Imidazolium ionic liquids as promoters and stabilising agents for the preparation of metal(0) nanoparticles by reduction and decomposition of organometallic complexes

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The organometallic complexes ([Ru(COD)(2-methylallyl)$_2$] and [Ni(COD)$_2$] (COD = 1,5-cyclooctadiene) dissolved in imidazolium ionic liquids (ILs) undergo reduction and decomposition, respectively, to afford stable ruthenium and nickel metal(0) nanoparticles (Ru(0)-NPs and Ni(0)-NPs) in the absence of classical reducing agents. Depending on the case, the reduction/auto-decomposition is promoted by either the cation and/or anion of the neat imidazolium ILs.

Introduction

In recent years, ILs have proven their versatility in synthetic and catalytic applications, provoking ever-growing interest in both academic and industrial research. One particularly intriguing field is the synthesis of nanoscale metal catalysts of controlled size and shape, namely metal(0) nanoparticles (M-NPs).[1–4] ILs have unique and tuneable properties useful in the synthesis of M-NPs *via* chemical routes. This can be controlled simply by incorporating coordinating groups,[5–7] varying the coordination strength of the anion,[8,9] or changing the length of the alkyl-chain in the cation.[10–15] In general, appropriate metal complexes or metal salts are dispersed/dissolved in the IL and subsequently reduced to the corresponding M-NPs, in the ubiquitous presence of reducing reagents such as molecular hydrogen gas, complex hydrides (NaBH$_4$ and LiAlH$_4$), hydrazine,[1–4] alcohols,[16] and thiols.[17] In some cases, the IL itself can carry the reducing agent, *e.g.* hydroxylated imidazolium salts,[18,19] and depending on the redox potential of the metal precursor, the imidazolium cation may even undergo oxidation. For example, in the case of Au(III), the imidazolium cation itself can act as a reducing agent to yield prismatic gold particles in BMI·PF$_6$.[20]

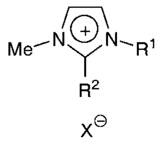
The preparation of M-NPs in ILs by simple decomposition of organometallic compounds in their formal zero oxidation states is invariably performed in the presence of hydrogen[11,21,22] or under thermal[8,15,23] or photolytic[9] conditions.

In this work, we report a novel approach for the synthesis of Ru(0)- and Ni(0)-NPs in imidazolium ILs, which act as incommensurably mild reducing/decomposing reagents for the organometallic complexes [Ru(COD)(2-methylallyl)$_2$] (COD = 1,5-cyclooctadiene) and [Ni(COD)$_2$] under very mild conditions. In these studies the role of both anion and cation is addressed and reaction pathways for the reduction/decomposition processes are proposed.

Results and discussion

The formation of Ru(0)-NPs using standard protocol with [Ru(COD)(2-methylallyl)$_2$] in IL (*i.e.* under 4 bar hydrogen at 50 °C)[7,14] was accompanied by the evolution of small amounts of odorous by-products (characteristic of ammonia/amines). This odour was particularly intense in the ILs BMI·NTf$_2$ and HM$_2$I·NTf$_2$ (Fig. 1).

The volatiles were thus analysed online in the gas phase with a mass gas-analyser. Indeed, compounds were detected with masses that could be assigned to small molecules formed due to the fragmentation of the imidazolium ring, such as acetonitrile/isocyanomethane (M^+ = 41), methylamine (M^+ = 29, MeN), ethylene (M^+ = 28) and hydrogen cyanide (M^+ = 27). Moreover, the observed C$_4$-fragment signals (M^+ = 56–58) provide strong evidence for the decomposition of the ruthenium complex [Ru(COD)(2-methylallyl)$_2$] involving the formation of isobutene/isobutane from the 2-methylallyl-ligand in the Ru(II) complex. Interestingly, the fragmentation of the IL seems to occur only during the reduction of Ru complex, but it is not promoted by the Ru(0)-NPs. The gaseous by-products were exclusively detected during the NP synthesis, but not when Ru(0)-NPs were stirred in BMI·NTf$_2$ and HM$_2$I·NTf$_2$ for a prolonged duration (several days) under identical conditions. A similar observation for the imidazolium ring fragmentation has previously been made, during the ultrasonic irradiation of imidazolium chloride



BMI.NTf$_2$, R^1= ^{n}Bu, R^2= H, X= N(SO$_2$CF$_3$)$_2$
HM$_2$I.NTf$_2$, R^1= ^{n}Hex, R^2= Me, X= N(SO$_2$CF$_3$)$_2$
BMI.BF$_4$, R^1= ^{n}Bu, R^2= H, X= BF$_4$
EMI.B(CN)$_4$, R^1= Et, R^2= H, X= B(CN)$_4$
BMI.N(CN)$_2$, R^1= ^{n}Bu, R^2= H, X= N(CN)$_2$
EMI.NTf$_2$, R^1= Et, R^2= H, X= N(SO$_2$CF$_3$)$_2$
BM$_2$I.NTf$_2$, R^1= ^{n}Bu, R^2= Me, X= N(SO$_2$CF$_3$)$_2$

Fig. 1 Structure of the ILs used in this study.

