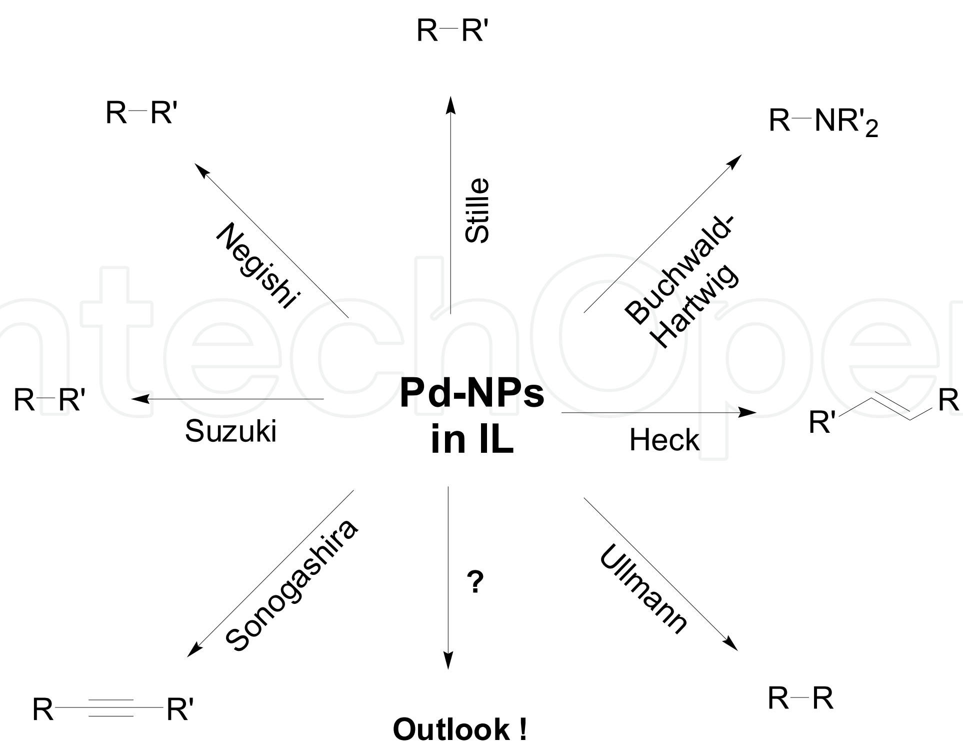
16

Palladium Nanoscale Catalysts in Ionic Liquids: Coupling and Hydrogenation Reactions

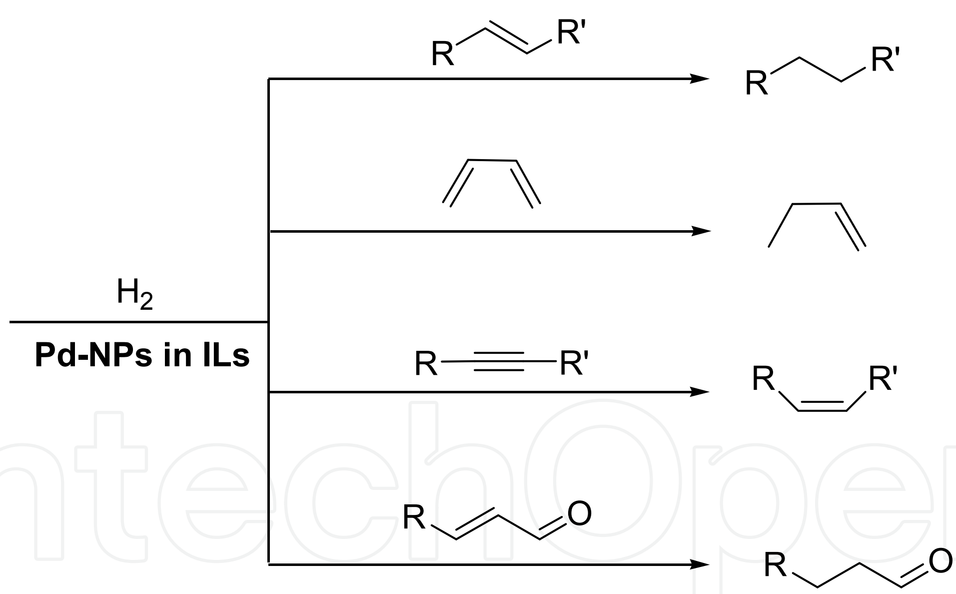
Martin H. G. Prechtl,[1,2]* Jackson D. Scholten[3] and Jairton Dupont[3]
[1]*Universität zu Köln, Köln,*
[2]*Humboldt Universität zu Berlin, Berlin,*
[3]*Universidade Federal do Rio Grande do Sul, Porto Alegre, RS,*
[1,2]*Germany*
[3]*Brazil*

