Gold imidazolium-based ionic liquids, efficient catalysts for cycloisomerization of γ-acetylenic carboxylic acids

Florentina Neaţu,[a] Vasile I. Pârvulescu,[a] Véronique Michelet,[b] Jean-Pierre Gênet,[b] Alexandre Goguet[c] and Christopher Hardacre[cd]

Received (in Durham, UK) 22nd July 2008, Accepted 8th September 2008
First published as an Advance Article on the web 20th October 2008
DOI: 10.1039/b812580e

Ionic liquid stabilized gold(III) chloride is shown to be a very active catalyst in the cyclization of sterically hindered and unhindered acetylenic carboxylic acid substrates even in the absence of a base.

Introduction

Ionic liquids (ILs) have received significant attention recently because they exhibit several advantages over molecular solvents with respect to their environmental impact.[1] Catalytic reactions in ILs have been examined for at least 20 years and have been used for a wide variety of carbon–carbon bond forming reactions, which were the first to be undertaken in this media, and a number of good reviews cover the area of ILs.[2–6] The extensive interest stems from the fact that the properties of ionic liquids may be tuned in order to suit a particular application by varying the cation–anion combination systematically and thereby are useful engineering solvents. In addition, for chemical reactions, the ionic liquid provides an ionic environment which can significantly alter the reactivity and selectivity of processes compared with molecular solvents.[7]

The transition metal-catalyzed cyclization of 4-alkynoic acids constitutes a major route[8] for the construction of 5-membered exocyclic lactones and has been the subject of a large number of investigations.[9–14] Recently, a very attractive route to perform this reaction under mild conditions in the presence of gold was reported.[15,16] In our laboratory, the catalytic properties of AuCl and $AuCl_3$ for *gem*-substituted substrates, in the absence of base, was described[15] as well as the use of two heterogeneous systems Au_2O_3[17] and Au/beta.[18] These systems were found to be active for both substituted and unsubstituted substrates. In addition, the optimized heterogeneously catalyzed system was found to be recyclable.[22] Whilst gold has been shown to be highly active, it commonly undergoes significant deactivation due to the ease by which it may change its oxidation state and, in the case of nanoparticles, the catalyst particle size leading to instability in the form of the active catalyst.[19] Therefore, modalities which can enhance the stability are extremely important for practical applications.[20] These can be in the form of the solvent used or the nature of the support.[21] For example, stabilization of gold in the form of nanoparticles in ionic liquids by imidazolium derivatives has been reported.[22–25]

In this report the behavior of a 4 wt% Au/beta catalyst and a series of 1,3-dialkylimidazolium tetrachloroaurate salts in ionic liquids as catalysts for the cyclization of acetylenic substrates has been studied. Gold has recently been reported as a catalyst in ionic liquids in the hydration of phenylacetylene[26,27] and the syntheses of substituted 3(2*H*)-furanones,[27] 2,5-dihydrofurans[28] and substituted indoles.[29] However, with the exception of the $Co_2(CO)_8$-catalyzed intramolecular and intermolecular Pauson–Khand annelation using 1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4mim][PF_6]$) and tetrafluoroborate ($[C_4mim][BF_4]$) ionic liquids as solvents, no other related reactions to the cyclization of acetylenic substrates have been reported in ILs, to date.[30]

Experimental

Catalysts preparation

1. Au-beta catalyst. The catalyst was prepared by stirring 1 g of beta zeolite (PQ Corporation) for 3 h with 100 cm^3 of 1 M NH_4NO_3 at 353 K.[22] The slurry was filtered off and carefully washed with deionized water, dried for 6 h at 333 K and calcined for 24 h at 773 K. Deposition of gold was performed using the deposition–precipitation method. The support (1 g) was added to 100 cm^3 of an aqueous solution of $HAuCl_4$ (2.1×10^{-3} M) at 343 K which had previously adjusted to a pH = 8.5 with 0.2 M NaOH. The temperature of the slurry was maintained at 343 K under vigorous stirring for 3 h. Thereafter, the sample was filtered off, washed with deionized water to remove the free chloride and then dried under vacuum at 333 K for 24 h. The resultant catalyst contained 4 wt% Au as determined by ICP-AES analysis. This catalyst has been used as a reference material in these experiments.

