 3681–3683.
- 32 A. Brunetta and G. Strukul, *Eur. J. Inorg. Chem.*, 2004, 1030–1038 and references therein.
- 33 C. Chiappe and D. Pieraccini, *J. Phys. Org. Chem.*, 2005, in press.
- 34 T. Welton, *Chem. Rev.*, 1999, **99**, 2071–2083.
- 35 P. Wasserscheid and W. Keim, *Angew. Chem., Int. Ed.*, 2000, **39**, 3772–3789.

-
- 36 R.A. Sheldon, *Chem. Commun.*, 2001, 2399–2407.
- 37 P. U. Naik, S. J. Nara, J. R. Harjani and M. M. Salunkhe, *Can. J. Chem.*, 2003, **10**, 1057–1060.
- 38 J. A. Boon, J. A. Levisky, J. L. Pflug and J. S. Wilkes, *J. Org. Chem.*, 1986, **51**, 480–483.
- 39 I. Meracz and T. Oh, *Tetrahedron Lett.*, 2003, **44**, 6465–6468.
- 40 A. Behr, F. Naendrup and S. Nave, *Eng. Life Sci.*, 2003, **8**, 325–327.
- 41 J. S. Yadav, B. V. S. Reddy, J. S. S. Reddy and R. S. Rao, *Tetrahedron*, 2003, **59**, 1599–1604.
- 42 J. S. Yadav, B. V. S. Reddy, K. U. Gayathri and A. R. Prasad, *Synthesis*, 2002, 2537–2541.
- 43 I. Hemeon, C. Deamicis, H. Jenkins, P. Scammells and R. D. Singer, *Synlett.*, 2002, 1815–1818.
- 44 J. Howarth, K. Hanlon, D. Fayne and P. Mc Cormac, *Tetrahedron Lett.*, 1997, **38**, 3097–3100.
- 45 E. T. Silveira, A. P. Umpierre, L. M. Rossi, G. Machado, J. Morais, G. V. Soares, I. J. R. Baumvol, S. R. Teixeira, P. F. P. Fichtner and J. Dupont, *Chem. Eur. J.*, 2004, **10**, 3734–3740.
- 46 G. S. Fonseca, A. P. Umpierre, P. F. P. Fichtner, S. R. Teixeira and J. Dupont, *Chem. Eur. J.*, 2003, **9**, 3263–3269.
- 47 P. J. Dyson, *Appl. Organomet. Chem.*, 2002, **16**, 495–500.
- 48 C. P. Menhert, E. J. Mozeleski and R. A. Cook, *Chem. Commun.*, 2002, 3010–3011.
- 49 Y. Chauvin, L. Mussmann and H. Oliver, *Angew. Chem., Int. Ed.*, 1995, **34**, 2698–2700.
- 50 O. Bortolini, V. Conte, C. Chiappe, G. Fantin, M. Fogagnolo and S. Maietti, *Green Chem.*, 2002, **4**, 94–96.
- 51 O. Bortolini, S. Campestrini, V. Conte, G. Fantin, M. Fogagnolo and S. Maietti, *Eur. J. Org. Chem.*, 2003, 4804–4809.
- 52 C. E. Song and E. J. Roh, *Chem. Commun.*, 2000, 837–838.
- 53 C. Chiappe, V. Conte and D. Pieraccini, *Eur. J. Org. Chem.*, 2002, 2831–2837.
- 54 J. S. Yadav, B. V. S. Reddy, A. K. Basak and A. V. Narsaiah, *Chem. Lett.*, 2004, **33**, 248–249.
- 55 R. Bernini, A. Coratti, G. Fabrizi and A. Goggiamani, *Tetrahedron Lett.*, 2003, **44**, 8991–8994.
- 56 S. P. Panchgalle, U. R. Kalkote, P. S. Niphadkar, P. N. Joshi, S. P. Chavan and G. M. Chaphekar, *Green Chem.*, 2004, **6**, 308–309.
- 57 P. Wasserscheid and T. Welton, *Ionic Liquids in Synthesis*, Wiley-VCH, Weinheim, 2003.
- 58 R. Gavagnin, M. Cataldo, F. Pinna and G. Strukul, *Organometallics*, 1998, **17**, 661–667.
- 59 M. Del Todesco Frisone, F. Pinna and G. Strukul, *Organometallics*, 1993, **12**, 148–156.
- 60 V. Farmer and T. Welton, *Green Chem.*, 2002, **4**, 97–102.
- 61 G. S. Owens and M. M. Abu Omar, *J. Mol. Cat. A: Chem.*, 2002, **187**, 215–225.
- 62 P. A. Z. Suarez, J. E. L. Dullius, S. Einloft, R. F. de Souza and J. Dupont, *Polyhedron*, 1996, **15**, 1217–1219.
- 63 P. A. Z. Suarez, S. Einloft, J. E. L. Dullius, R. F. De Souza and J. Dupont, *J. Chim. Phys.*, 1998, 1626–1639.
- 64 L. Cammarata, S. G. Kazarian, P. A. Salter and T. Welton, *Phys. Chem. Chem. Phys.*, 2001, **3**, 5192–5200.
- 65 V. Conte, B. Floris, P. Galloni, V. Mirruzzo, A. Silvagni and D. Sordi, submitted.