1. Introduction

Palladium nanoparticles (Pd-NPs) stabilised by ionic liquids (ILs) revealed a promising potential to act as recyclable catalysts for plethora reaction types. These include typical homogeneous as well as heterogeneous catalytic reactions such as hydrogenation of multiple bonds, (Dupont et al., 2002; Huang et al., 2003; Scheeren et al., 2003; Kim et al., 2004; Silveira et al., 2004; Umpierre et al., 2005; Migowski & Dupont, 2007; Rossi et al., 2007; Scholten et al., 2007; Hu et al., 2008; Prechtl et al., 2008; Gelesky et al., 2009; Hu et al., 2009; Prechtl et al., 2009; Redel et al., 2009; Rossi & Machado, 2009; Dupont & Scholten, 2010) and carbon-carbon cross-coupling reactions.(Calo et al., 2003; Calo et al., 2003; Calo et al., 2004; Calo et al., 2004; Calo et al., 2005; Calo et al., 2005; Cassol et al., 2005; Calo et al., 2006; Chiappe et al., 2006; Dubbaka et al., 2006; Phan et al., 2006; Calo et al., 2007; Fei et al., 2007; Dieguez et al., 2008; Calo et al., 2009; Calo et al., 2009; Cui et al., 2010) It is well accepted that Pd-NPs serve as reservoir for active molecular Pd species in carbon-carbon cross coupling reactions (Scheme 1), for example. Moreover, Pd-NPs have been employed as efficient catalyst for typical heterogeneous reactions (Scheme 2).(Phan et al., 2006; Migowski & Dupont, 2007; Gu & Li, 2009) In order to avoid the formation of bulk metal, ILs can be used as suitable stabilisers for the synthesis of mono-dispersed NPs.(Prechtl et al., 2008; Prechtl et al., 2009) ILs form also a protective liquid-film on the sensitive and highly active metal surface, preventing the metal surface from oxidation.(Migowski & Dupont, 2007) One additional property of Pd-NPs/ILs systems is the feature for multiphase catalysis that the NPs are immobilised in the dense IL-phase ("stationary phase"), and are, therefore easily recyclable by simple phase separation of the organic "mobile phase", containing the substrates and product.(Dupont et al., 2002) In many cases, the well-immobilised NPs in ILs can be used as catalyst-phase several times, showing the potential to recyclability of this system. General limitations are reached in the following cases: (I) palladium leaching into the organic layer, (Cassol et al., 2005; Consorti et al., 2005) (II) retention of organic molecules in the IL-phase,(Cassol et al., 2007) and (III) a delayed mass transfer between the organic and the IL-layer due to the relatively high viscosity of the IL.(Dupont & Suarez, 2006)



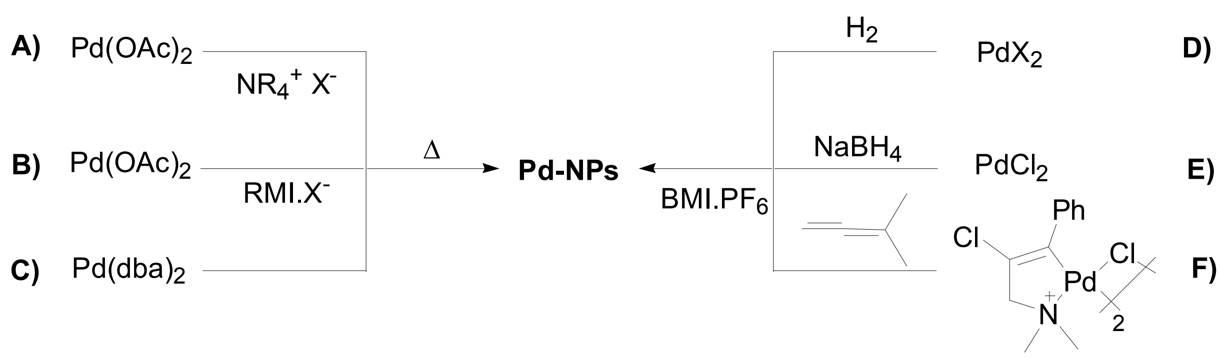
Scheme 1. Exemplary coupling reactions catalysed by metal Pd-NPs in ILs.



Scheme 2. Hydrogenation reactions catalysed by metal Pd-NPs in ILs.

Pd-based carbon-carbon cross-coupling reactions were discovered more than three decades ago, and remain under the most investigated transition-metal catalysed reactions.(Beletskaya & Cheprakov, 2000; Moreno-Manas & Pleixats, 2003; Phan et al., 2006; Yin & Liebscher, 2007; Liu et al., 2009) These reactions use Pd complexes with strong ligands (e. g. PR_3, NHC), palladacycles, PdX_2 (e. g. X= halide, acetate) or even ligand-free approaches, in which Pd(0) species are catalytically active.(Reetz et al., 1998; de Vries et al., 2002; Bedford, 2003; de Vries et al., 2003; de Vries et al., 2003; Reetz & de Vries, 2004; Dupont et al., 2005) The Heck reaction for instance, with aryl iodides or bromides is catalysed by a plethora of Pd(II) or Pd(0) sources.(Cassol et al., 2005; Migowski & Dupont, 2007) This indicates, at least for ligand-free Pd sources, that soluble Pd-NPs are involved as a reservoir of active species.(Reetz & Westermann, 2000; Rocaboy & Gladysz, 2003; Tromp et al., 2003) The first article of a zero-valent Pd complex suitable for the formation of Pd-NPs, by Takahashi and co-workers was published in 1970, used $Pd(dba)_2$ (dba = dibenzylideneacetone) under thermal decomposition conditions forming metallic palladium and dba in solution.(Takahashi et al., 1970) More studies of Pd-NP synthesis and its applications followed in the 1980s and 1990s by, for example Bönnemann, Reetz and their respective co-workers.(Bonnemann et al., 1990; Bonnemann et al., 1991; Reetz & Helbig, 1994; Reetz & Quaiser, 1995; Reetz et al., 1996; Reetz & Lohmer, 1996) In the last decade, metal NP synthesis in ILs had their breakthrough and numerous detailed studies about Pd-NPs in ILs are available in the literature.