2. Ionic liquids synthesis. Gold ionic liquids were synthesized using the method reported previously by Hasan *et al.*[25] Four 1-alkyl-3-methylimidazolium tetrachloroaurate ($[C_nmim][AuCl_4]$, n = 2, 4, 6, 18) ionic liquids were prepared by adding a 10% molar excess of $[C_nmim]Cl$ to tetrachloroauric

[a] *Department of Chemical Technology and Catalysis, University of Bucharest, B-dul Regina Elisabeta 4-12, 030016 Bucharest, Romania. E-mail: v_parvulescu@chem.unibuc.ro; Fax: +40 21 4010241*
[b] *Laboratoire de Synthèse Sélective Organique et Produits Naturels, ENSCP, UMR 7573, 11 rue P. et M. Curie, F-725231 Paris Cedex 05, France. E-mail: veronique-michelet@enscp.fr; Fax: +33 1 44071062*
[c] *CenTACat School of Chemistry and Chemical Engineering, Queen's University, Stranmillis Road, Belfast, Northern Ireland, UK BT9 5AG*
[d] *QUILL School of Chemistry and Chemical Engineering, Queen's University, Stranmillis Road, Belfast, Northern Ireland, UK BT9 5AG. E-mail: c.hardacre@qub.ac.uk; Fax: +44 28 90974687*

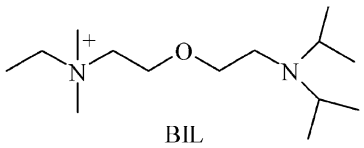


Fig. 1 Schematic of the cation of the basic ionic liquid (BIL) used as solvent for the cyclization of the functionalized acetylenic substrates **1a** and **1b**.

acid ($HAuCl_4{\cdot}4H_2O$, Alfa Aesar) resulting in the rapid formation of a yellow solid. Following heating to above its melting points with stirring for 0.5 h, the product was purified by recrystallization from benzene–acetonitrile in the volume ratio of 4 : 1. [$C_n$mim]Cl were prepared in house using standard literature methods.[31] Trihexyltetradecylphosphonium hydrogen sulfate ([P_{66614}][HSO_4]) was supplied by Cytec. 1-Butyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}-imide ([C_4mim][NTf_2]) and trihexyltetradecylphosphonium bis{(trifluoromethyl)sulfonyl}imide ([P_{66614}][NTf_2]) were formed by metathesis from [C_4mim]Cl and [P_{66614}]Cl (Cytec), respectively, according to literature methods.[32] The base functionalized ionic liquid 5-diisopropylamino-3-oxapentyl)-dimethylethylammonium bis{(trifluoromethyl)sulfonyl}imide (BIL) shown in Fig. 1 was synthesized as previously reported.[33] In all cases prior to reaction the ionic liquids were dried under vacuum at 50 °C overnight. All ionic liquids contained <0.16 wt% water determined by Karl–Fischer analysis and <5 ppm halide by suppressed ion chromatography. All other reagents were used as received.

Catalyst characterization

The solid catalysts were characterized by nitrogen adsorption–desorption isotherms at 77 K (Micromeritics ASAP 2000) after out-gassing the samples at 393 K for 12 h.

The XPS spectra were recorded using a Kratos Axis UltraDLD spectrometer with monochromatic Al-Kα radiation. The data were analyzed using Casa-XPS (v2.3.13) employing a Shirley-background subtraction prior to fitting. EXAFS data were collected at the Synchrotron Radiation Source in Daresbury, UK, using station 9.3. The spectra were recorded at the Au L_{III} edge using a double crystal Si(111) monochromator. Scans were collected and averaged. Data were processed using EXCALIB which was also used to convert raw data into energy *vs.* absorption data. EXBROOK was used to remove the background. The analysis of the EXAFS was performed using EXCURV98.[34] The gold concentration was determined by ICP-AES.

