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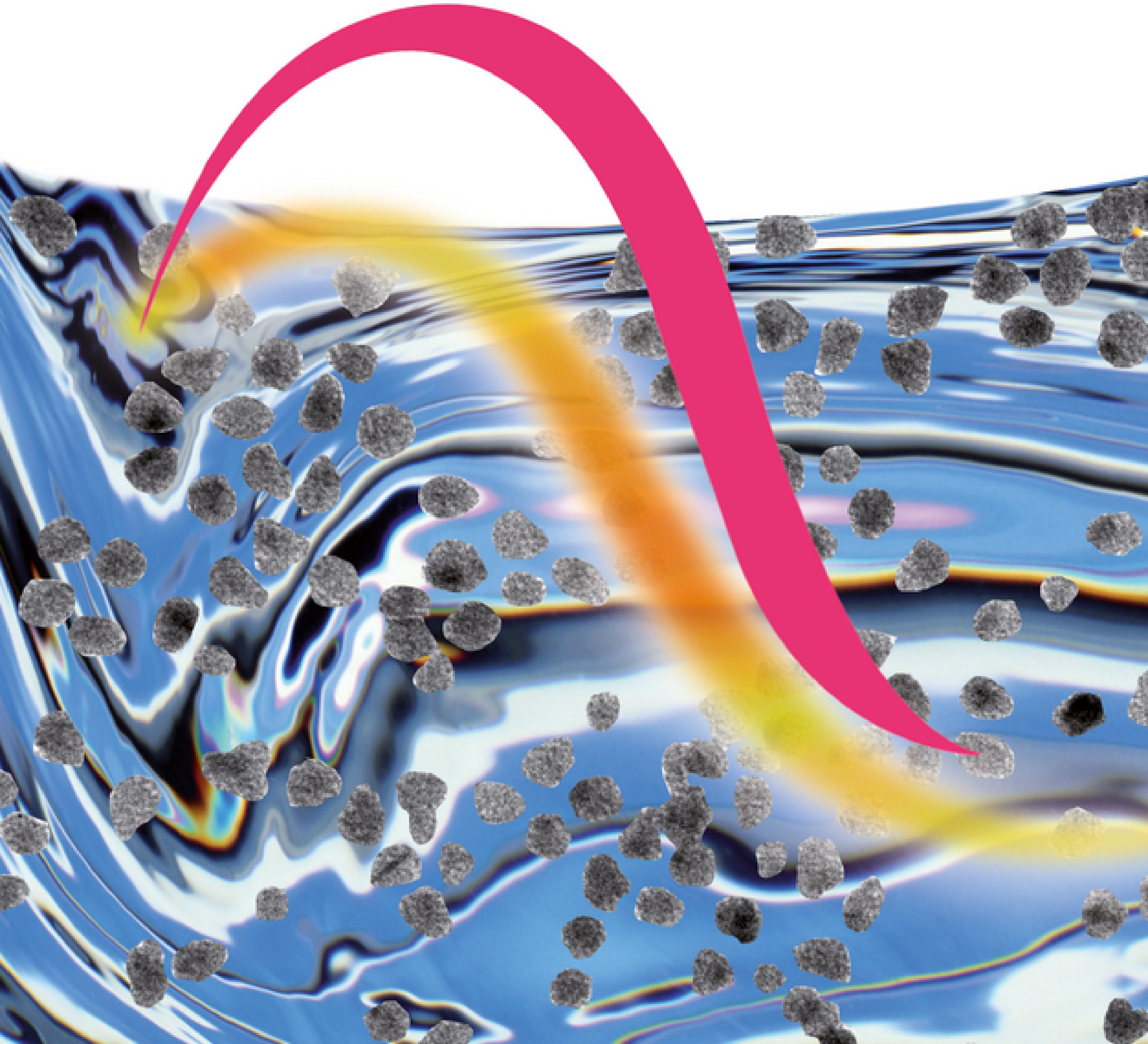
Nanocatalysis in Ionic Liquids

