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Nitrene transfer reactions catalysed by copper(I) complexes in ionic liquid using chloramine-T†

Israel Cano, M. Carmen Nicasio* and Pedro J. Pérez*

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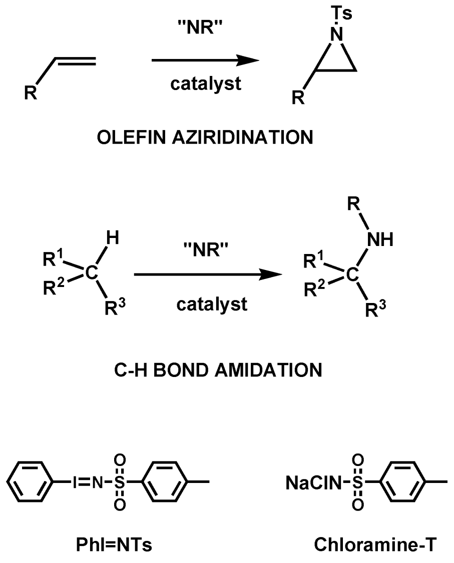
The complex [Tpm^{*,Br}Cu(NCMe)]BF$_4$ (Tpm^{*,Br} = HC(3,5-Me$_2$-4-Br-pyrazolyl)$_3$) catalyses the aziridination of alkenes and the amidation of cyclic ethers with chloramine-T as the nitrene source and the ionic liquid [bmim]PF$_6$ as the reaction medium (bmim = 1-*n*-butyl-3-methylimidazolium). High conversions have been obtained over several cycles of catalyst recovery and reuse.

Introduction

The catalytic formation of carbon-nitrogen bonds is an area of continuous research.[1] Aziridines represent valuable intermediates not only for the synthesis of wide range of nitrogen-containing products,[2] but also due to its presence in a number of naturally occurring compounds with cytotoxic activity.[3] Transition metal-catalyzed nitrene transfer to olefins is an efficient route to the direct synthesis of aziridines (Scheme 1).[4] A reaction which sometimes competes with aziridination is the insertion of the nitrene unit into C-H bond of substrates to yield amidation products (Scheme 1). Most of the work carried out in this area corresponds to homogeneous systems in which, at the end of the reaction, product purification supposes catalyst loss.[4] On the other hand, very few systems have been reported to promote the aziridination reaction under conditions that allow easy catalyst and product separation and further catalyst recycling.[5,6] In the last decade ionic liquids have emerged as a convenient reaction medium to favour catalyst and product separation,[7] although their use in these nitrene transfer catalytic transformations is yet scarce. We are only aware of two examples reporting the use of ionic liquids as reaction media in aziridination reactions by nitrene transfer to olefins. Kantam *et al.*[8] performed the aziridination of alkenes in [bmim]X (bmim = 1-*n*-butyl-3-methylimidazolium; X = BF$_4$, PF$_6$) using PhI=NTs[9] as the nitrene donor and Cu(acac)$_2$ as catalyst. Jain and Sain[10] reported the use of [bmim]X as reaction media as well as promoters for the metal-free aziridination of alkenes with chloramine-T and N-bromosuccinimide as catalyst. Regarding the amidation reaction, and to the best of our knowledge, there is no report on the use of ionic liquids as solvents to perform catalytic nitrene insertion into carbon-hydrogen bonds.



Scheme 1 Nitrene transfer reactions and nitrene sources.

During the last decade, we have developed a family of copper(I) complexes which contain hydrotris(pyrazolyl)borate[11] (Tp^x) ligands for carbene[12] and nitrene[13] transfer reactions to a variety of organic substrates in conventional organic solvents. In search of recyclable catalytic systems, we have recently developed a methodology involving the use of ionic liquid (IL) to immobilise the catalyst. This approach has been successfully applied in carbene transfer reactions[14] mediated by cationic Cu(I) complexes of formula [Tpm^{x}Cu(NCMe)]BF$_4$ containing tris(pyrazolyl)methane ligands (Tpm^x), the neutral analogue of anionic Tp^x ligands. On the basis of the aforementioned lack of reported catalytic systems for nitrene transfer and catalyst recycling, we have studied the use of those cationic copper complexes as catalysts for such process. Herein, we describe the catalytic capabilities of [Tpm^{x}Cu(NCMe)]BF$_4$ complexes immobilised in [bmim]PF$_6$[15] for alkene aziridination and C–H amidation reactions using chloramine-T as the nitrene source. It is worth mentioning that the most widely used nitrene source is N-tosyliminophenyl-iodinane, PhI=NTs,[4] in spite of the fact that its use supposes the generation of stoichiometric amounts of iodobenzene as by-product. In recent years chloramine-T (sodium N-chloro-*p*-toluensulfonamide), an inexpensive and commercially available oxidant, has become an alternative nitrogen source for aziridination and amidation reactions in the homogenous phase.[16]