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at 135 °C, causing degradation of ILs.[24–26] However, herein the observed decomposition of the imidazolium ring is not clearly understood.

More interestingly, further investigations of the Ru(II)/IL reaction system revealed a more important result: the presence of hydrogen gas as a reducing reagent for the Ru complex seems to be obsolete. Stirring a mixture of the complex in $HM_2I \cdot NTf_2$ under argon atmosphere at 50 °C for a prolonged period (2 days) resulted in a dark brown/black colloidal solution. Samples for TEM analysis were prepared by placing a small amount of the Ru(0)-NPs dispersed in $HM_2I \cdot NTf_2$ onto a holey carbon film supported by a copper grid. The diameters of the particles in the micrographs were measured using the software Sigma Scan Pro 5. Size distribution histograms of the NPs were obtained by measuring the diameter of randomly selected particles, resulting in the particle size of 2.0 ± 0.3 nm (see Fig. 2) with a monomodal distribution.

The crystalline structure of the particles was confirmed by HR-TEM micrographs, analysed using *Gatan Digital Micrograph Software*. By means of HR-TEM measurements it was possible to obtain the Fourier transform images from which lattice spacings of 2.04 Å and 2.13 Å were measured. These lattice spacings correspond to the interplanar distances (1 0 1) and (0 0 2), respectively, of hcp Ru(0). Isolation of the Ru(0)-NPs for analysis by XRD was not possible, corroborating previous reports.[14,22] The size and size distribution of the ruthenium NPs were similar to those of Ru(0)-NPs previously generated using hydrogen gas as a reducing agent for the reduction of [Ru(COD)(2-methylallyl)$_2$] or decomposition of [Ru(COD)(COT)] (COT = 1,3,5-cyclooctatriene).[7,11,14,22]

The Ru(0)-NP formation led us to propose a reaction pathway in which the imidazolium ILs $BMI \cdot NTf_2$ and $HM_2I \cdot NTf_2$ might act as reducing agents for [Ru(COD)(2-methylallyl)$_2$]. Here the NTf_2 anion would act as a nucleophile[27,28] and attack the allylic-ligand of the complex (Schemes 1 and 2).

This stoichiometric reaction would cause the concomitant reduction of the Ru(II) complex and subsequent decomposition of the IL. Consequently, the ruthenium would lose its ligand-sphere and be reduced to ruthenium(0) atoms that coalesce generating the Ru(0)-NPs. It is proposed that during the reduction process of the Ru(II) complex, the first step involves a ligand exchange between the COD and a stronger coordinating ligand, occurring readily under the given reaction conditions.[29] A stronger coordinating ligand is easily provided in *neat* imidazolium ionic liquid as solvent, where classical and abnormal *N*-heterocyclic carbenes (NHCs) formed *in situ* might act as a ligand.[30,31] As a consequence, the NTf_2 anion would "lose" its counterion, thus enhancing its nucleophilicity. And this would favour its subsequent attack on the allylic species of the Ru(II) complex. The resulting ruthenium(0) metal atoms in the IL go on to generate the M-NPs. The isobutene by-product was detected by MS analysis of the gas phase (see above). However, attempts to detect the hypothesised by-product *N*-isobutene *N*-triflate in the liquid-phase by NMR were unsuccessful, presumably due to the very low concentration.

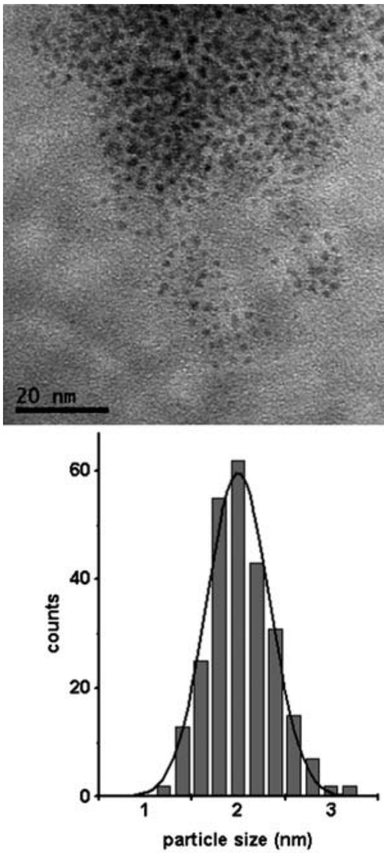
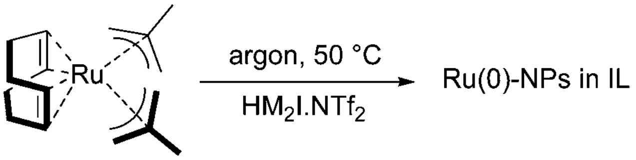
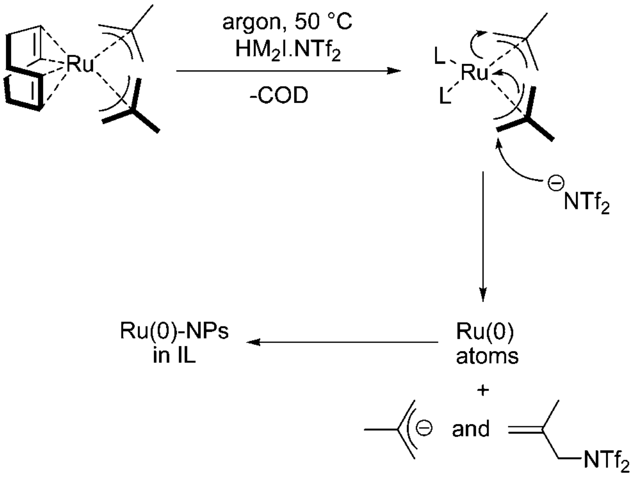