With a Foreword by Jairton Dupont



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Preface

The first room-temperature organic molten salt was reported by Peter Walden over 100 years ago in 1914 [1]. In the next decades, molten salts have been tested as solvents for biomass processing (1920s), and later as electrolytes (1950s) for the electrodeposition of aluminum. Interestingly it took again more than 20 years until molten salts, now also called *ionic liquids*, were reported as solvents for organic synthesis in the 1980s [2]. The first applications of ionic liquids (ILs) in catalysis was reported just in 1990, when Yves Chauvin (Nobel laureate 2005; 1930–2015) published the first nickel-catalyzed olefin dimerization reaction performed in water-sensitive organochloroaluminate molten salts under biphasic reaction conditions [3]. Later, in the mid-1990s, two manuscripts were submitted almost simultaneously (26 June 1995 and 18 August 1995) about rhodium-catalyzed hydrogenation in biphasic systems using for the first time air and water-stable ILs [4, 5]. Both Yves Chauvin and Jairton Dupont focused on imidazolium-based ionic liquids for the immobilization of the catalysts. Already these early works reported promising turnover numbers (15 000) and good catalyst recyclability. The robustness of these systems in terms of air- and moisture stability was a crucial factor for the later and wide spread application of such ILs. However, it has taken some more years, until for the new millennium more perspectives and future directions have been envisioned and propagated especially in review articles [6–8].

Contrary to the advent of the ILs application, the use of colloidal metals, hence solvated nanoparticles, goes back at least 2000 years and had been subject of scientific researches early as in the nineteenth century by Michael Faraday [9]. Nanoscale metals have been synthesized from chemical vapor in 1927 by Roginsky and Schalnikoff, [10] and applied in catalysis in the 1940s by Nord and coworkers [11]. Since then, the synthesis and uses of metal nanoparticles has spread over all fields of chemistry. Again in the 1990s, Manfred Reetz reported the synthesis of metal nanoparticles in zwitterionic surfactants [12] and the use of palladium nanoclusters stabilized by propylene carbonate for their use as active catalysts for the Mizoroki-Heck reaction [13]. At the same institute, already in 1991 Helmut Bonnemann reported the synthesis of metal nanoparticles using tetraalkyl ammonium hydrotriorganoborates as reducing agent for metal salts and the formed ammonium salts acted as stabilizing agent for the metal nanoparticles [14]. At about the same time, Bradley, Chaudret and colleagues turned their attention from synthesis of organometallic complexes to a novel approach toward the controlled decomposition of organometallics for the defined synthesis of metal nanoparticles for industrial application [15].

These early observations and applications about "laboratory curiosities" such as the use of molten salts in organic synthesis and the decomposition of metal precursors obviously have not fully revealed their potential. The above-mentioned contributions are examples of the vivid research activities toward the end of the last century and of course many other researchers were active as well.

It was only in the early 2000s that the above mentioned aspects of (i) multiphase catalysis in ionic liquids and (ii) controlled decomposition of metal precursors for metal nanoparticle formation started to merge into a single application: nanocatalysis in ionic liquids. These nanocatalysts revealed properties between single-site catalysts in homogeneous catalysis and multisite catalysts in heterogeneous catalysis. It was again Dupont *et al.* who presented a pioneering work about the use of ionic liquids as template for the synthesis of nanomaterials in ionic liquids and hybrid systems consisting of nanoparticles as catalysts and ionic liquids for multiphase catalysis [16]. In the next years, this new field started to take full ride and the field of application of those nanocatalysts in ILs broadened its diversity. Nowadays there are many examples in literature for different reaction types including hydrogenation, dehydrogenation, cross-coupling, C–H activation, and applications such as in organic synthesis (drug design, fine chemicals), new materials, biomass conversion, hydrogen storage, energy conversion, industrial implementation, flow processes, and so on.

This book presents a collection of selected topics about the progress of nanocatalysis in ionic liquids. The individual chapters are divided into two sections: (i) metals and (ii) specific applications. The chapters cover pioneering works, recent achievements, and discussion for future advancements in sustainable synthetic methods, technologies, and energy research. Besides hydrogenation and cross-coupling reactions, that is, hydrogen storage, water-splitting, biomass processing are subject to discussion as well as bottom-up and top-down synthetic methods for the preparation of metal nanoparticles.

It has been a pleasure and an inspiration to act as editor in this book. I am grateful to all the authors for their efforts in the production of this informative collection about nanocatalysis in ionic liquids. Thirty authors working in eight different countries contributed to 13 chapters reflect international diversity. Nanocatalysis and ionic liquids have become promising research fields in the last 20 years and there are many interesting things to investigate in the future.

Moreover, I am thankful to Dr Claudia Ley who has taken the initiative to discuss with me the adventure and idea for this book project in March 2014. Moreover, I thank Mrs Samanaa Srinivas as supportive project editor along the project. Last but not least, I am grateful to all my current and former collaboration partners, coauthors, students, mentors, family, and friends over the years.