Laboratorio de Catálisis Homogénea, Departamento de Química y Ciencia de los Materiales, Unidad Asociada al CSIC, Campus de El Carmen s/n, Universidad de Huelva, 21007, Huelva, Spain. E-mail: perez@dqcm.uhu.es, mcnica@dqcm.uhu.es; Fax: +34 959219942; Tel: +34 959219956

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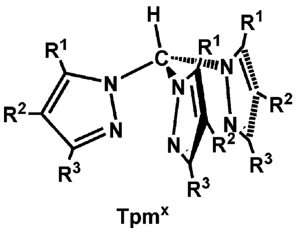
Results and discussion

Olefin aziridination

Initially, we screened a series of four [Tmp^{x}Cu(NCMe)]BF$_4$ (Fig. 1) complexes[14] dissolved in [bmim]PF$_6$ as potential catalysts for the aziridination of styrene using anhydrous chloramine-T[17] and different reaction conditions. The results are summarized in Table 1. In all cases, the desired aziridine was obtained in good yield (60–90%) along with small amounts of TsNH$_2$ as the only by-product. No aziridine formation was observed in the absence of catalysts. The best results (84% isolated yield) were obtained when using 5 mol% of **3** in [bmim]PF$_6$ (3 mL) over activated 4 Å molecular sieves with a styrene to chloramine-T mole ratio of 5:1 (entry 3). Such degree of conversion found for **3** was better than those previously described for metal mediated aziridination of styrene with chloramine-T,[16a–c,e,j] or bromamine-T[18] as nitrene sources in organic solvents and it is comparable to that reported by Xia and co-workers[16g] for aziridinations in aqueous media using CuI and a phase-transfer catalysts. However, in the only reported[10] example of chloramine-T employed under ionic liquid conditions, styrene was converted into the corresponding aziridine in 75% yield, slightly lower than in our case for **3** as the catalyst.

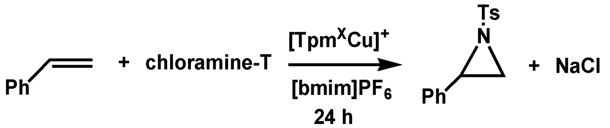


Ligand	R1	R2	R3
Tpm	H	H	H
Tpm*	Me	H	Me
Tpm*,Br	Me	Br	Me
TpmMs	H	H	Ms[a]

[a]Ms = Mesityl

Fig. 1 Tris(pyrazolyl)methane ligands used in this work.

Table 1 Aziridination of styrene with chloramine-T (CT) catalysed by [Tpm^{x}Cu(NCMe)]BF$_4$ in [bmim]PF$_6$[a]



Entry	Catalyst	Styrene/CT[b]	Yield (%)[c]
1	[TpmCu(NCMe)]BF$_4$, **1**	5:1	70 (51)[d]
2	[Tpm*Cu(NCMe)]BF$_4$, **2**	5:1	65 (50)[d]
3	[Tpm^{*,Br}Cu(NCMe)]BF$_4$, **3**	5:1	84 (73)[d]
4	[Tpm^{*,Br}Cu(NCMe)]BF$_4$, **3**	5:1	65[e]
5	[Tpm^{Ms}Cu(NCMe)]BF$_4$, **4**	5:1	70
6	[TpmCu(NCMe)]BF$_4$, **1**	10:1	62
7	[Tpm*Cu(NCMe)]BF$_4$, **2**	10:1	57
8	[Tpm^{*,Br}Cu(NCMe)]BF$_4$, **3**	10:1	70
9	[TpmCu(NCMe)]BF$_4$, **1**	2:1	61
10	[Tpm*Cu(NCMe)]BF$_4$, **2**	2:1	50
11	[Tpm^{*,Br}Cu(NCMe)]BF$_4$, **3**	2:1	76