Synthetic approaches using controlled thermal decomposition for the generation of Pd-NPs in ILs use for example: $Pd(dba)_2$,(Takahashi et al., 1970) $Pd(OAc)_2$ or palladium carbene complexes (Scheme 3).(Reetz & Westermann, 2000; Xu et al., 2000; Deshmukh et al., 2001; Calo et al., 2003) Furthermore, palladium salts such as $PdCl_2$, Na_2PdCl_4 can be reduced with metal hydrides or simply dihydrogen. Pd-NPs are also formed starting from palladacycles by reaction with dienes (Scheme 3).(Bonnemann et al., 1990; Cassol et al., 2005; Umpierre et al., 2005)



Scheme 3. Metal Pd-NPs formation in ILs by thermal/ultrasonic treatment of Pd salts and Pd carbene complexes where the imidazolium salt (RMI.X) acts as NHC-carbene source (A-C; X = halide or BF_4). Reduction with dihydrogen or hydrides (D-E; X = OAc, halide) or reductive elimination of a palladacycle by reaction with a diene (F). Adapted from references (Takahashi et al., 1970; Reetz & Westermann, 2000; Xu et al., 2000; Deshmukh et al., 2001; Calo et al., 2003; Cassol et al., 2005; Umpierre et al., 2005).

The particle size of Pd-NPs is often strongly related to the type of precursor, and small-sized particles are easily obtained starting from $Pd(OAc)_2$. Besides the Pd-precursor, the state of agglomeration/dispersion also depends on the coordination properties of the IL media and the concentration/solubility of the Pd-precursor in the IL.(Dupont & Scholten, 2010) Especially low concentration and high solubility of the Pd-precursor is quite helpful in obtaining a high dispersion and low agglomeration. It is important to note, that the lifetime of Pd-NPs as catalysts depend, on their stability, which is often related to the preparative protocol used. Also Pd-NPs tend to form large aggregates with smaller surface which often show lower activity. To obtain prolonged catalyst lifetime of the Pd-NPs, these particles may be stabilised by the addition of polymers, which give access for tuning the particle size and their topology.(Yang et al., 2008) A more detailed discussion on the synthesis of metal NPs in ILs can be found in a recently published critical review.(Dupont & Scholten, 2010)

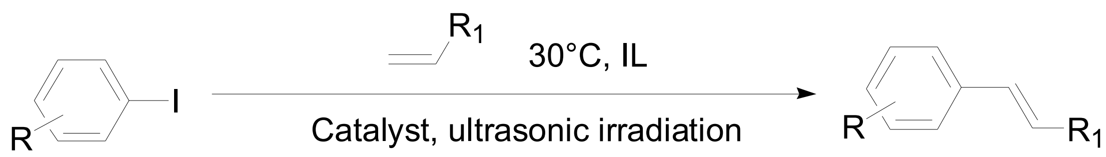
2. Nanoscale Pd-Catalysts in ILs for C-C coupling reactions

2.1 Mizoroki-Heck reaction

The Mizoroki-Heck coupling reaction is one of the best methods in modern organic chemistry.(Beletskaya & Cheprakov, 2000; Moreno-Manas & Pleixats, 2003; Phan et al., 2006; Yin & Liebscher, 2007; Liu et al., 2009) The coupling involves the reaction of an unsaturated halide with olefins catalysed by Pd precursors in organic solvents in presence of a base. Pointing out, that often the active species is not the palladium complex but molecular Pd species derived from Pd-NPs stabilised by the IL serving as reaction medium.(Reetz & Westermann, 2000; Astruc, 2007) These Pd-NPs are resulting from the reduction of the Pd(II) species to Pd(0) in the presence of bases employed in the reaction. In the last two decades, classical solvents have been substituted by ILs in chemical reactions.(Dupont et al., 2002) In fact, ILs are more environmentally benign, which is due to their ability to act as stationary phase for catalysts in recyclable multiphase catalysis. In such multiphase systems, ILs are suitable together with apolar solvents as well as with polar solvents, depending on the polarity of the IL. Moreover, certain ILs such as those with imidazolium cations, show selectivity for a specific product as the ILs are feasible to stabilise ionic transition states due to their inherent physico-chemical properties.(Hardacre et al., 2003; Dupont, 2004; Gozzo et al., 2004; Tsuzuki et al., 2005) One of the first results reported on the role of ILs in Heck reactions was published by Deshmukh and co-workers in 2001. (Deshmukh et al., 2001) For instance, ILs based on the cation [1,3-di-*n*-butylimidazolium] and bearing bromide (BBI.Br) and tetrafluoroborate ($BBI.BF_4$) as anions promote a significant improve in the rate of Heck reactions. It was observed that under ultrasonic irradiation and in the presence of base, the C-C couplings of several substituted iodobenzenes and alkenes/alkynes at 30 ºC were performed successfully affording solely the *trans*-product in high yields (Scheme 4). The authors also proved that a Pd *bis*-carbene took part in the transformation and was reduced to metal Pd-NPs in the process. Moreover, the molecular Pd as the active species is most likely coming from Pd-NPs. Once no reaction was observed for classical organic solvents under the same conditions, the advantage of ILs toward the stabilisation of intermediates can be evidenced in this case.