March 2016

Martin H. G. Prechtl
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Foreword

Metal nanoparticles are only kinetically stable and consequently nanoparticles that are freely dissolved in solution must be stabilized in order to prevent their agglomeration. Unchecked, they can diffuse together and coalesce, eventually leading to the formation of the thermodynamically favored bulk metal. Indeed, since Faraday, various capping agents have been used to stabilize metal nanoparticles in aqueous or organic solvent solutions, rendering the investigation of the properties of freely dissolved metal nanoparticles a complex challenge. The advent of low-volatility ionic liquids as “liquid” support for the formation and stabilization of metal nanoparticles has opened not only a new avenue for the preparation of soluble “naked” metal nanoparticles but also the possibility to investigate the properties of these materials *in situ* employing techniques once almost restricted to solid state such as TEM and XPS. Moreover, ionic liquid is proved to be the ideal medium for multiphase catalytic systems, allowing not only the preparation and stabilization of transition-metal nanoparticles but also easy catalyst recycling and product separation, thus avoiding the environmental problems associated with the related aqueous and organic biphasic regimes. Doubtless ionic liquids are the most versatile liquid platform for the design and preparation of a new generation of modular soluble metal nanoparticle materials for catalytic transformations.

The field defined by *Nanocatalysis in Ionic Liquids* has had a transformative effect upon “soluble” metal nanoparticle catalysts and has given rise to an immense and exponentially growing field of literature: from fundamental understanding of the transformations occurring in a metal surface to applied advanced catalysis such as biomass transformation and water splitting. The editor Dr Prechtl has captured the essence of such a fast-moving field and has assembled an outstanding team of authors with many pioneering and leading contributions on the field. The end product is not only a state-of-the art collection of reports on the field, but constitutes an instructive guide for both experienced practitioners and newcomers, detailing new ways to approach soluble metal nanoparticle catalysis. Virtually all the areas of nanocatalysis are covered in this monograph encompassing the synthesis (bottom-up and top-down approaches), classical biphasic catalytic reactions (including reductions, oxidations, and coupling), and more advanced subjects such as supported ionic liquid phase catalysis and photocatalytic transformations.

This monograph provides new information and will certainly inspire and foster new avenues in the fascinating field of soluble metal nanoparticle catalysis in ionic liquids.

Nottingham, 18 April 2016 *Jairton Dupont*

Symbols and Abbreviations

Selected and Common Ionic Liquid Abbreviations

Cations

[Hmim]$^+$	1-Methylimidazolium
C$_1$, C$_2$, C$_4$, etc.	Methyl, ethyl, butyl, and so on
[C$_n$C$_{n'}$Im]$^+$	1,3 functionalized imidazolium
[C$_n$C$_{n'}$C$_{n''}$Im]$^+$	1,2,3 functionalized imidazolium
[C$_2$mim]$^+$/Emim	1-Ethyl-3-methylimidazolium
[C$_3$mim]$^+$	1-Propyl-3-methylimidazolium
[C$_4$mim]$^+$/Bmim	1-Butyl-3-methylimidazolium
[C$_4$mmim]$^+$	1,2-Dimethyl-3-butylimidazolium
[C$_5$mim]$^+$	1-Pentyl-3-methylimidazolium
[C$_6$mim]$^+$	1-Hexyl-3-methylimidazolium
[(C$_3$CN)C$_1$Im]$^+$	1-Butyronitrile-3-methylimidazolium
[C$_1$C$_1$(EG)Im]$^+$	1-(2,3-Dihydroxypropyl)-2,3-dimethylimidazolium
[C$_2$OHmim]$^+$	1-(2-hydroxyethyl)-3-methylimidazolium
[Cmmim]$^+$	1-Carboxymethyl-3-methylimidazolium
[ammim]$^+$	1-(3-Aminopropyl)-2,3-dimethylimidazolium
[C$_4$mPyr]$^+$/[C$_4$mp]$^+$	1-Butyl-1-methylpyrrolidinium
[C$_2$C$_6$Pip]$^+$	1-Ethyl-1-hexylpiperidinium
[P$_{6,6,6,14}$]$^+$	Trihexyl(tetradecyl)phosphonium
[N$_{6,6,6,14}$]$^+$	Trihexyl(tetradecyl)ammonium
[C$_4$mPy]$^+$	1-Butyl-3-methylpyridinium
[C$_4$CNpy]$^+$	*N*-Butyronitrile pyridinium
[C$_4$mmimDPA]$^+$	2,3-Dimethyl-1-[3-*N*,*N*-bis(2-pyridyl)propylamido]imidazolium
[TMG]$^+$	1,1,3,3-Tetramethylguanidinium