Fig. 2 Selected TEM image of Ru(0)-NPs (2.0 ± 0.3 nm) in $HM_2I \cdot NTf_2$ and the histogram of the NPs size distribution.



Scheme 1 Formation of Ru(0)-NPs in $HM_2I \cdot NTf_2$.



Scheme 2 Proposed reductive elimination of the allyl-ligand induced by the NTf_2 anion (L = ligand/solvent-IL).

To prove this pathway, the anion-effect in different imidazolium ILs was therefore investigated. When using the IL BMI·BF_4 (BF_4 = tetrafluoroborate), for example, a green suspension that showed no indication of IL decomposition or Ru(0)-NPs formation was obtained. Also, using EMI·$B(CN)_4$ and BMI·$N(CN)_2$, the strongly coordinating nature of the anions prevented the reduction of the Ru(II) complex and the reaction solution remained clear and colourless, even when subjected to a longer reaction time (5 days). Furthermore, the typical catalytic properties of nanoscale ruthenium catalysts in arene hydrogenation were tested with these Ru/IL-systems.[14] Indeed, the Ru(0)-NPs produced in HM_2I·NTf_2 showed the highest activity in toluene hydrogenation, resulting in conversions above 95% (4 bar H_2 at 75 °C, 18 h), similar to results previously reported.[14] The Ru(0)-NPs in BMI·NTf_2 were also active in toluene hydrogenation, but with a poorer conversion (55%) under the same conditions. In addition, the systems using the ILs BMI·BF_4, EMI·$B(CN)_4$ and BMI·$N(CN)_2$ were subjected to identical conditions, to gauge whether Ru(0)-NPs would form *in situ* during toluene hydrogenation. Indeed, the green suspension in BMI·BF_4 turned dark brown and the toluene was hydrogenated, albeit with low conversion (<20%), indicating the formation of Ru(0)-NPs. In contrast, the clear solutions in EMI·$B(CN)_4$ and BMI·$N(CN)_2$ turned slightly yellow, but no hydrogenation of toluene was observed.

The stability of [Ni(COD)$_2$] in imidazolium ILs was also investigated. This complex can be easily decomposed affording Ni(0)-NPs under hydrogen in organic solvents such as THF, in the presence of hexadecylamine (HDA) as the stabilising ligand or polyvinylpyrrolidone (PVP) as the polymer support.[32,33] In this case, cyclooctane is produced as a side product. Moreover, Ni(0)-NPs from the decomposition of [Ni(COD)$_2$] under hydrogen in imidazolium-based ILs have also been reported.[12,34] However, it is worth noting that in this previous work a substantial amount of benzene was used to aid the dissolution of [Ni(COD)$_2$] (6 mL of benzene for 2 mL of IL), and although effort was made to remove the volatiles before decomposition, it is not possible to be sure of the complete removal of benzene and therefore the media in which the decomposition actually occurred.[12,34]

In this work, spontaneous decomposition of [Ni(COD)$_2$] occurred upon dissolution at 25 °C, in both EMI·NTf_2 and BMI·NTf_2, in the absence of hydrogen. TEM was performed on the resulting black solutions and revealed in each case a mixture of Ni(0)-NPs (<10 nm) and sponge-like agglomerates of larger particles (Fig. 3). It can be seen from the TEM image that these sponge-like structures clearly consist of agglomerates of individual particles. This is completely different from previous findings, highlighting the important role of co-solvents.[12,34]

Notably ^{1}H NMR spectroscopy and gas chromatography performed on the resulting solution showed only a trace of cyclooctane, resulting from the hydrogenation of 1,5-COD ligand, the by-product of decomposition reported in the literature.[32,33] Instead, the presence of both 1,5-COD and its isomer 1,3-cyclooctadiene (1,3-COD) was detected by both gas chromatography and ^{1}H/^{13}C NMR spectroscopy. 1,3-COD must be a result of the isomerisation of 1,5-COD, which could only take place at a metal centre in the presence of Ni–H bond (Scheme 3).