The formation of similar palladium carbene complexes derived from imidazolium ILs were also reported elsewhere, as well as the deprotonation of imidazolium cations during the catalysis.(Xu et al., 2000; Dupont & Spencer, 2004; Lebel et al., 2004; Bernardi et al., 2009)

In the same context, metal Pd-NPs (1.5–6 nm) dispersed in a tetraalkylammonium salt (tetrabutylammonium bromide, TBAB) could be used as catalysts for the Heck reaction of bromoarenes with 1,1-disubstituted olefins in the presence of tetrabutylammonium acetate (TBAA) as base at 120 ºC (entry 1, Table 1).(Calo et al., 2003) In most cases the main products were terminal olefins, which suggest that Pd-hydride species is immediately neutralised by the base avoiding the isomerisation of the olefin. Notably, bromoarenes may couple with less reactive 1,2-disubstituted alkenes, like cinnamates, in presence of Pd-NPs in TBAB at 130 ºC.(Calo et al., 2003) Here, $Pd(OAc)_2$ and a Pd *bis*-benzothiazole carbene compound were used as a source of Pd-NPs. The same research group reported recently that aryl chlorides undergo coupling reaction with deactivated alkenes using Pd-NPs in TBAB and TBAA (entry 2, Table 1).(Calo et al., 2009) It has to be pointed out, that it is generally accepted that the true catalyst of the reaction is most likely molecular Pd species detached from the NPs surface.



Yields = 73-87%

R = H, 4-OMe, 4-Cl
$R_1 = CO_2Me, CO_2Et, Ph$

Scheme 4. Selected examples of Heck reaction of substituted iodobenzenes and alkenes in imidazolium-based ILs at 30 ºC under ultrasonic conditions. (Deshmukh et al., 2001)

Mechanistic details concerning the role of Pd-NPs in C-C cross-coupling reactions, were investigated by Dupont and co-workers.(Cassol et al., 2005; Consorti et al., 2005) The palladacycle (see Scheme 3) was rapidly transformed into Pd-NPs by reaction with dimethylallene even at room-temperature. These Pd-NPs were suspended in $BMI.PF_6$ (BMI: 1-*n*-butyl-3-methylimidazolium; PF_6: hexafluorophosphate). Following the analysis of the Pd-powder in IL was conducted with TEM and EDS techniques. The micrographs depict the presence of Pd-NPs and the XRD results of the isolated Pd-NPs confirmed the presence of metallic Pd. The evaluation of the Pd-NPs/IL-system for catalysis was performed in particular with the Heck reaction as benchmark model using with aryl halides and *n*-butyl acrylate (substrate:Pd ratio = 1000:1) at various temperatures and bases (entry 5, Table 1). The addition of $NEt(iPr)_2$ to the dark suspension resulted then in a yellow solution. Contrary with other bases the colour of the suspension remained unchanged. Highest conversions (92-100%) are accessible with aryl iodides and bromides using $NEt(iPr)_2$ as base and lower conversion (<30%) to other bases between 80–130 °C (14 h). The analysis of the organic fraction, after catalysis, by ICP-MS showed leaching of considerable quantities of palladium from the IL into the organic phase. The TEM and ICP-MS data indicate that Pd-NPs in IL simply serve as reservoir for molecular active Pd species. Pointing out, that Pd isolated from the organic layer showed no activity in the Heck reaction also after prolonged period of time in a recycling experiment (20 h). Also attempts to locate Pd-NPs in the organic phase by means of TEM failed. The authors suggested that the reaction pathway starts with oxidative addition of the aryl halide onto the metal surface. The oxidised molecular Pd species is immediately cleaved from the metal surface, which then enters the typical catalytic cycle