[a] Reactions carried out for 24 h at room temperature in the presence of molecular sieves using 0.05 mol of the catalyst, 5% respect to chloramine-T (CT) in ionic liquid (3 mL) as the solvent. [b] Styrene/CT = styrene to chloramine-T mole ratio. [c] Isolated yields based on chloramine-T (average of two runs), TsNH$_2$ accounted for the remaining nitrene source. [d] In the absence of molecular sieves. [e] In biphasic medium ([bmim]PF$_6$-hexane).

Table 2 Reuse of [Tpm^{x}Cu(NCMe)]$^+$/[bmim]PF$_6$ in the catalytic aziridination of styrene with chloramine-T[a]

	Catalyst		
	1	2	3
Run	Yield[b] (conversion)[c]	Yield[b] (conversion)[c]	Yield[b] (conversion)[c]
1	52 (60)	64 (70)	83 (90)
2	70 (81)	65 (71)	85 (90)
3	70 (80)	70 (76)	92 (95)
4	60 (70)	60 (64)	83 (90)
5	35 (40)		81 (85)
6			61 (65)

[a] Reactions carried out for 24 h at room temperature in the presence of molecular sieves using 0.025 mol of the catalyst (5 mol%), 0.5 mmol of chloramine-T, 2.5 mmol of styrene in 3 mL of [bmim]PF$_6$. [b] Isolated yield (average of two runs). [c] Substrate conversion determined by NMR analysis using a internal standard.

Having optimized the reaction conditions, we examined the recyclability of the Cu(I)/[bmim]PF$_6$ catalytic systems in the aziridination of styrene. The Cu(I) complex (5 mol%) was dissolved in [bmim]PF$_6$ (3 mL) in the presence of molecular sieves and the substrate and chloramine-T (5:1 mol ratio respect to styrene) were added. Reactions were stirred for 24 h at room temperature. The aziridine was extracted from the reaction mixture with diethyl ether, leaving the catalyst[19] and NaCl in the ionic liquid phase, which was loaded with more chloramine-T and styrene. The results are displayed in Table 2 and plotted in Fig. 2. For catalysts **1** and **2** the yields were comparable for the first four runs, the low yield for the former in the first cycle being probably due to the presence of adventitious water. After the fourth run the yield decreased considerably suggesting a deactivation process of the catalytic system. However, complex **3** demonstrated to have better catalytic performance during five cycles, in an unprecedented behaviour compared to other recyclable systems for olefin aziridination reactions.[5,6,8,10] Only some deactivation was observed in the sixth run (Table 2, entry 6). It is interesting to point out that we did not attempt the removal of NaCl by-product from ionic liquid after each run. The role of the chloride anion will be discussed below.

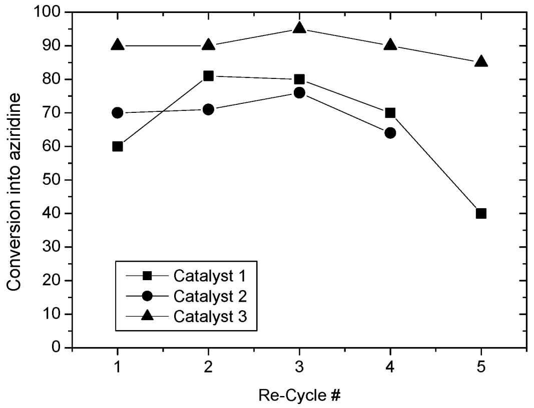
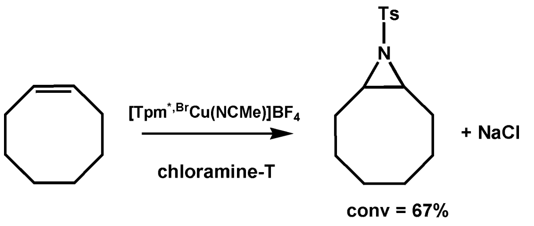