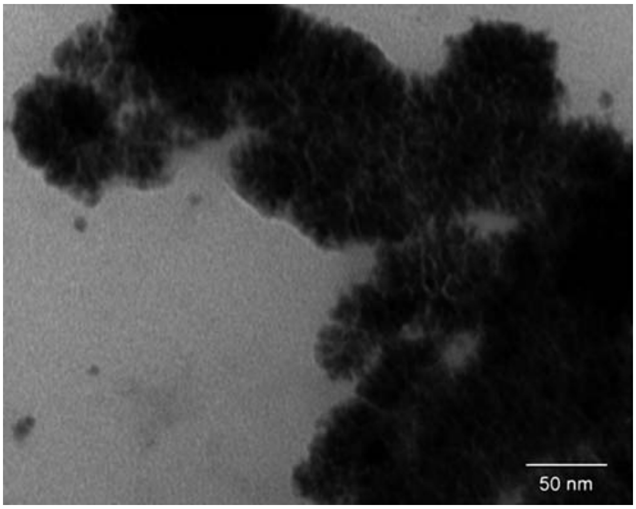
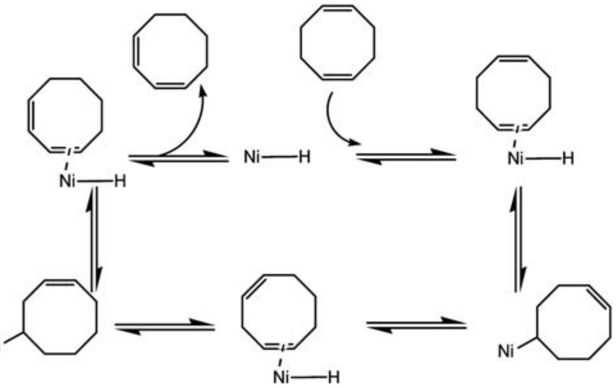


Fig. 3 Sponge-like agglomerates of Ni(0)-NPs formed by auto-decomposition of [Ni(COD)$_2$] in BMI·NTf_2.

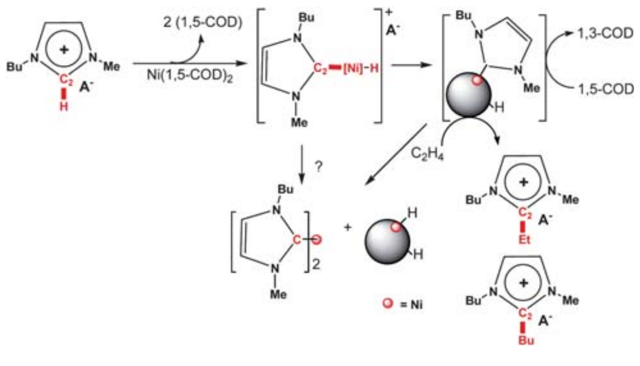


Scheme 3 Mechanism for the isomerisation of COD necessitating a Ni–H specie.

With Ru(0)-NPs, the presence of surface hydrides has been proven by hydrogenation of ethylene without the addition of H_2 by a solution of Ru(0)-NPs in IL.[35] This experiment was repeated for the Ni(0)-NPs formed by auto-decomposition of [Ni(COD)$_2$] in BMI·NTf_2. After treatment under ethylene atmosphere (4 bars, 100 °C, 24 h) no ethane was detected by GC as a result of ethylene hydrogenation, however, significant amounts of butenes and hexenes were detected, probably a result of oligomerisation of the ethylene. Interestingly, the formation of an ethyl substituted IL BMEI·NTf_2 (BMEI = 1-*n*-butyl-2-ethyl-3-methylimidazolium) was also observed by NMR spectroscopies (COSY, HETCOR and DOSY) and confirmed by electrospray mass spectrometry where cations at m/z = 139 and 167 were observed with similar abundances, corresponding to [BMI]$^+$ and [BMEI]$^+$, respectively. A small amount of the cation [B_2MI]$^+$ (B_2MI = 1,2-di-*n*-butyl-3-methylimidazolium) was also observed by mass spectrometry, m/z = 195, probably a result of oligomerisation of ethylene to 1-butene before reaction with the imidazolium cycle. The evidence gathered suggests that the observed decomposition could be due to the cleavage of the very acidic C2–H bond and the consequent *in situ* generation of NHC species, as already reported in the case of Ir(0)-NP preparation in ILs,[36–40] and with homogeneous complexes of Ni,[41] Pd,[42–44] Rh,[30,45] and Ir.[45] Cavell and co-workers have proposed a mechanism for the possible catalytic cycle for the imidazolium/alkene coupling reaction where the organometallic starting material was [Ni(OAc)$_2$].[46] The same phenomenon has also been observed in work by Lecocq and Olivier-Bourbigou who were investigating the oligomerisation behaviour of Ni in imidazolium ILs.[41] At this point it is impossible to determine whether the observed reactions (isomerisation of COD and formation of BMEI·NTf$_2$) occur on molecular or colloidal species. However, these results do prove that the cleavage of the C2–H bond occurs during the spontaneous decomposition on dissolution. The proposed mechanism of the reaction of imidazolium salts with low valent M(0) (M = Pd and Ni) hypothesises the formation of a molecular carbene–M–H species, as also proposed in the catalytic cycle for oligomerisation and formation of trialkylimidazolium species.[47,48] The presence of bis(imidazolylidene)nickel complexes [(NHC)$_2$NiH]$^+$ was also detected by mass spectrometry, implying that a molecular intermediate is in fact present as proposed. This may act as a transient species and could be the active species for the above mentioned reactions. Similar bis-carbene iodide nickel complexes have already been prepared in imidazolium ILs and isolated by Wasserscheid's group.[46] These were indeed found to be active in the dimerisation of butene carried out in ILs, although no production of Ni(0)-NPs was noted here, perhaps due to the presence of the strongly coordinating iodides. Although the exact mechanism remains unclear, from our investigations it is certain that the spontaneous decomposition of [Ni(COD)$_2$] on dissolution into the ILs with short alkyl chains involves attack on the acidic C2–H (Scheme 4).