Anions

[OAc]$^-$	Acetate
[TFA]$^-$	Trifluoroacetate
[DBS]$^-$	Dodecylbenzene sulfonate

$[OTf]^-$	Trifluoromethanesulfonate
$[N(Tf)_2]^-$	Bis(trifluoromethylsulfonyl)imide
$[N(CN)_2]^-$/DCA	Dicyanamide
$[EtSO_4]^-$	Ethyl sulfate
$[HCO_2]^-$	Formate
$[PF_6]^-$	Hexafluorophosphate
$[NO_3]^-$	Nitrate
$[BF_4]^-$	Tetrafluoroborate
$[SCN]^-$	Thiocyanate
$[CF_3CO_2]^-$	Trifluoroacetate
$[CF_3SO_3]^-$	Trifluoromethanesulfonate
$[FAP]^-/[FEP]^-$	Trifluorotris(pentafluoroethyl)phosphate
tppts	Triphenylphosphine-3,3′,3″-trisulfonic acid trisodium salt

Part I
Synthesis, Characterization, and Evaluation of Nanocatalysts in Ionic Liquids

Nanocatalysis in Ionic Liquids, First Edition. Edited by Martin H.G. Prechtl.

1
Fe, Ru, and Os Nanoparticles

Madhu Kaushik, Yuting Feng, Nathaniel Boyce, and Audrey Moores

1.1
Introduction

Although Fe, Ru, and Os are transition metals all belonging to Group 8 of the periodic table, their prevalence, chemistry, and applications differ greatly. Iron is an earth abundant element, playing a key role in life with implications in some of the most difficult biological processes [1]. Iron is a current topic of interest in the context of catalysis, both in its homogeneous [2, 3] and heterogeneous forms [4, 5], as a means to replace more toxic and less abundant transition metals. Iron has interesting properties in this context, including magnetic properties, a rich redox chemistry, with implications both in molecular and material sciences, an affordable price and nontoxicity. Iron complexes, oxides, and metal-based materials have been applied to a wide array of chemical processes, including oxidation processes, hydrogenation, C–C coupling, and aromatic substitutions [3, 6–9]. Ruthenium belongs to the platinum series and is obtained as a by-product to platinum or nickel mining. Within the platinum series, ruthenium is comparably cheaper than its counterparts and thus desirable as a replacement to more expensive, catalytically active transition metals. Compared to iron, it is less prone to oxidation when in its reduced form. Ruthenium has established itself as an important and industrially relevant catalyst, in both its homogeneous and heterogeneous forms for a number of important processes including the Haber-Bosch process (dinitrogen to ammonia) [10, 11], the Fischer-Tropsch process (syngas to hydrocarbons) [12, 13], hydrogenation reactions [14], including the partial and selective hydrogenation of benzene and phenol, olefin metathesis [15], CH activation [16], and organic oxidations just to name a few. Osmium has been comparatively less explored. Osmium tetroxide and related compounds have demonstrated early on their ability to catalyze the oxidative cleavage of olefins with molecular oxygen [17]. Other osmium complexes have now been developed for a number of reactions including complete and partial hydrogenation, dehydrogenation, and hydroformylation [18, 19]. Nanoparticulate osmium counterparts

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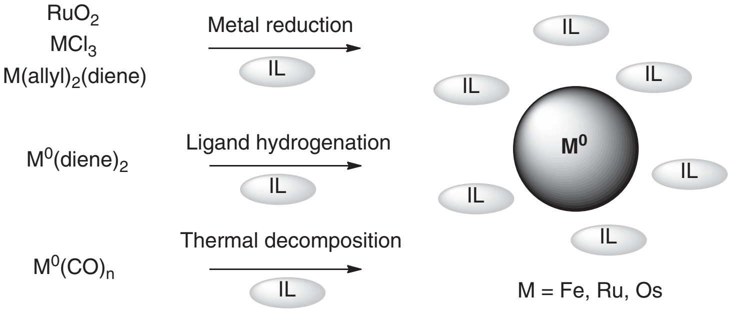
have been studied for their catalytic properties toward Fischer–Tropsch reaction, the homologation of alkenes under H_2 and the hydrogenolysis of alkanes [20], and electrocatalytic activity useful in fuel cell research [21].