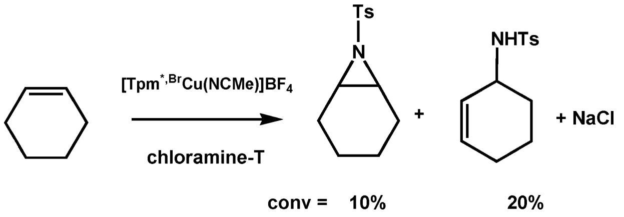
Fig. 2 Plot of the conversion *vs.* number of cycles for the aziridination of styrene with chloramine-T using complexes **1–3** as catalysts.

We have also studied the aziridination with chloramine-T of a series of cycloalkenes using **3** as catalyst (eqn (1)–(2)).

The yields of aziridines were significantly reduced relative to that obtained with styrene as substrate (the remaining of the initial nitrene precursor was converted into $TsNH_2$). Interestingly, cyclohexene was converted to a mixture of the 3-cyclohexenyl sulfonamide (20%), the allylic amidation product, together with the corresponding N-tosyl aziridine as the minor product (10%). It is worth mentioning that allylic insertion is rarely observed for copper-based aziridination catalysts.[16c,h,i]



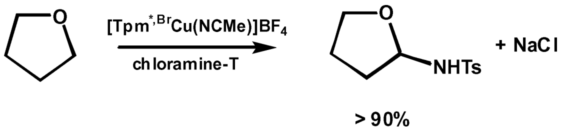
(1)



(2)

C–H bond amidation of tetrahydrofuran

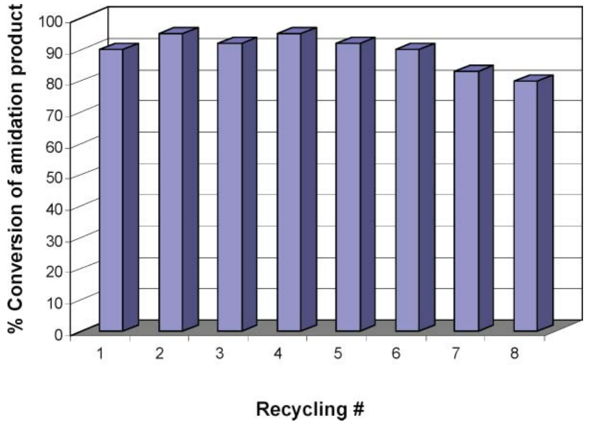
In view of the results found for cyclohexene, in which the amidation of a C–H bond was observed, we decided to use **3** in the amidation of the C–H bonds of tetrahydrofuran. In a typical experiment, chloramine-T (0.5 mmol) was added to a solution of **3** in $[bmim]PF_6$ (5 mol% with respect to the nitrene source) containing THF in excess (2 mL) in the presence of molecular sieves. The mixture was stirred at room temperature for 3 h and the product and excess of THF were extracted with diethyl ether. The conversion was examined by ^1H NMR affording 93% yield of α-tosylamino tetrahydrofuran (eqn (3)). The use of tetrahydropyran was also successful albeit with a lower conversion (60%). As mentioned above, there are no examples of catalytic amidation of C–H bonds by nitrene insertion in ionic liquids. We have previously reported the use of $Tp^{Br3}Cu(NCMe)$ as the catalyst and chloramine-T as the nitrene source for the quantitative conversion of thf into the nitrene insertion product.[13d] Other systems have also been reported with such degree of conversions but using PhI=NTs as the nitrene source.[13d,20] But the most interesting feature of this system is its potential to be reused. As shown in Table 3, up to eight cycles were run with an overall loss of efficiency of only 10%, again proving the potential of this system to separate catalyst and products and to be recycled for several times with an acceptable decrease of activity. It seems reasonable to propose that the differences in activity shown between cyclohexene and tetrahydrofuran must be related to their solubilities into the ionic liquid, since both C–H bonds display similar bond dissociation energies.[21]



(3)

Table 3 Reuse of $[Tpm^{*,Br}Cu(NCMe)]BF_4$ (**3**)/$[bmim]PF_6$ in the catalytic amidation of THF with chloramine-T[a]