To achieve the controlled generation of small-size Ni(0)-NPs, we must find a way of inhibiting this auto-decomposition in imidazolium ILs with short alkyl chains. Another strategy attempted in order to circumvent the problem was to use an IL which does not contain the most acidic C2–H proton such as BM$_2$I·NTf$_2$. Surprisingly, the [Ni(COD)$_2$] still decomposed on stirring, but this time afforded well dispersed Ni(0)-NPs (7.0 ± 2.0 nm, Fig. 4). This can only be explained by attack on the two less acidic protons C4–H, C5–H of the imidazolium ring and generation of transient non-classical NHC ligands.[31]

In another attempt to avoid auto-decomposition the NTf$_2$-anion was exchanged for the more strongly coordinating BF$_4$-anion, yielding important results. In this case, similarly to the case of [Ru(COD)(2-methylallyl)$_2$] the decomposition of [Ni(COD)$_2$] in BMI·BF$_4$ occurred not spontaneously but very slowly at 25 °C only under 4 bar of H$_2$, once again highlighting the importance of the NTf$_2$-anion. Therefore, as the auto-decomposition of [Ni(COD)$_2$] to Ni(0)-NPs was also observed uniquely in NTf$_2$-ILs, it is possible that the NTf$_2$ anion intervenes in the Ni(0)-NP formation through interaction with the COD ligands, similarly to the case of the Ru(II) complex.



Scheme 4 Reactions occurring during the auto-decomposition of [Ni(COD)$_2$] in imidazolium ILs.

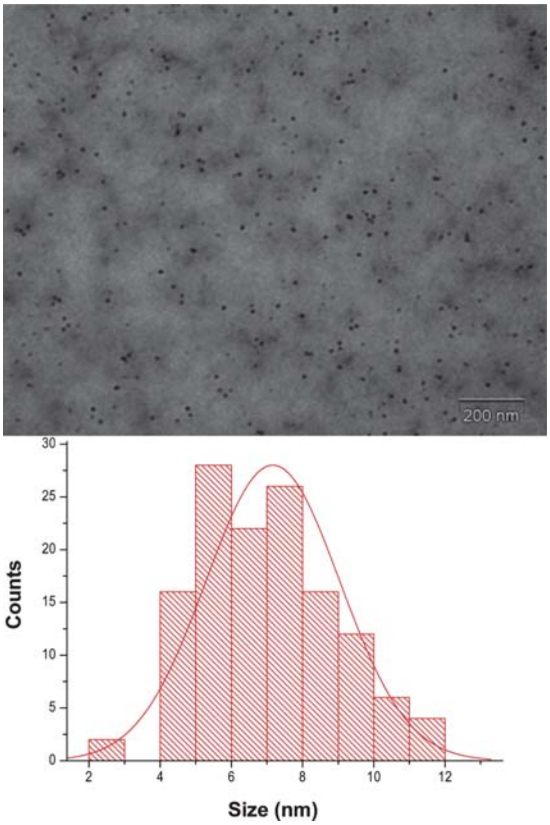


Fig. 4 TEM image of Ni(0)-NPs (7.0 ± 2.0 nm) formed by auto-decomposition of [Ni(COD)$_2$] in BM$_2$I·NTf$_2$ and size distribution histogram.