Ionic liquids (ILs) are defined as salts with melting points below 100 °C. Over the last two decades, research on ILs has developed with a focus on liquid ones at or near room temperature [22, 23]. Typically such systems are constituted of flexible organic ion pairs with delocalized charges and tunable lipophilic domains [24]. Because of their liquid nature and specific properties, ILs are used as solvents to substitute volatile molecular liquids and specialty materials for a number of important applications, including synthesis, catalysis and biocatalysis, separation technology, biomass processing and transformation, electrochemical devices including capacitors, fuel cells and solar cells, nanotechnology, sensing, lubricants, hypergolic materials, and pharmaceutics [22, 25–30]. ILs rapidly emerged as a privileged environment for catalysis because of their unique intrinsic properties. ILs are attractive as potential solvents for a number of reasons: (i) they are nonvolatile under ambient conditions; (ii) they are colorless and little viscous; (iii) they possess good solvation properties for a large number of species; (iv) they are immiscible with many conventional solvents; (v) The properties of ILs can be easily tuned by a careful choice of the cation and anion entities, making them “designer solvents” [31]; and (vi) they are commercially available [30]. The combination of properties (i), (iii), (iv), and (v) explain that they are perfectly suited as catalyst stabilizers in biphasic systems [32, 33]. ILs have also been developed in supported versions to afford heterogenized systems of interest in catalysis [27].

Metal nanoparticles (NPs) have been intensely researched in the context of catalysis [34, 35]. Their high surface-over-volume ratio and unique effects linked to their nano size (role of defects, photon, and electron-linked properties) explain unique activities at the crossroads of homogeneous and heterogeneous catalysis [36–38]. They are appealing as highly active catalysts and materials easily amenable to recovery and recycling strategies [37]. Metal NPs and ILs, as privileged catalysts and catalysis media respectively, have thus been naturally explored in partnership and have opened a unique and rich research field, which has already been largely reviewed. Among the papers published over the last 10 years, the reader is directed to reviews on ILs in catalysis [25, 39], functionalized ionic liquids (FILs) [40, 41], FILs in catalysis [42], NPs in ILs [36, 43–46], NPs in ILs for catalysis [26, 47–55], and Ru NPs in IL [56]. In this chapter, we focused on the synthesis, stabilization properties, and catalytic applications of Fe, Ru, and Os NPs in ILs. For Fe, we extended the review to iron oxide NPs as well, as under aerobic condition, reduced iron NPs lead to such species.

1.2
Synthesis of Fe, Ru, and Os NPs in ILs

In general, the synthetic methods to access metal and metal oxide NPs in ILs have focused on providing materials with key features relevant for catalysis, that is, small sizes, good monodispersity, and high purity [26]. These properties are achieved using bottom-up synthetic approaches, either by reduction of metal salts, by the direct use of zero-valent molecular species, which can be freed from their ligands via hydrogenation, or simply decomposed (Scheme 1.1). The use of additional stabilizers [46] or functional ILs [42] has been reported to improve the properties of the end product. Top-down approaches are known for the synthesis of Au, Rh, Pd, and Pt NPs in ILs but are not a classic approach to access NPs of metals of Group 8 [26]. Also, although synthetic routes via phase transfer [57] from another organic or aqueous medium have been reported for other metals such as gold [58] and rhodium [59], Group 8 NPs are typically prepared directly in neat ILs. Because of the preorganized structure of ILs via electrostatic, hydrogen bonding, and van der Waals interactions, especially those with imidazolium and phosphonium functionalities, the IL medium is described as made of polar and nonpolar nanodomains. Those tunable domains act as nanoreactors and stabilizing chambers via noncovalent interactions [44, 46]. Thanks to the polarity, thermal stability, and preorganized supermolecular structure of ILs, the synthesis of Ru, Fe, and Os NPs could be attained in ambient conditions [44, 60]. In ILs, such strategies have unlocked access to metal NPs with precise size control and narrow size distributions [56]. Further comments on the stabilization properties of ILs for NPs are provided in Section 1.3.



Scheme 1.1 Summary of the synthetic schemes for accessing Fe, Ru, and Os NPs in ILs.

A complete list of Ru NPs synthesis in ILs was established by Campbell *et al.* in 2013 [56]. In the following sections, we focused on the most distinctive and recent examples for synthesis of Fe, Ru, and Os NPs. One of the specifics of the synthesis of metal NPs directly within an IL is the difficulty in washing the resulting material from any salt by-product generated during the reaction. Hence it is important to select "salt-free" precursors or organometallic precursors decomposing into easily washable organic species or volatile [61, 62] ones, such as [Ru(COD)(2-methylallyl)$_2$], [Ru(COD)(COT)], or carbonyl compounds such as (COD = 1,5-cyclooctadiene and COT = 1,3,5-cyclooctatriene) [63], as discussed below.