Run	1	2	3	4	5	6	7	8
Yield[b] (Conv)[c]	83 (90)	80 (95)	84 (92)	83 (95)	77 (92)	78 (90)	74 (83)	76 (80)



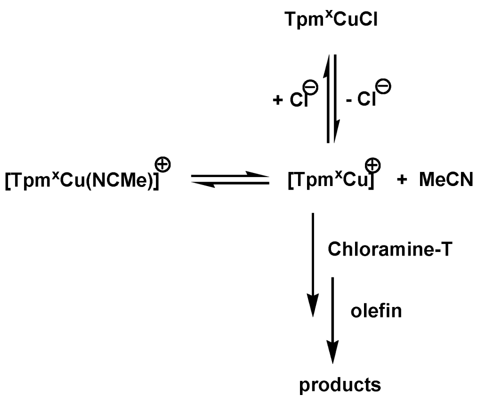
[a] Reactions carried out for 3 h at room temperature in the presence of molecular sieves using 0.025 mol of the catalyst (5 mol%), 0.5 mmol of chloramine-T, 2 mL of substrate in 3 mL of $[bmim]PF_6$. [b] Isolated yield (average of two runs). [c] Substrate conversion determined by NMR analysis using a internal standard.

The reaction medium and the catalytic species

In the system reported herein the ionic liquid $[bmim]PF_6$ acts as the sole reaction medium, in contrast to other examples reported in which the IL is part of a biphasic system. In our case, the reactants, the catalyst and the products are contained in the ionic liquid. It is worth mentioning that NMR studies carried out with a sample of the reaction mixture after the chloramine-T was consumed showed only the expected products and the ionic liquid, the latter remaining unaffected by the catalytic reaction. The catalytic reactions are performed in the presence of activated 4 Å molecular sieves to eliminate adventitious water from the reaction medium which is responsible for the formation of $TsNH_2$ as by-product. Blank experiments performed with molecular sieves in the absence of the copper complexes were unproductive, the molecular sieves being not active to induce these nitrene transfer reactions.

An interesting feature is the presence of chloride ions in the reaction mixture, formed upon decomposition of the nitrene source, chloramine-T. Davies and co-workers[22] have reported that halide impurity in ionic liquids dramatically drops the yield and enantioselectivity in the asymmetric cyclopropanation reaction of styrene catalysed by bis(oxazoline) Cu(I) complexes in ionic liquids. It seems that in our system, the presence of sodium chloride in high concentration in the ionic liquid had no influence on the yields at least during the first four catalytic runs. However, in a separate experiment, when chloramine-T was reacted with styrene in the presence of complex **3** as the catalysts and [bmim]Cl was added (80 equiv with respect to the catalyst), the reaction was completed inhibited. Since the cation is identical to that in the IL, it seems obvious that such inhibition is due to the chloride anions. The lack of observation of such effect due to accumulation of NaCl could be explained in terms of the different degree of dissociation of [bmim]Cl and NaCl in the IL, the latter being more associated in this medium.

To account for the above experimental results, we could invoke to the formation, in the reaction medium, of a neutral complex of composition Tpm^{x}CuCl, that would be in equilibrium with the cationic complex, the real catalytic species (Scheme 2). The relative amount of chloride ion in solution would govern the amount of such catalytic species. It is also worth mentioning that theoretical studies have shown that chloride ions in ionic liquids can interact with the medium, and therefore a competition with the above equilibrium could also occur.[23] When Tpm^{*,Br}CuI was employed as the catalyst precursor, in methylene chloride as the solvent, minor conversions (below 15–20%) were observed. This is in good accord with the cationic species [Tpm^{x}Cu]$^+$ being the real catalytic species: the neutral precursor delivers small amounts of the cationic species through the equilibrium shown in Scheme 2.



Scheme 2 Role of chloride ion.

Conclusions

In summary, we have shown that cationic tris(pyrazolyl)methane copper(I) complexes can be employed as catalysts in nitrene transfer reactions with readily available chloramine-T as nitrene source and the ionic liquid [bmim]PF$_6$ as the solvent. This protocol has proved to be efficient for the preparation of aziridines and C–H bond amidation products. The recovery and reuse of the catalytic system have been successfully demonstrated in both type of transformations. The use of [bmim]PF$_6$ as reaction medium in amidation reactions is unprecedented and opens up the scope of application of ionic liquids as alternative solvents in catalytic processes.