Conclusions

In summary, IL decomposition and simultaneous Ru(0)-NP formation are limited to imidazolium salts containing the NTf$_2$ anion. These results may explain how the Ru(0)-NPs formation is induced by imidazolium *N*-triflate ILs, but cannot explain the exact mechanism for the imidazolium ring fragmentation in small quantities. Most importantly, the formation of small-sized active ruthenium nanoscale hydrogenation catalysts is possible at low temperature and atmospheric pressure in the absence of classical and potentially dangerous reducing agents such as hydrogen gas (under elevated pressure), pyrophoric LiAlH$_4$ or hazardous hydrazine. Moreover, an unexpected spontaneous decomposition of [Ni(COD)$_2$] occurred without the addition of hydrogen for imidazolium ILs with short alkyl chains: ILs BMI·NTf$_2$, EMI·NTf$_2$ and BM$_2$I·NTf$_2$. In the case of ILs BMI·NTf$_2$ and EMI·NTf$_2$, TEM micrographs showed that Ni(0)-NPs of fairly large diameter were formed as well as sponge-like super agglomerates. However, for IL $BM_2I \cdot NTf_2$ well dispersed Ni(0)-NPs are formed. An explanation for the activation of the acidic protons on the imidazolium ring and the subsequent NHC formation that led to a rapid decomposition of the complex has been proposed. The additional interaction between the NTf_2 anion and the COD ligands on the Ni complex, which also may support the Ni(0)-NPs formation, cannot be excluded nonetheless. It is conceivable that this novel approach may be extended as a general access to M-NPs in imidazolium NTf_2-ILs, starting from organometallic complexes bearing only COD, allylic and/or olefinic ligands, such as [Co(COD)$_2$], [Ru(COD)(COT)], [Rh(allyl)$_3$], [Pd(COD)$_2$], [Pt(COD)$_2$] or [Pt(norbornene)$_3$].

Experimental

General

All manipulations were carried out under argon atmosphere. The organometallic complexes [Ru(COD)(2-methylallyl)$_2$] and [Ni(COD)$_2$] were purchased from Sigma-Aldrich and Strem Chemicals, respectively. For the ruthenium experiments, a Hiden QIC20 MS-QTOF gas-analyser was used for the gas phase analysis after the synthesis of Ru(0)-NPs. TEM analyses were performed in a JEOL-JEM 2010 microscope operating at 200 kV (*UFRGS-CME*, Brazil) and EDS, and used for catalytic experiments as previously described.[14] The HR-TEM was performed at the *"Centro de Tecnologias Estratégicas do Nordeste" (CETENE)*, Recife/Brazil. The ILs were synthesised as previously reported,[49] and ILs $EMI \cdot B(CN)_4$ and $BMI \cdot N(CN)_2$ were purchased from *Merck KGaA*, Germany.

In the case of nickel experiments, conventional TEM micrographs were obtained at the *"Centre Technologique des Microstructures"*, France, using a Philips 120 CX electron microscope operating at 120 kV. Size distribution histograms were constructed from the measurement of at least 200 different NPs assuming a near spherical shape and random orientation. Solution NMR spectra were recorded on Bruker Avance 300 MHz spectrometer for ^1H and ^{13}C. DRX 500 MHz for ^2H. Gas phase ^1H NMR spectra were obtained on a Bruker DRX 500 instrument at 298 K (nominal). Mass spectra were acquired on a ThermoFinnigan LCQ Advantage ion trap instrument, detecting positive (+) and negative (−) ions in the ESI mode. Samples (1 to 10 $\mu g\ mL^{-1}$ in acetonitrile) were infused directly into the source (5 $\mu L\ min^{-1}$) using a syringe pump. The following source parameters were applied: spray voltage 3.0–3.5 kV, nitrogen sheath gas flow 5–20 arbitrary units. The heated capillary was held at 200 °C. MS spectra were obtained by applying a relative collision energy of 25 to 40% of the instrumental maximum. The products were quantitatively analysed by gas chromatography on a P6890 chromatograph equipped with a flame ionisation detector (FID) and an Al_2O_3/KCl column (*L*: 50 m, diameter: 0.32 mm, and film thickness: 5 μm). The injector and detector temperature was 230 °C, and the injection volume was 1 μL. The temperature was fixed at 190 °C. The synthesis of ILs was carried out as previously reported.[43]

Synthesis of Ru(0)-NPs

In a typical experiment, a Fischer–Porter bottle was loaded with [Ru(COD)(2-methylallyl)$_2$] (30 mg, 0.094 mmol) under argon. Then, the IL $HM_2I \cdot NTf_2$ (1.5 mL) was added *via* syringe under an argon flow. The mixture was stirred at room temperature for 60 min, resulting in a turbid dispersion. The system was heated to 50 °C, and stirred under argon for two days resulting in a black suspension. The Fischer–Porter bottle was connected to a mass gas-analyser in order to evaluate the gas phase. After analysis the Fischer–Porter bottle was then kept under reduced pressure to eliminate the organic volatiles formed. An aliquot of the Ru(0)-NPs embedded in the IL was analysed by TEM.