Catalytic tests

Typically 0.26 mmol of acetylenic acid was stirred with 2.5 mol% [$C_n$mim][$AuCl_4$] dissolved in 0.5 g [$C_n$mim]Cl in air at room temperature, until completion of the reaction. After the completion of the reaction, the reaction products were extracted three times with diethyl ether and the solvent completely removed under vacuum to give the corresponding lactone. ^{1}H and ^{13}C NMR were recorded on a Bruker AV 300 instrument operating at 300 Hz to identify the products. The measured NMR spectra for 3-phenyl-5-methylene-γ-butyrolactone (**2a**), 3-*n*-butyl-3-ethoxycarbonyl-5-methylene-γ-butyrolactone (**2b**), 3-methoxycarbonyl-5-methylene-3-(3′-phenylprop-2′-enyl)-γ-butyrolactone (**2c**), 3-allyl-3-methoxycarbonyl-5-methylene-γ-butyrolactone (**2d**), 3-benzyl-3-ethoxycarbonyl-5-methylene-γ-butyrolactone (**2e**) and 3-methoxycarbonyl-5-methylene-γ-butyrolactone (**2f**) were in good agreement were those reported previously.[19–21] In all cases, no cyclization is observed in the absence of any of the gold catalysts irrespective of the solvent used.

Results and discussion

Catalysts characterization

The beta zeolite used in these experiments had a surface area of 464 $m^2\ g^{-1}$ and a pore volume of 0.96 $cm^3\ g^{-1}$. After the deposition of gold (4 wt%) the surface area decreased to 383 $m^2\ g^{-1}$ and the pore volume to 0.80 $cm^3\ g^{-1}$. TEM analysis of this material shown an uniform size distribution with an average of 3 nm. The characterization of IL-stabilized gold(III) chloride was examined using TEM, XPS and EXAFS. Fig. 2 shows the XPS spectra of the Au 4f photoelectron emission corresponding to the mixture of the catalyst ([C_6mim][$AuCl_4$]) with the ionic liquid [C_6mim]Cl after the reaction. The binding energies of Au $4f_{7/2}$ and Au $4f_{5/2}$ levels were located at 90.0 eV and 86.3 eV, respectively. EXAFS of [C_6mim][$AuCl_4$] dissolved in [C_6mim]Cl showed a single peak at 0.22 nm associated with 4 chlorine atoms in the first coordination shell. During reaction, this peak decreases slightly and a small decrease in the white line of the XANES is observed. This variation may indicate that chlorine is being replaced by a lighter element such as coordination by the substrate during reaction, as would be expected. TEM analysis is in agreement with the XPS and EXAFS measurements and showed no nanoparticle formation. These observations are

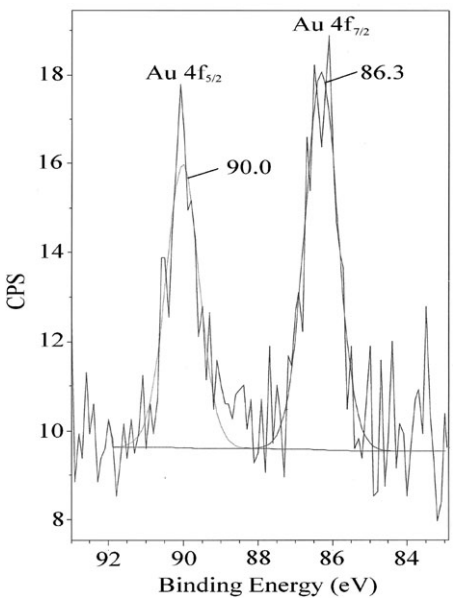


Fig. 2 The XPS spectra in the Au 4f region of the [C_6mim][$AuCl_4$] after reaction.

consistent with the presence of a dissolved Au(III) species with ~4 chlorines in the first coordination sphere.[35]

Catalytic tests

Table 1 shows the activity of Au/beta in a range of ionic liquids for the cyclization of the functionalized acetylenic substrates **1a** and **1b**.