Experimental

General

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents and hydrocarbons were dried and degassed before use. Chloramine-T trihydrate was purchased from Aldrich and was dried by heating at 60 °C in an oil bath under vacuum for 6 h. Ionic liquid [bmim]PF$_6$[15] and the complexes [Tpm^{x}Cu(NCMe)]BF$_4$[24] were prepared according to literature procedures. NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer. ^{1}H chemical shifts were measured relative to partially deuterated solvent peaks but are reported relatively to tetramethylsilane.

General catalytic procedure for aziridination reactions

The catalyst (0.025 mmol, 5 mol%) was dissolved in [bmim]PF$_6$ (3 mL) in an ampoule containing 4 Å activated molecular sieves. The olefin (2.5 mmol) and dried chloramine-T (0.5 mmol) were added to the solution under a nitrogen atmosphere. The reaction mixture is stirred at room temperature for 24h. The product was extracted with diethyl ether (4 × 4 mL) and the organic solvent was evaporated to dryness to yield a crude solid residue which was investigated by ^{1}H NMR to determine the conversion using trimethyl vinyl silane (0.5 mmol) as internal standard. The crude residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (5:1) as eluent to afford the aziridination product. Aziridines and allylic amidation products were characterised by comparison of their spectroscopic data with those previously reported.

General catalytic procedure for amidation reactions of cyclic ethers

The catalyst (0.025 mmol, 5 mol%) was dissolved in [bmim]PF$_6$ (3 mL) in an ampoule containing molecular sieves. The substrate (2 mL) and dried chloramine-T (0.5 mmol) were added to the solution under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for the specified time period (see Table 5). Diethyl ether (4 mL) was added to separate the organic layer. The ionic liquid phase was washed with diethyl ethyl (3 × 4 mL). The combined organic solution was evaporated to dryness and the residue was investigated by ^{1}H NMR to determine the conversion (using trimethyl vinyl silane as internal standard). We observed that the amidation products decomposed on chromatography. To avoid decomposition, the crude residue was treated with hexane and filtered to remove *p*-toluenesulfonamide. The filtrates were evaporated and dried under vacuum to yield the pure amidation products. Compounds were characterised by comparing their ^{1}H NMR with the previously reported data.

Study of reuse of catalytic systems

The aziridination or amidation reaction was performed as described above. Once the product was extracted with diethyl ether the ionic liquid phase was dried under vacuum and charged with a second load of the substrate and chloramine-T (0.5 mmol) under nitrogen. The mixture was stirred at room temperature for a specific reaction period. After this time, the products were extracted with diethyl ether and the remaining solution of the catalyst in the IL was reused following the same procedure (see Tables 2 and 3).

Acknowledgements

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Notes and references

1 (*a*) S. V. Ley and W. A. Thomas, *Angew. Chem. Int. Ed.*, 2003, **42**, 5400; (*b*) M. Johannsen and K. A. Jorgensen, *Chem. Rev.*, 1998, **98**, 1689;

(*c*) T. E. Müller and M. Beller, *Chem. Rev.*, 1998, **98**, 675; (*d*) J. P. Wolfe, S. Wagaw, J. F. Marcoux and S. L. Buchwald, *Acc. Chem. Res.*, 1998, **31**, 805.

2 (*a*) I. D. Watson, L. Yu and A. K. Yudin, *Acc. Chem. Res.*, 2006, **39**, 194; (*b*) J. B. Sweeney, *Chem. Soc. Rev.*, 2002, **31**, 247.

3 (*a*) T. Fukuyama and L. Yang, *J. Am. Chem. Soc.*, 1989, **111**, 8303; (*b*) R. S. Coleman and J.-S. Komg, *J. Am. Chem. Soc.*, 1998, **120**, 3538.

4 (*a*) P. Müller and C. Fruit, *Chem. Rev.*, 2003, **103**, 2905; (*b*) J. A. Halfen, *Curr. Org. Chem.*, 2005, **9**, 657; (*c*) H. M. L. Davies and J. R. Meaning, *Nature*, 2008, **451**, 417.