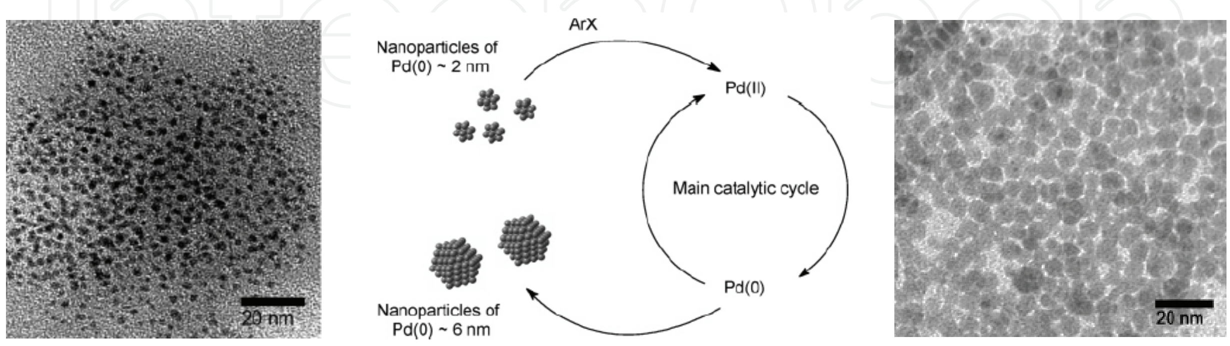
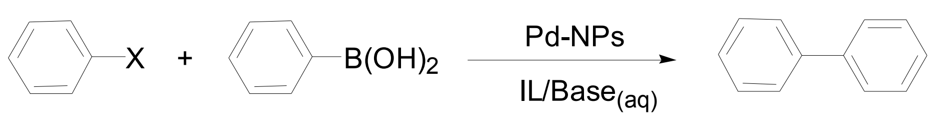


Fig. 1. TEM micrographs of the Pd-NPs in $BMI.PF_6$: before catalysis (1.7 ± 0.3 nm), left; after catalysis (6.1 ± 0.7 nm), right. The proposed catalytic cycle for the Heck reaction promoted by Pd-NPs is indicated in the middle. Reprinted with permission from reference (Cassol et al., 2005) (Copyright American Chemical Society).

(Figure 1). The molecular Pd species may remain in the catalytic cycle or Pd(0) may agglomerate and precipitate again as Pd-NPs, which stays in agreement with previous reports by de Vries and Reetz for ligand-free Heck reactions.(Reetz & Westermann, 2000; Reetz & de Vries, 2004)

2.2 Suzuki-Miyaura reaction

The Suzuki reaction represents another important example for C-C bond formation. Today, rather few works have been published using Pd-NPs in ILs as catalyst in this reaction.(Pathak et al., 2000; Ramarao et al., 2002; Gopidas et al., 2003; Narayanan & El-Sayed, 2003; Pittelkow et al., 2003; Kim et al., 2004; Liu et al., 2004; Calo et al., 2005; Corma et al., 2005; Fernandez et al., 2007; Durand et al., 2008) For example, Calo and Nacci reported on Pd-NPs in tetraalkylammonium ILs, starting from $Pd(OAc)_2$ in the presence of TBAA at 90 °C, which were used as precursor for the coupling of aryl halides (Scheme 5; entry 6, Table 1).(Calo et al., 2005)



X = Cl, Br

Base = Na_2CO_3, KOH, NBu_4OH

Yields = 20-95%

Scheme 5. Suzuki cross-coupling reactions catalysed by Pd-NPs in TBAB or THeptAB (THeptA = tetraheptylammonium) ILs at different temperatures (60-140 °C). (Calo et al., 2005)

Interestingly, with tetrabutylammonium hydroxide as base, the catalytic efficiency increased significantly, thus, the reaction was performed even under milder conditions. This can be explained by the elevated concentration of tetraalkylammonium in water, contributing through partitioning equilibrium, keeping the concentration of the cations in the IL constant. Consequently, the Pd-NPs were effectively stabilised against aggregation. Furthermore, with more hydrophobic IL such as tetraheptylammonium bromide (THeptAB) containing longer side chains than TBAB, the results were improved in the Suzuki reaction, which might be due to the better stabilisation of the Pd-NPs provided by this IL. Moreover, the Pd/THeptAB-system is recyclable for at least three runs. Again, the metal NPs were identified simply as reservoir for the molecular active catalyst in Suzuki reactions, when $Pd(OAc)_2$ as precursor in $BMI.PF_6$ in the presence of functionalised ligands derived from norborn-5-ene-2,3-dicarboxylic anhydride were employed.(Fernandez et al., 2007) Noteworthy is that in organic solvents the molecular catalyst is adequately stabilised by ligands, but in ILs the catalyst is active due to the in situ formation of NPs. Consequently, the formation of Pd-NPs is crucial to obtain an active catalyst in ILs as reaction medium.

2.3 Stille reaction

As another important tool for C-C coupling, the Stille reaction has also been catalysed by Pd-NPs in ILs. It was demonstrated that nitrile-functionalised ILs are superior for Pd-NP stabilisation to non-functionalised ILs (Figure 2).(Zhao et al., 2004; Calo et al., 2005; Chiappe et al., 2006; Fei et al., 2007; Cui et al., 2010) Moreover, tetraalkylammonium bromides are also suitable as reaction medium for the Stille reaction with Pd-NPs catalysts.(Calo et al.,

2005) A library of imidazolium, pyridinium and pyrrolidinium ILs with nitrile groups was designed to improve prolonged catalyst lifetime in the Stille reaction, among other cross-coupling reactions.(Zhao et al., 2004)