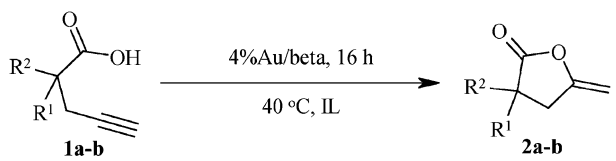
Although cycloisomerization of substrate **1a** did occur in the BIL and $[P_{66614}][HSO_4]$ with conversions of 75 and 70%, respectively, (Table 1, entries 1, 2), the ILs could not be separated from the reaction products due to the high solubility of the ionic liquid–substrate mixture in diethyl ether. In the case of the reaction performed in $[C_4mim][NTf_2]$ and $[P_{66614}][NTf_2]$, the ionic liquid could only be partially separated from the reactants and products and showed conversion of the substrate of 80% and 70%, respectively (Table 1, entries 3, 4). In each case, the conversions were obtained from NMR determination in the ionic liquid. $[C_6mim]Cl$ was found to separate efficiently from diethyl ether and the cycloisomerization of **1a** (Table 1, entry 5) resulted in the desired compound **2a** in 79% isolated yield.

Due to the ease of workup $[C_6mim]Cl$ was also examined as a medium for the cyclization of **1b** over Au/beta. From an analysis of the ^1H NMR, a conversion of 91% was obtained with an isolated yield of the lactone of 58% (Table 1, entry 6). Similar activities and selectivities were also found in conventional molecular solvents, such as acetonitrile (Table 1, entry 7).

The heterogeneously catalyzed reaction results were compared with the use of the ionic liquid as a catalyst in the form of the tetrachloroaurate based ionic liquids. Since $[C_6mim][AuCl_4]$ is a solid at room temperature, $[C_6mim]Cl$ was used as solvent. The results are summarised in Table 2.

To date, it has only been possible to exclude a base from the homogeneous reaction conditions if the two substituents on a tetrahedral centre were of a significant size, as understood by the Thorpe–Ingold effect.[36] In the case of the ionic liquid catalyst system, all the γ-acetylenic carboxylic acids examined

Table 1 Cyclization of functionalized acetylenic substrate over Au/beta in a range of ionic liquids



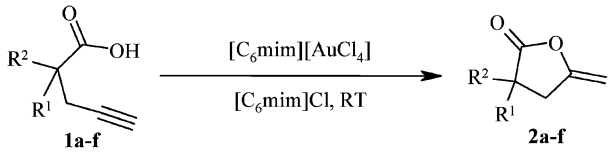
1a-b **2a-b**

1a: R^1 = Ph; R^2 = H
1b: R^1 = CO_2Et; R^2 = n-Bu

Entry	R^1	R^2	Solvent	Product	Yield[a] (Conv.) (%)
1	Ph	H	BIL	**2a**	(75)[b]
2	Ph	H	$[P_{66614}][HSO_4]$	**2a**	(70)[b]
3	Ph	H	$[P_{66614}][NTf_2]$	**2a**	(70)[b]
4	Ph	H	$[C_4mim][NTf_2]$	**2a**	(80)[b]
5	Ph	H	$[C_6mim]Cl$	**2a**	79 (83)
6	CO_2Et	*n*-Bu	$[C_6mim]Cl$	**2b**	58 (91)
7	CO_2Et	*n*-Bu	CH_3CN	**2b**	60 (90)

[a] Isolated yield. [b] IL inseparable from the system.

Table 2 Au-catalyzed cyclization of functionalized carboxylic acids



1a-f **2a-f**

1a: R^1 = Ph; R^2 = H
1b: R^1 = CO_2Et; R^2 = *n*-Bu
1c: R^1 = CO_2Et; R^2 = cinnamyl
1d: R^1 = CO_2Me; R^2 = allyl
1e: R^1 = CO_2Et; R^2 = Bn
1f: R^1 = CO_2Me; R^2 = H

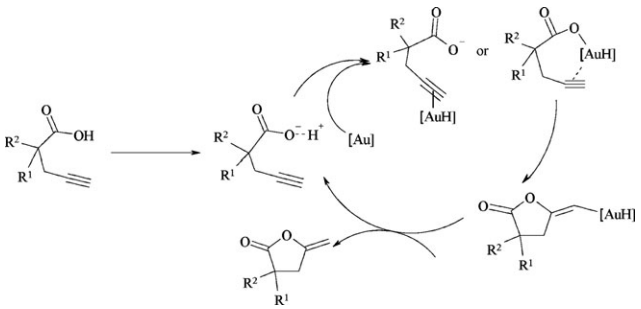
Entry	R^1	R^2	Product	Temp./°C	Time/h	Yield[a] (%)
1	CO_2Et	*n*-Bu	**2b**	RT	1	96
2	CO_2Me	Cinnamyl	**2c**	40	2	90
3	CO_2Me	Allyl	**2d**	RT	2	91
4	CO_2Et	Bn	**2e**	RT	1	85
5	CO_2Et	Bn	**2e**	RT	2	95
6	CO_2Me	H	**2f**	RT	1	84
7	Ph	H	**2a**	RT	1	96