5 (*a*) P. McMorn and G. J. Hutchings, *Chem. Soc. Rev.*, 2004, **33**, 108; (*b*) C. Jonsson, K. Hallman, H. Andersson, G. Stemme, M. Malkoch, E. Malmstrom, A. Hult and C. Moberg, *Bioorg. Med. Chem. Let.*, 2002, **12**, 1857.

6 (*a*) A. R. Silva, J. L. Figueiredo, C. Freire and B. de Castro, *Catal. Today*, 2005, **102**, 154; (*b*) J. M. Fraile, J. I. García, G. Lafuente, J. A. Mayoral and L. Salvatella, *Arkivoc*, 2004, 67; (*c*) J. Gullick, S. Taylor, P. McMorn, D. Bethell, P. C. Bulman-Page, F. E. Hancock, F. King and G. J. Hutchings, *J. Mol. Catal. A Chem.*, 2002, **182**, 571.

7 (*a*) H. Weingärtner, *Angew. Chem. Int. Ed.*, 2008, **47**, 654; (*b*) V. I. Parvulescu and C. Hardacre, *Chem. Rev.*, 2007, **107**, 2615; (*c*) P. Wasserscheid and W. Keim, *Angew. Chem. Int. Ed.*, 2000, **39**, 3772; (*d*) M. J. Earle and K. R. Seddon, *Pure Appl. Chem.*, 2000, **39**, 3772; (*e*) T. Welton, *Chem. Rev.*, 1999, **99**, 2071.

8 M. L. Kantam, V. Neeraja, B. Kavita and Y. Haritha, *Synlett*, 2004, **3**, 525.

9 Y. Yamada, T. Yamamoto and M. Okawara, *Chem. Lett.*, 1975, 361.

10 S. L. Jain and B. Sain, *Green Chem.*, 2006, **8**, 943.

11 S. Trofimenko, *Scorpionates, The Coordination Chemistry of Polypyrazolylborate Ligands*, Imperial College Press, London, 1999.

12 (*a*) M. M. Diaz-Requejo, T. R. Belderrain, M. C. Nicasio, S. Trofimenko and P. J. Pérez, *J. Am. Chem. Soc.*, 2002, **124**, 896; (*b*) A. Caballero, M. M. Díaz-Requejo, T. R. Belderrain, M. C. Nicasio, S. Trofimenko and P. J. Pérez, *J. Am. Chem. Soc.*, 2003, **125**, 1446; (*c*) A. Caballero, M. M. Díaz-Requejo, T. R. Belderrain, M. C. Nicasio, S. Trofimenko and P. J. Pérez, *Organometallics*, 2003, **22**, 4145; (*d*) M. M. Diaz-Requejo, T. R. Belderrain, M. C. Nicasio, S. Trofimenko and P. J. Pérez, *Dalton Trans.*, 2006, 5559 and references therein.

13 (*a*) Aziridination:M. A. Mairena, M. M. Díaz-Requejo, T. R. Belderrain, M. C. Nicasio, S. Trofimenko and P. J. Pérez, *Organometallics*, 2004, **23**, 253; (*b*) M. M. Díaz-Requejo, P. J. Pérez, M. Brookhart and J. L. Templeton, *Organometallics*, 1997, **16**, 4399; (*c*) C–H amidation:M. M. Díaz-Requejo, T. R. Belderrain, M. C. Nicasio, S. Trofimenko and P. J. Pérez, *J. Am. Chem. Soc.*, 2003, **125**, 12078; (*d*) M. R. Fructos, S. Trofimenko, M. M. Díaz-Requejo and P. J. Pérez, *J. Am. Chem. Soc.*, 2006, **128**, 11784.

14 (*a*) P. Rodríguez, A. Caballero, M. M. Díaz-Requejo, M. C. Nicasio and P. J. Pérez, *Org. Lett.*, 2006, **8**, 557; (*b*) P. Rodríguez, E. Álvarez, M. C. Nicasio and P. J. Pérez, *Organometallics*, 2007, **26**, 6661.