Synthesis of Ni(0)-NPs

[Ni(COD)$_2$] (50 mg, 0.14 mmol) was stirred under argon in the ILs $BMI \cdot NTf_2$, $EMI \cdot NTf_2$ and $BM_2I \cdot NTf_2$ (10 mL) producing a pale yellow solution at 25 °C. After 1 h the solution had turned green and after a further hour a black solution resulted. Samples for TEM observations were prepared by placing a thin film of the Ni(0)-NPs dispersed in ILs on a copper grid coated with holey carbon film.

Oligomerisation of ethylene by Ni(0)-NPs in IL

A 2 mL sample of the Ni(0)-NPs solution in the IL was introduced under argon into a Schlenk of known volume. The sample was treated under flow of argon for 18 h. The argon atmosphere was replaced with a known pressure of ethylene using a vacuum line and the system was stirred. A decrease of the internal pressure was observed, and the composition of the gas phase was monitored by gas chromatography. After 12 h, the atmosphere was replaced by a H_2 atmosphere and the system was heated and stirred for 12 h. The composition of the gas phase was again monitored by gas chromatography.

Acknowledgements

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References

1 J. Dupont and J. D. Scholten, *Chem. Soc. Rev.*, 2010, **39**, 1780–1804.
2 P. Migowski and J. Dupont, *Chem.–Eur. J.*, 2007, **13**, 32–39.
3 H. Boennemann and K. S. Nagabhushana, *Nanoclusters in Catalysis and Materials Science: the Issue of Size Control*, ed. B. Corain, G. Schmid and N. Toshima, Elsevier B.V., Amsterdam, 2008, pp. 21–48.
4 H. Boennemann, K. S. Nagabhushana and R. M. Richards, *Nanoparticles and Catalysis*, Wiley-VCH, Weinheim, 2008.
5 Y. G. Cui, I. Biondi, M. Chaubey, X. Yang, Z. F. Fei, R. Scopelliti, C. G. Hartinger, Y. D. Li, C. Chiappe and P. J. Dyson, *Phys. Chem. Chem. Phys.*, 2010, **12**, 1834–1841.
6 Z. F. Fei, D. B. Zhao, D. Pieraccini, W. H. Ang, T. J. Geldbach, R. Scopelliti, C. Chiappe and P. J. Dyson, *Organometallics*, 2007, **26**, 1588–1598.
7 M. H. G. Prechtl, J. D. Scholten and J. Dupont, *J. Mol. Catal. A: Chem.*, 2009, **313**, 74–78.
8 E. Redel, R. Thomann and C. Janiak, *Inorg. Chem.*, 2008, **47**, 14–16.
9 E. Redel, R. Thomann and C. Janiak, *Chem. Commun.*, 2008, 1789–1791.