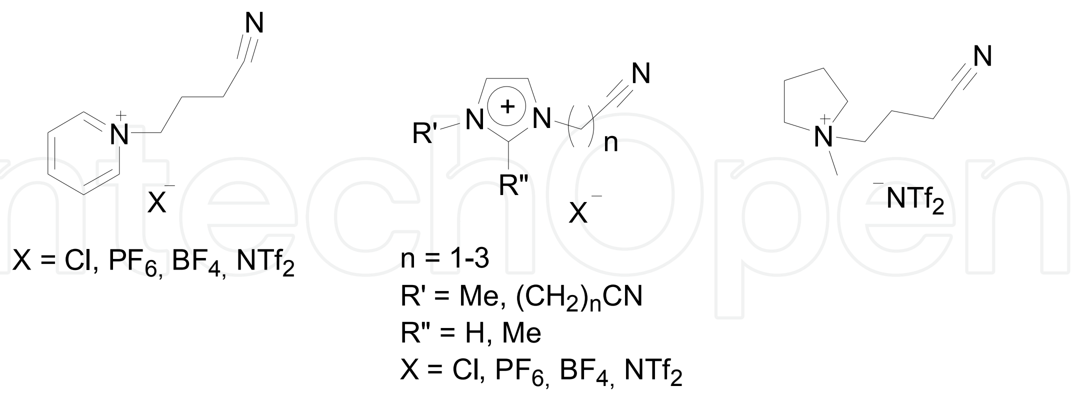
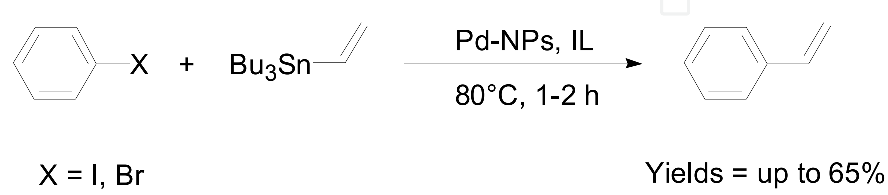


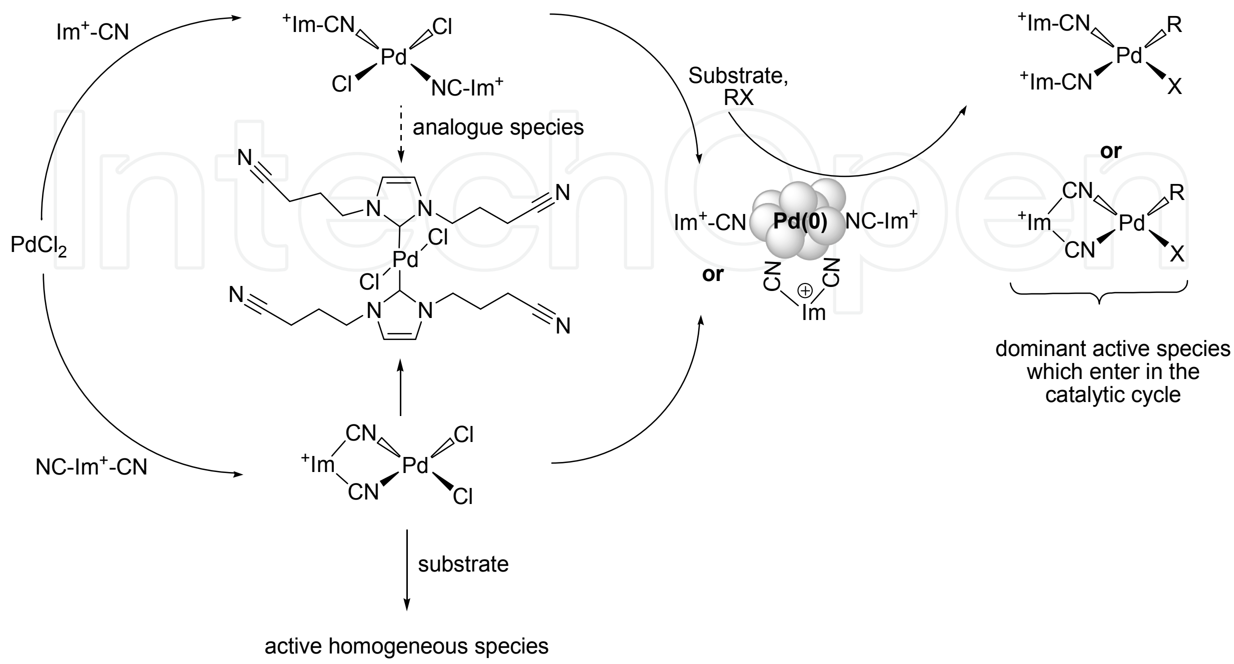
Fig. 2. Selection of ILs with nitrile-groups: pyridinium ((BCN)Py$^+$; left), imidazolium ((RCN)I$^+$ or (RCN)$_2$I$^+$; middle), pyrrolidinium salts ((BCN)P$^+$; right) with various anions. (Calo et al., 2005; Zhao et al., 2004; Chiappe et al., 2006; Fei et al., 2007; Cui et al., 2010)