15 (*a*) J. S. Wilkes, J. A. Levisky, R. A. Wilson and C. L. Hussey, *Inorg. Chem.*, 1982, **21**, 1263; (*b*) P. A. Z. Suarez, J. E. L. Dullius, S. Einloft, R. F. de Souza and J. Dupont, *Polyhedron*, 1996, **15**, 1217.

16 (*a*) T. Ando, D. Kano, S. Minakata, I. Ryu and M. Komatsu, *Tetrahedron Lett.*, 1998, **39**, 309; (*b*) R. Vyas, B. M. Chanda and A. V. Bedekar, *Tetrahedron Lett.*, 1998, **39**, 4715; (*c*) D. P. Albone, P. S. Aujila, P. C. Taylor, S. Challenger and A. M. Derrick, *J. Org. Chem.*, 1998, **63**, 9569; (*d*) D. Kano, S. Minakata and M. J. Komatsu, *Chem. Soc. Perkin Trans. 1*, 2001, 3186; (*e*) L. Simkhovich and Z. Gross, *Tetrahedron Lett.*, 2001, **42**, 8089; (*f*) J. Gullick, S. Taylor, P. McMorn, D. Bethell, P. C. Bulm-Page, F. E. Hancock, F. King and G. Huchings, *J. Mol. Catal. A*, 2002, **180**, 85; (*g*) H. Wu, L.-W. Xu, C.-G. Xia, J. Ge, W. Zhou and L. Yang, *Catal. Commun.*, 2005, **6**, 221; (*h*) D. P. Albone, S. Challeger, A. M. Derrick, S. M. Fillery, J. L. Irwin, C. M. Parsons, H. Takada, P. C. Taylor and D. J. Wilson, *Org. Biomol. Chem.*, 2005, **3**, 107; (*i*) R. Bhuyan and K. M. Nicholas, *Org. Lett.*, 2007, **9**, 3957; (*j*) H. Martínez-García, D. Morales, J. Pérez, D. J. Coady, C. W. Bielawski, D. E. Gross, L. Cuesta, M. Márquez and J. L. Sessler, *Organometallics*, 2007, **26**, 6511.

17 Commercial chloramine-T·$3H_2O$ was dried heating the solid under vacuum at 60 °C in an oil bath for 5 h.

18 (*a*) B. M. Chanda, R. Vyas and A. V. Bedekar, *J. Org. Chem.*, 2001, **66**, 30; (*b*) A. M. M. Antunes, S. J. L. Marto, P. S. Branco, S. Prabhakar and A. M. Lobo, *Chem. Commun.*, 2001, 405; (*c*) R. Vyas, G.-Y. Gao, J. D. Harden and X. P. Zhang, *Org. Lett.*, 2004, **6**, 1907.

19 Due to the cationic nature of complexes used in this study, the amount of catalyst leached in the organic solution was negligible. This was confirmed by adding chloramine-T and styrene to the diethyl ether solution obtained after extraction. No aziridine formation was observed in any case after several days of stirring.

20 See: L. He, J. Yu, J. Zhang and X.-Q. Yu, *Org. Lett*, 2007, **9**, 2277 and references cited therein.

21 S. J. Blanksby and G. B. Ellison, *Acc. Chem. Res.*, 2003, **36**, 255.

22 D. L. Davies, S. K. Kandola and R. K. Patel, *Tetrahedron: Asymmetry*, 2004, **15**, 77.

23 (*a*) N. Sieffert and G. Wipff, *J. Phys. Chem. B*, 2007, **111**, 7253; (*b*) M. G. Del Pópolo, J. Kohanoff and R. M. Lynden-Bell, *J. Phys. Chem. B*, 2006, **110**, 8798.

24 (*a*) $Tpm^X = Tpm^*$ (see Fig. 1): D. L. Reger, J. E. Collins, A. L. Rheingold and L. M. Liable-Sands, *Organometallics*, 1996, **15**, 2029; (*b*) $Tpm^X = Tpm^{*,Br}$: M. Cvetkovic, S. R. Batten, B. Moubaraki, K. S. Murray and L. Spiccia, *Inorg. Chim. Acta*, 2001, **324**, 131; (*c*) $Tpm^X = Tpm^{Ms}$: ref. 14b.