10 P. S. Campbell, C. C. Santini, F. Bayard, Y. Chauvin, V. Collière, A. Podgorsek, M. F. Costa Gomes and J. Sá, *J. Catal.*, 2010, **257**, 99–107.
11 T. Gutel, C. C. Santini, K. Philippot, A. Padua, K. Pelzer, B. Chaudret, Y. Chauvin and J. M. Basset, *J. Mater. Chem.*, 2009, **19**, 3624–3631.
12 P. Migowski, G. Machado, S. R. Texeira, M. C. M. Alves, J. Morais, A. Traverse and J. Dupont, *Phys. Chem. Chem. Phys.*, 2007, **9**, 4814–4821.
13 P. Migowski, D. Zanchet, G. Machado, M. A. Gelesky, S. R. Teixeira and J. Dupont, *Phys. Chem. Chem. Phys.*, 2010, **12**, 6826–6833.
14 M. H. G. Prechtl, M. Scariot, J. D. Scholten, G. Machado, S. R. Teixeira and J. Dupont, *Inorg. Chem.*, 2008, **47**, 8995–9001.
15 M. Scariot, D. O. Silva, J. D. Scholten, G. Machado, S. R. Teixeira, M. A. Novak, G. Ebeling and J. Dupont, *Angew. Chem., Int. Ed.*, 2008, **47**, 9075–9078.
16 H. J. Ryu, L. Sanchez, H. A. Keul, A. Raj and M. R. Bockstaller, *Angew. Chem., Int. Ed.*, 2008, **47**, 7639–7643.
17 L. Zhao, C. Y. Zhang, L. Zhuo, Y. G. Zhang and J. Y. Ying, *J. Am. Chem. Soc.*, 2008, **130**, 12586–12587.
18 S. Choi, K. S. Kim, S. H. Yeon, J. H. Cha, H. Lee, C. J. Kim and I. D. Yoo, *Korean J. Chem. Eng.*, 2007, **24**, 856–859.
19 K. S. Kim, S. Choi, J. H. Cha, S. H. Yeon and H. Lee, *J. Mater. Chem.*, 2006, **16**, 1315–1317.
20 Y. Gao, A. Voigt, M. Zhou and K. Sundmacher, *Eur. J. Inorg. Chem.*, 2008, 3769–3775.
21 E. T. Silveira, A. P. Umpierre, L. M. Rossi, G. Machado, J. Morais, G. V. Soares, I. L. R. Baumvol, S. R. Teixeira, P. F. P. Fichtner and J. Dupont, *Chem.–Eur. J.*, 2004, **10**, 3734–3740.
22 T. Gutel, J. Garcia-Anton, K. Pelzer, K. Philippot, C. C. Santini, Y. Chauvin, B. Chaudret and J. M. Basset, *J. Mater. Chem.*, 2007, **17**, 3290–3292.
23 D. O. Silva, J. D. Scholten, M. A. Gelesky, S. R. Teixeira, A. C. B. Dos Santos, E. F. Souza-Aguiar and J. Dupont, *ChemSusChem*, 2008, **1**, 291–294.
24 D. J. Flannigan, S. D. Hopkins and K. S. Suslick, *J. Organomet. Chem.*, 2005, **690**, 3513–3517.
25 J. D. Oxley, T. Prozorov and K. S. Suslick, *J. Am. Chem. Soc.*, 2003, **125**, 11138–11139.
26 S. Sowmiah, V. Srinivasadesikan, M. C. Tseng and Y. H. Chu, *Molecules*, 2009, **14**, 3780–3813.
27 S. Chowdhury, R. S. Mohan and J. L. Scott, *Tetrahedron*, 2007, **63**, 2363–2389.
28 R. Bini, C. Chiappe, E. Marmugi and D. Pieraccini, *Chem. Commun.*, 2006, 897–899.
29 J. P. Genet, S. Mallart, C. Pinel, S. Juge and J. A. Laffitte, *Tetrahedron: Asymmetry*, 1991, **2**, 43–46.
30 J. D. Scholten and J. Dupont, *Organometallics*, 2008, **27**, 4439–4442.
31 S. Grundemann, A. Kovacevic, M. Albrecht, J. W. Faller and R. H. Crabtree, *Chem. Commun.*, 2001, 2274–2275.
32 N. Cordente, C. Amiens, B. Chaudret, M. Respaud, F. Senocq and M. J. Casanove, *J. Appl. Phys.*, 2003, **94**, 6358–6365.
33 N. Cordente, M. Respaud, F. Senocq, M. J. Casanove, C. Amiens and B. Chaudret, *Nano Lett.*, 2001, **1**, 565–568.
34 P. Migowski, S. R. Teixeira, G. Machado, M. C. M. Alves, J. Geshev and J. Dupont, *J. Electron Spectrosc. Relat. Phenom.*, 2007, **156**, 195–199.
35 P. S. Campbell, C. C. Santini, D. Bouchu, B. Fenet, K. Philippot, B. Chaudret, A. A. H. Padua and Y. Chauvin, *Phys. Chem. Chem. Phys.*, 2010, **12**, 4217–4223.
36 L. S. Ott, S. Campbell, K. R. Seddon and R. G. Finke, *Inorg. Chem.*, 2007, **46**, 10335–10344.
37 L. S. Ott, M. L. Cline, M. Deetlefs, K. R. Seddon and R. G. Finke, *J. Am. Chem. Soc.*, 2005, **127**, 5758–5759.
38 L. S. Ott and R. G. Finke, *Inorg. Chem.*, 2006, **45**, 8382–8393.
39 J. D. Scholten, G. Ebeling and J. Dupont, *Dalton Trans.*, 2007, 5554–5560.
40 J. D. Scholten and J. Dupont, in *Iridium Complexes in Organic Synthesis*, ed. L. A. Oro and C. Claver, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2009, pp. 369–389.
41 V. Lecocq and H. Olivier-Bourbigou, *Oil Gas Sci. Technol.*, 2007, **62**, 761–773.
42 C. M. Crudden and D. P. Allen, *Coord. Chem. Rev.*, 2004, **248**, 2247–2273.
43 L. Magna, Y. Chauvin, G. P. Niccolai and J. M. Basset, *Organometallics*, 2003, **22**, 4418–4425.
44 M. H. G. Prechtl, J. D. Scholten and J. Dupont, *Molecules*, 2010, **15**, 3441–3461.
45 U. Hintermair, T. Gutel, A. M. Z. Slawin, D. J. Cole-Hamilton, C. C. Santini and Y. Chauvin, *J. Organomet. Chem.*, 2008, **693**, 2407–2414.
46 D. S. McGuinness, W. Mueller, P. Wasserscheid, K. J. Cavell, B. W. Skelton, A. H. White and U. Englert, *Organometallics*, 2002, **21**, 175–181.
47 N. D. Clement, K. J. Cavell, C. Jones and C. J. Elsevier, *Angew. Chem., Int. Ed.*, 2004, **43**, 1277–1279.
48 D. C. Graham, K. J. Cavell and B. F. Yates, *Dalton Trans.*, 2007, 4650–4658.
49 C. C. Cassol, G. Ebeling, B. Ferrera and J. Dupont, *Adv. Synth. Catal.*, 2006, **348**, 243–248.