In these works an anion-dependence was described using pyridinium ILs with palladium chloride as precursor. It is a direct approach to various molecular palladium species with cations and anions in the coordinating sphere of the palladium. These palladium complexes were tested in C-C coupling reactions in ILs with aliphatic and nitrile side-chains. An encouraging catalytic activity was observed in the coupling of iodobenzene with phenyltributylstannane. And, also recycling with no significant loss of activity was observed exclusively for the nitrile-functionalised IL (entry 8, Table 1). The following facts are characteristic for the nitrile-ILs: (I) the nitrile-group avoids leaching remarkably, (II) Pd-NPs act as reservoir for the active Pd species in the Stille reaction and (III) Pd-NPs were analysed by means of TEM techniques depicted well-dispersed small sized Pd-NPs (5 nm).(Zhao et al., 2004) Similar results were observed with imidazolium ILs including the nitrile-groups. In the entitled reaction, the influences of the cations (BMI, (RCN)$_{1-2}$I) and anions (BF_4, NTf_2, $N(CN)_2$), and the catalyst source ($Pd(OAc)_2$; $Pd_2(dba)_3$) have been evaluated (entry 10, Table 1).(Chiappe et al., 2006) The nitrile group in the cations and also the cyanamide anion affects the cross-coupling and the catalyst stability. In fact, it was shown that the relative coordination strengths of the ions played a role and that under certain conditions NPs have been observed. In all cases, the nitrile-functionalised ILs are superior to alkylimidazolium ILs for the immobilisation of Pd-catalysts and vinylation of aryl halides with tributylvinylstannane (Scheme 6).



Scheme 6. Example for the Stille reaction of aryl halides with tributylvinylstannane catalysed by Pd-NPs in ILs.(Zhao et al., 2004)

In additional studies, molecular intermediate complexes were found, where (I) the nitrile group is ligated to the metal core, and (II) carbenes (derived from the imidazolium IL reaction media) are coordinated to the central palladium atom.(Fei et al., 2007) Such complexes were tested for C-C coupling reactions, and Pd-NPs were observed in, for instance, the (BCN)MI.BF_4.

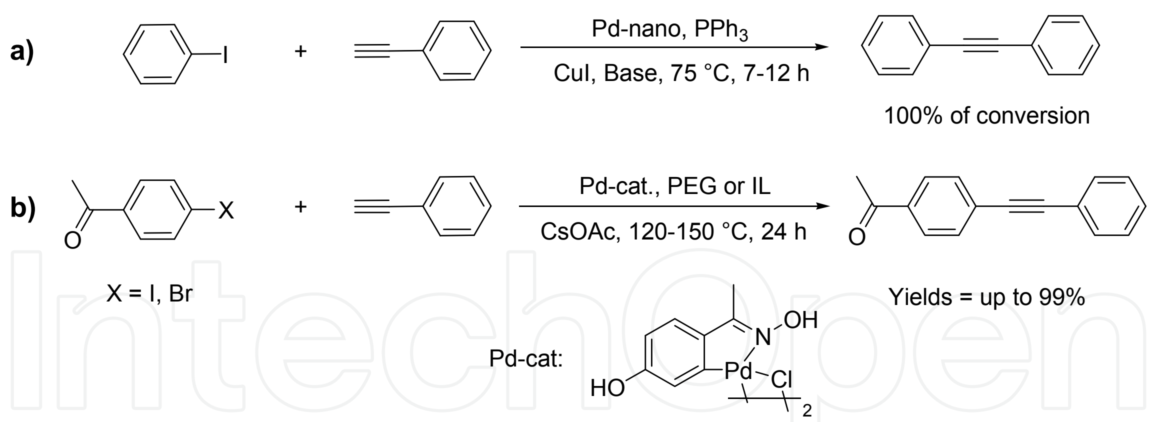


Scheme 7. Proposed mechanism for the formation of nitrile-IL stabilised Pd-NPs. Adapted with permission from reference (Fei et al., 2007) (Copyright American Chemical Society).

However, Pd-NPs are reservoirs for molecular Pd(II) species, the presumably the true active catalyst. The nitrile-functionality and carbenes (derived from the IL) stabilises these molecular intermediates via transient coordination, and they protect Pd-NPs (Scheme 7).(Fei et al., 2007) Most interestingly, palladium leaching into the organic layer was ten times lower in nitrile-ILs than in alkylimidazolium ILs, and the coordinating nitrile-group supports also the solubility of $PdCl_2$. These properties make this catalyst system, achieving high conversions in the Stille reaction, attractive for recycling catalyst.

2.4 Sonogashira reaction

Two different approaches were reported for the Sonogashira reaction with palladium nanocatalysts in IL. (Corma et al., 2005; Gao et al., 2005) One method used Pd-nanowires in IL, and in another protocol a palladacycle was thermally decomposed in IL resulting in Pd-NPs. The palladium nanowires were prepared in a thiol-functionalised IL (TFIL) by use of the seed growth method.(Gao et al., 2005) H_2PdCl_4 was reduced with $NaBH_4$ in a solution of gold colloids (2.2 nm) as seeds in the TFIL. Interestingly, the Pd-nanowires (2-4 nm in diameter) were exclusively obtained with specific ratios of Au and Pd precursors and IL. With low (high) Au concentrations core/shell nanostructures were obtained. The catalytic activity of the Pd nanowires were evaluated for the Sonogashira coupling. They revealed a remarkable activity and catalyst retention with iodoarene and phenyl acetylene as substrates, in presence of CuI and phosphine. Complete conversion was obtained in a few hours at 75 °C using the nanowires (Scheme 8a), contrary to the bimetallic (Pd_{Shell}@Au_{Core})-NPs where a conversion of 82% was obtained.