[a] Isolated yield.

were cleanly transformed to the corresponding γ-alkylidene γ-butyrolactones. Moreover, similar activity and selectivity was found for the ionic liquid catalyst compared with the homogeneous AuCl catalysts system in acetonitrile.[15] Irrespective of the alkenyl side chain length the lactones were isolated in 85–96% yields (Table 2, entries 1–5) even at room temperature. In all cases, the catalytic amount of gold ionic liquid used in these reactions was equivalent to the amount used under heterogeneous conditions. No side reactions were observed on the alkenyl side chains during the course of the reaction.

Using the gold based ionic liquid system, complete transformations of 2-prop-2-ynylmalonic acid monomethyl ester **1f** with an 84% isolated yield (Table 2, entry 6) and of 2-phenylpent-4-ynoic acid **1a** with an 96% isolated yield (Table 2, entry 7) after 1 h at room temperature were obtained. Similar results were found for the reaction of **1a** in the presence of $[C_2mim][AuCl_4]$, $[C_4mim][AuCl_4]$ and $[C_{18}mim][AuCl_4]$ at room temperature. These results for unsubstituted substrates are comparable with those obtained under heterogeneous Au_2O_3 conditions (3 h),[21] or homogeneous $AuCl/K_2CO_3$ conditions (2 h)[20] and show significant advantages over other homogeneous gold chloride based catalysts.[19] In the case of the homogeneous catalysts, the formation of degradation products or the corresponding methylketone was observed for the sterically unhindered substrates and the reaction only occurred in the presence of a base. In the ionic liquid catalyzed reactions, excellent reactivity was found without the need for additives. Furthermore, the IL-catalysts were recycled three times without any loss in conversion or yields.

A comparison of the homogeneous reaction (Table 2, entries 7 and 1) with that of the heterogeneous reaction (Table 1, entries 5 and 6) indicates that the former is more active requiring a lower temperature and resulting in a higher conversion/yield after 1 h. This is reflected in the turnover frequencies (TOF) for the homogeneous catalysts compared with the supported catalysts which are ~19.8 h^{-1} (at RT) and ~1.3 h^{-1} (at 40 °C), respectively, for the formation of **2b**, for example. The lower rate is unlikely to be due to mass transfer



Scheme 1 The mechanism of cyclization of acetylenic carboxylic acid using Au^{3+} derived catalysts. It should be noted that representation of the gold as [Au] is for illustrative purposes only and will exist in the form of a $[AuCl_x]^{y+}$ complex.

limitations in the heterogenous case which has been observed in other solid catalyzed reactions in ionic liquids[37] as the acetonitrile reaction (Table 1, entries 6 and 7) also shows reduced activity. The higher TOF may be expected due to the inaccessibility of the bulk gold atoms; however, even taking into account the lower dispersion of the heterogeneous catalyst, which contains 3 nm gold particles, the homogeneous catalyst has a higher intrinsic activity compared with the heterogeneous system.

Scheme 1 shows a proposed mechanism for the gold based ionic liquid catalyzed reaction. From the XPS and EXAFS, the active catalyst is thought to be Au^{3+} which activates the acetylenic group.[20] The ionic liquid provides a medium which eliminates the use of a base. This role of the ionic liquid may be to shift the acid equilibrium of the starting material to favour the carboxylate anion, either by hydrogen bonding with the chloride, for example, or *via* stabilizing the anion in the ionic environment. This increase in concentration of the active intermediate allows reaction and activation of the carbon–carbon triple bond by the Au^{3+} centre and nucleophilic addition to the alkyne. After the cyclization a hydrogen mediated demetalation ends the catalytic cycle. It should be noted that the scheme does not preclude the possibility that the cation of the ionic liquid may play an important role in creating the active catalyst. For example, imidazolium based ionic liquids have been shown to form carbenes with homogeneous catalysts in C–C bond forming reactions.[10]

Conclusions

Gold chloride based ionic liquids have been shown to be very active catalysts in the cyclization of acetylenic substrates. The ionic liquid medium prevents nanoparticle formation *via* stabilization of the gold in the form of isolated species by chlorine coordination. The ionic liquid also allows activation of the carboxylic acid in the starting material and provides a medium which eliminates the need for added base in order to cyclize unhindered acetylenic carboxylic acid.