1.2.1
Synthesis via Reduction of Metal Precursors or Ligands

Despite the long list of reducers used with this metal, Ru precursors in ILs are reduced by H_2 in reported procedures [36, 48, 56, 64]. In a common scheme, a Ru precursor, such as [Ru(COD)(2-methylallyl)$_2$] or [Ru(COD)(COT)] is dissolved or suspended into a specific IL under argon and exposed to mild H_2 pressure and heating (<90 °C) from a few hours to days to obtain a black suspension. The size of the resulting Ru NPs – usually between 1.0 and 3.0 nm – and their size distribution may be tuned depending on reaction conditions, namely, stirring, temperature, and IL cations/anions (Figure 1.1) [56, 65–70]. From a formal standpoint, [Ru(COD)(2-methylallyl)$_2$] and [Ru(COD)(COT)] precursors differ in that the latter is a Ru(0) complex which should not necessitate the use of a reducer. Under H_2 pressure, however, the COD and COT ligands are hydrogenated to release atomic Ru(0) and allow the growth of Ru NPs [61, 62]. $RuCl_3$ and RuO_2 have also been reported as precursors being easily reduced by H_2 to access the desired NPs. In some ILs, precursor solubility may be a limitation that has been circumvented via the use of an auxiliary solvent. Our group showed that tetrahydrofuran (THF) could be successfully used to mix [Ru(COD)(2-methylallyl)$_2$] with phosphonium and imidazolium ILs, before being easily removed *in vacuo*. Subsequent reduction under H_2 pressure afforded small Ru NPs (between 1.5 and 2.5 nm) [71]. Although not necessarily required for subsequent catalytic applications, the separation of the obtained NPs from imidazolium ILs may be performed and depends on the anion in the IL [65]. Prechtl *et al.* also showed that

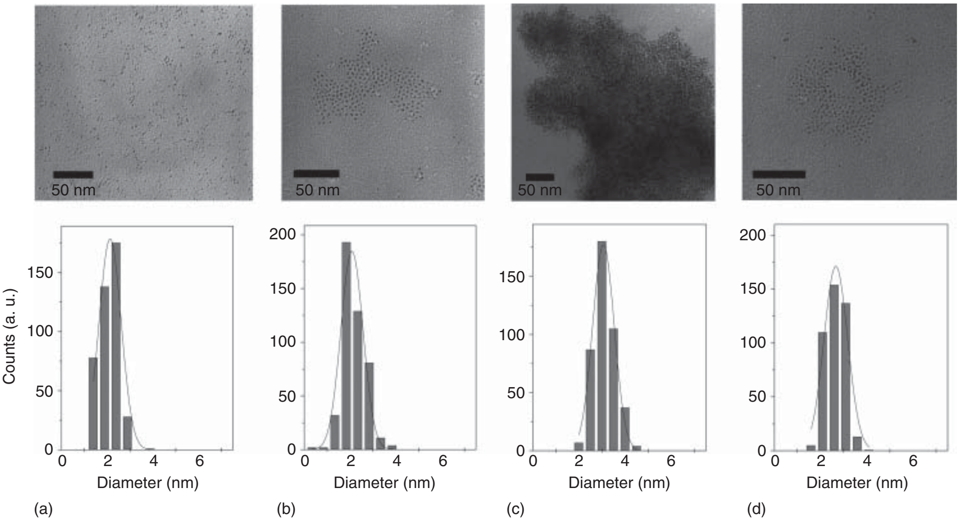


Figure 1.1 *In situ* transmission electron microscopy (TEM) images of Ru NPs generated from the reduction of [Ru(COD)(2-methylallyl)$_2$] by H_2 in (a) [C_4C_1Im][NTf_2], (b) [$C_{10}C_1$Im][NTf_2], (c) [C_4C_1Im][BF_4], and (d) [$C_{10}C_1$Im][BF_4]. (Prechtl *et al.* [65]. Reproduced with the permission of American Chemical Society.)

imidazolium ILs containing NTf_2 (bis(trifluoromethylsulfonyl)imide) anions such as $[C_4Im][NTf_2]$ and $[C_6C_1Im][NTf_2]$ could be used directly as reducing agents toward $[Ru(COD)(2\text{-methylallyl})_2]$ [72]. Small and monodisperse 2.0 ± 0.3 nm Ru NPs were obtained at low temperature and atmospheric pressure without the participation of classical reducing agents such as H_2, $LiAlH_4$, or hydrazine. The $^-NTf_2$ anion was shown to have a key role in the reduction mechanism; imidazolium ring decomposition was also observed.