Acknowledgements

This work was financially supported by the Consiliul National al Cercetarii Stiintifice din Invatamantul Support (CNCSIS) and the Centre National de la Recherche Scientifique (CNRS), a Portfolio partnership from the EPSRC and an EU transnational grant. CCLRC are thanked for providing EXAFS beamtime.

References

1 J. A. Boon, J. A. Levinsky, J. I Pflug and J. S. Wilkes, *J. Org. Chem.*, 1986, **51**, 480.
2 *Ionic Liquids IIIA and B: Fundamentals, Progress Challenges and Opportunities–Properties and Structure*, eds. R. D. Rogers and K. R. Seddon, American Chemical Society, Washington DC, 2005.
3 J. S. Wilkes, *J. Mol. Catal., A: Chem.*, 2004, **214**, 11.
4 *Ionic Liquids in Synthesis*, eds. P. Wasserscheid and T. Welton, Wiley-VCH, Weinheim, 2007.
5 C. Hardacre, *Annu. Rev. Mater. Res.*, 2005, **35**, 29.
6 V. Pârvulescu and C. Hardacre, *Chem. Rev.*, 2007, **106**, 2615.
7 C. Hardacre, J. D. Holbrey, M. Nieuwenhuyzen and T. G. A. Youngs, *Acc. Chem. Res.*, 2007, **40**, 1146.
8 (*a*) F. Alonso, I. P. Beletskaya and M. Yus, *Chem. Rev.*, 2004, **104**, 3079; (*b*) M. Beller, J. Seayad, A. Tillack and H. Jiao, *Angew. Chem., Int. Ed.*, 2004, **43**, 3368; (*c*) I. Nakamura and Y. Yamamoto, *Chem. Rev.*, 2004, **104**, 2127; (*d*) for Ru-catalyzed intermolecular reactions, see C. Bruneau and P. H. Dixneuf, *Acc. Chem. Res.*, 1999, **32**, 311.
9 H. Imagawa, Y. Fujikawa, A. Tsuchihiro, A. Kinoshita, T. Yoshinaga, H. Takao and N. Nishizawa, *Synlett*, 2006, 639.
10 C. H. Oh, H. J. Yi and J. H. Lee, *New J. Chem.*, 2007, **31**, 835.
11 R. W. Spencer, T. F. Tam, E. Thomas, V. J. Robinson and A. Krantz, *J. Am. Chem. Soc.*, 1986, **108**, 5589.
12 Z. Huo, N. T. Patil, T. Jin, N. K. Pahadi and Y. Yamamoto, *Adv. Synth. Catal.*, 2007, **349**, 680; Z. Ahmed, U. Albrecht and P. Langer, *Eur. J. Org. Chem.*, 2005, 3469; A. Duchêne, J. Thibonnet, J.-L. Parrain, E. Anselmi and M. Abarbri, *Synthesis*, 2007, 597.
13 M. Jimenez-Tenotio, M. C. Puerta, P. Valerga, F. J. Moreno-Dorado, F. M. Guerra and G. M. Massanet, *Chem. Commun.*, 2001, 2324.
14 S. Elgafi, L. D. Field and B. A. Messerle, *J. Organomet. Chem.*, 2000, **607**, 97.
15 (*a*) E. Genin, P. Y. Toullec, S. Antoniotti, C. Brancour, J.-P. Genêt and V. Michelet, *J. Am. Chem. Soc.*, 2006, **128**, 3112; (*b*) E. Genin, P. Y. Toullec, S. Antoniotti, C. Brancour, J.-P. Genêt and V. Michelet, *ARKIVOC*, 2007, **v**, 67.
16 H. Harkat, J.-M. Weibel and P. Pale, *Tetrahedron Lett.*, 2006, **47**, 6273; for a recent Au-catalyzed cyclization of γ- and δ-acetylenic acids, see: E. Marchal, P. Uriac, B. Legoin, L. Toupet and P. van de Weghe, *Tetrahedron*, 2007, **63**, 9979.
17 P. Y. Toullec, E. Genin, S. Antoniotti, J.-P. Genêt and V. Michelet, *Synlett*, 2008, 707.
18 F. Neaţu, Z. Li, R. Richards, P. Y. Toullec, J.-P. Genêt, K. Dumbuya, J. M. Gottfried, H.-P. Steinrück, V. I. Pârvulescu and V. Michelet, *Chem.–Eur. J.*, 2008, **14**, 9412.
19 A. Abad, A. Corma and H. Garcia, *Chem.–Eur. J.*, 2008, **14**, 212 and references therein.
20 R. J. David, *Science*, 2003, **301**, 926, and references therein.
21 (*a*) Z.-R. Tang, J. K. Edwards, J. K. Bartley, S. H. Taylor, A. F. Carley, A. A. Herzing, C. J. Kiely and G. J. Hutchings, *J. Catal.*, 2007, **249**, 208; (*b*) S. Carrettin, A. Corma, M. Iglesias and F. Sanchez, *Appl. Catal., A*, 2005, **291**, 247.
22 K.-S. Kim, D. Demberelnyamba and H. Lee, *Langmuir*, 2004, **20**, 556.
23 H. Itoh, K. Naka and Y. Chujo, *J. Am. Chem. Soc.*, 2004, **126**, 3026.
24 R. Tatumi and H. Fujihara, *Chem. Commun.*, 2005, 83.
25 M. Hasan, I. V. Kozhevikov, M. R. H. Siddiqui, A. Steiner and N. Winterton, *Inorg. Chem.*, 1999, **38**, 5637.
26 M. Deetlefs, H. G. Raubenheimer and M. W. Esterhuysen, *Catal. Today*, 2002, **72**, 29.
27 Y. Liu, M. Liu, S. Guo, H. Tu, Y. Zhou and H. Gao, *Org. Lett.*, 2006, **8**, 3445.
28 O. Aksin and N. Krause, *Adv. Synth. Catal.*, 2008, **350**, 1106.
29 I. Ambrogio, A. Arcadi, S. Cacchi, G. Fabrizi and F. Marinelli, *Synlett*, 2007, 1775.
30 P. Mastrorilli, C. F. Nobile, R. Paolillo and G. P. Suranna, *J. Mol. Catal., A: Chem.*, 2004, **214**, 103.

31 C. M. Gordon, J. D. Holbrey, A. R. Kennedy and K. R. Seddon, *J. Mater. Chem.*, 1998, **8**, 2627; J. D. Holbrey and K. R. Seddon, *J. Chem. Soc., Dalton Trans.*, 1999, 2133; A. Downard, M. J. Earle, C. Hardacre, S. E. J. McMath, M. Nieuwenhuyzen and S. J. Teat, *Chem. Mater.*, 2004, **16**, 43.
32 P. Bonhôte, A. P. Dias, N. Papageorgiou, K. Kalyanasundram and M. Grätzel, *Inorg. Chem.*, 1996, **5**, 1168.
33 U. Fröhlich, PhD Thesis, Queens University, Belfast, 2005U. Fröhlich, P. Goodrich, H. Q. N. Gunaratne, C. Hardacre, A. McKeown and K. R. Seddon, to be published; C. Paun, J. Barklie, P. Goodrich, H. Q. N. Gunaratne, A. McKeown, V. I. Pârvulescu and C. Hardacre, *J. Mol. Catal., A: Chem.*, 2007, **269**, 64.
34 N. Binstead, EXCURV98: CCLRC Daresbury Laboratory computer program, 1998.
35 H. Kitagawa, N. Kojima and T. Nakajima, *J. Chem. Soc., Dalton Trans.*, 1991, 3121.
36 C. K. Ingold and J. F. Thorpe, *J. Chem. Soc., Trans.*, 1915, **107**, 1080.
37 P. N. Davey, S. A. Forsyth, H. Q. N. Gunaratne, C. Hardacre, A. McKeown, S. E. J. McMath, D. W. Rooney and K. R. Seddon, *Green Chem.*, 2005, **7**, 224.