On the other hand, the use of Grignard reagents with $FeCl_3$ successfully afforded catalytically active Fe(0) NPs of 4–5 nm diameter [73].

Upon intensive use in catalysis or through simple aging, IL-stabilized NPs have been shown to grow, coalesce, or leach. A study by Scott and coworkers showed that tetraalkylphosphonium ILs were a good environment to produce metal NPs of Au, Pd, Pt, Ru, Rh, Ni, Co, Fe, Ag, and Cu from halide salts, using appropriate reducers, for example, $LiBH_4$ for Ru and Fe [74]. These NPs could be oxidized back into salts in the presence of oxygen for oxidizable metals such as Fe or *tert*-butyl hydroperoxide for Ru. Further addition of reducer allowed recovery of the metal NPs within the IL.

1.2.2
Synthesis via Decomposition of Metal Precursors

The decomposition of metal complexes in IL involves various energy forms such as heat, microwave, and light irradiation [46]. The Thomann and Janiak groups [75] reported successful synthesis of Fe, Ru, and Os NPs by the decomposition of their respective di- and trinuclear metal carbonyls in *n*-butyl-methylimidazolium tetrafluoroborate $[C_4C_1Im][BF_4]$. Under argon, the deoxygenized dry IL with dissolved or suspended metal carbonyl was heated to 250 °C for several hours; alternatively, the mixture was irradiated with UV light at 200–450 nm for 15 min. The products are in the range of several nanometers and with a uniform, monodisperse, and narrow size distribution. By varying the metal loading, the NP size could be varied as well. For Fe, Fe(0) and Fe_2O_3 NPs were produced under inert and aerobic conditions respectively, with sizes of 5.2 ± 1.6 and 4.2 ± 1.1 nm, respectively. For Ru and Os, the sizes achieved were smaller, between 1.6 ± 0.4 and 2.0 ± 0.5 nm for Ru and 2.5 ± 0.4 nm for Os. Under inert atmosphere, the products could be retained for months. This procedure was updated later so that the reaction is finished in 3 min (for 0.48 g IL in a 1 ml vial) by microwave irradiation (10 W) [76]. The same group also synthesized chemically derived graphene (CDG)-supported Ru NPs from $Ru_3(CO)_{12}$ in $[C_4C_1Im][BF_4]$ [77]. $Ru_3(CO)_{12}$ was added into preformed CDG/IL slurry (0.2 wt%) and stirred for 18 h under argon. The whole mixture then went through a 6-min microwave irradiation (20 W). The dried flakes after centrifugation and decantation were analyzed and proved to be Ru NPs attached to mini CDG sheets (Ru NP/CDG) with 17.4 wt% Ru content. In another example, Lee *et al.* synthesized Fe_2O_3 nanobars and nanowires in $[C_8C_1Im][BF_4]$/dimethylformamide mixture by thermal decomposition of $Fe(CO)_5$ followed by oxidation [78]. The IL $[C_8C_1Im][BF_4]$

played an important role in stabilizing NPs, directing crystal growth to obtain high aspect ratio particles as well as boosting thermal decomposition of the precursor. The resulting high aspect ratio NPs showed good superparamagnetic properties, useful for contrast enhancement applications.

1.2.3
The Use of Additional Stabilizers and Functional ILs

ILs are privileged media used to generate and maintain small metal NPs useful in catalysis. However, upon using and reusing IL-stabilized metal NPs, it has been noted that the NPs could aggregate and lose their catalytic activity [55]. Also, for specialty applications, highly monodisperse metal NPs may be needed, which are difficult to achieve with straight IL. To overcome these hurdles, additional stabilizers have been used, either in the form of small molecules [46] or in the form of FILs [40–42]. In the context of NP stabilization, *FILs* are defined as an IL featuring a metal-binding moiety such as a phosphine, an amine, or a thiol. A few examples of such strategies have been reported with Fe and Ru metals. Highly monodispersed, iron oxide NPs of 10.6 ± 1.6 nm were made in 1-butyl-3-methylimidazolium bis(triflylmethyl-sulfonyl) imide ($[C_4C_1Im][NTf_2]$) by thermal decomposition of $Fe(CO)_5$ in the presence of oleic acid as an additional stabilizer, followed by oxidation (Figure 1.2a) [79]. The control over the particle size was attributed to the oversaturation of oleic acid in the system.

The resulting particles could be allowed to settle and be separated from the IL, which was recycled and reused for another synthesis. In this example, Fourier-transform infrared (FTIR) spectroscopy was used to establish that the oleic acid alone was responsible for the NP stabilization. The size of these iron oxide NPs could be tuned by using a mixture of stabilizers composed of oleic acid, oleylamine, and 1,2-hexadecanediol [79]. Using a similar procedure, the same group synthesized iron oxide NPs in $[C_4C_1Im][NTf_2]$ with different

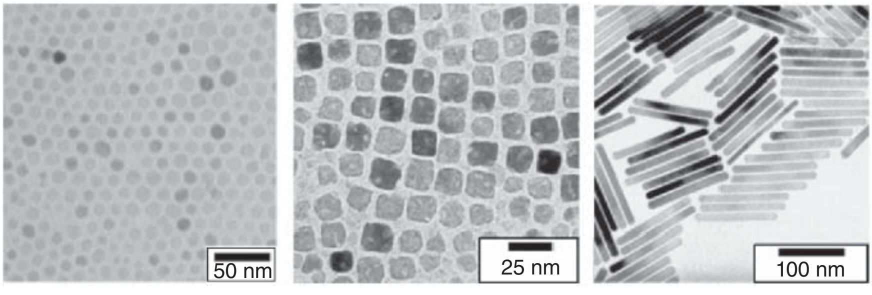


Figure 1.2 TEM images of iron oxide (a) nanospheres, (b) nanocubes, and (c) nanorods synthesized in $[C_4C_1Im][NTf_2]$ by thermal decomposition of $Fe(CO)_5$ using oleic acid and/oleylamine as capping agent. (Panel (a) Wang *et al*. [79]. Reproduced with the permission of Royal Society of Chemistry. Panels (b) and (c) Wang and Yang [80]. Reproduced with the permission of Elsevier.)

morphologies, such as nanorods and nanocubes, by playing on the reaction temperature, the nature of the stabilizer (oleic acid and oleylamine), as well as the concentration of these stabilizers (Figures 1.2b and c) [80].

Besides small molecules, FILs were also shown to provide improved stabilization compared to classic ILs. A few examples of Group 8 NPs produced in FILs were recently reported. With Ru, phosphine-functionalized imidazolium-based ILs were used as stabilizers to access catalytically active 2.2 nm Ru NPs [81]. Nitrile [82] and hydroxy [83]-functionalized imidazolium IL were also used to access Ru NPs, which proved particularly appealing as selective catalysts for partial hydrogenation of nitriles, hydrogenation of C═O, and hydrogenation of C═C bonds. Interestingly, the 1-butyronitrile-3-methylimidazolium bis(trifluoromethanesulfonyl)imidate IL ($[(C_3CN)C_1Im][NTf_2]$) afforded small Ru NPs (2.2 ± 0.5 nm), comparable to the ones obtained in nonfunctionalized ILs, while 1-(2,3-dihydroxypropyl)-2,3-dimethylimidazolium bis(trifluoromethanesulfonimide) $[C_1C_1(EG)Im][NTf_2]$ gave larger NPs (6.9 ± 1.3 nm) [82, 83]. With Fe, polymer-based ILs, namely, an imidazolium-modified poly(ethylene glycol) was used as the medium to access ferrite NPs. The resulting system functioned as a ferrofluid and served as electrolyte in an AC circuit [84]. Jacobi von Wangelin and coworkers reported the synthesis of Fe(0) NPs stabilized with nitrile-functionalized imidazolium generated within an imidazolium-based IL. This system was used for the selective hydrogenation of alkynes into alkene, as further detailed in Section 1.4.2 [73].

1.3
Ionic Liquid Stabilization of Metal Nanoparticles

1.3.1
Ionic Liquid Properties

Metal NPs are intrinsically unstable materials that easily grow into bulk metal by particle coalescence. In the liquid phase, they thus require the use of stabilizers in the form of small molecules or polymeric materials to ensure that they remain stable as a suspension. ILs are quite unique in this context, as they provide an environment that has the intrinsic ability to stabilize NPs extensively without the use of a stabilizer. ILs have thus been termed “nanosynthetic templates” [75, 85]. The origin of this stabilization has been studied using a number of techniques and remains an active area of research with open questions and debates. The structure of free, pure ILs is complex and has been explored using experimental and theoretical approaches [22]. Neutron scattering experiments have allowed to establish that structural order in imidazolium-based ILs extends over a longer range than conventional liquids, although this effect is dependent upon the nature of the counter anion [86–88]. ILs also differ from convention solvents in that they feature mesoscopic organizations. The surfactant properties of ILs originating from the presence of hydrophilic and hydrophobic functionalities translate in the liquid phase into the presence of polar and nonpolar mesodomains.