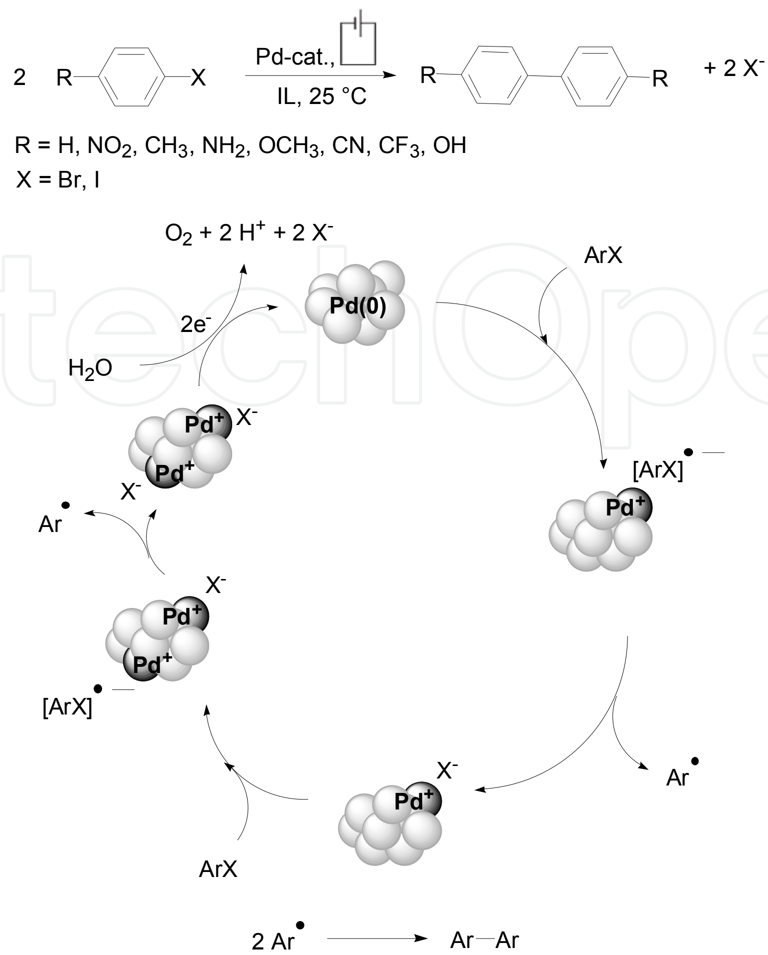
Scheme 8. a) Sonogashira reaction catalysed by Pd-nanowires and b) Pd-catalysed C-C coupling in PEG or ILs (BMI.PF_6 and $BM_2I.PF_6$).(Corma et al., 2005; Gao et al., 2005)

A palladacycle complex of 4-hydroxyacetophenone oxime was used for a recyclable multiphase system (Scheme 8b; entry 11, Table 1). This palladacycle is known to be a highly active catalyst for C-C bond forming reactions in water.(Corma et al., 2005) The stability of the complex was evaluated at elevated temperature in ILs and in PEG. The palladacycle decomposed in H_2O, BMI.PF_6 and BMI.Cl forming Pd-NPs in water and BMI.PF_6 (2–5 nm) and $PdCl_4^{2-}$ in the latter case. In contrast, the Pd complex remained stable in hot 1-*n*-butyl-2,3-dimethylimidazolium hexafluorophosphate ($BM_2I.PF_6$) and in PEG. The activity of the complex in PEG was superior to the one in ILs, likely to be related to the stability of the complex. However, the palladacycle also decomposed in PEG during the cross coupling yielding Pd-NPs (2–5 nm) which were stabilised by PEG. This copper- and ligand-free Pd/PEG-system can be applied for Sonogashira coupling on air with moderate to good yields (Scheme 8b). The authors explained that the lower catalytic activity in the ILs is related to the low solubility of CsOAc and unconsidered ILs as suitable media for this Pd-catalyst. Contrary, PEG was identified as more convenient medium for these reactions, due the higher stability of the palladacycle and of the Pd-NPs and the better solubility of cesium acetate.

2.5 Ullmann reaction

One established approach for the synthesis of biaryls is the dimerisation of aryl halides. For this purpose the Ullmann reaction is a traditional method, although the original protocol uses an excess of copper and harsh thermal conditions with temperatures above 200 °C.(Calo et al., 2009) Without doubt, a convenient alternative uses Pd-catalysts for the coupling of aryl halides to symmetrical biaryls. However, reductive conditions are crucial, and reductive agents such as amines, molecular hydrogen, hydroquinone, alcohols, or formic acid salts are commonly used in this approach.(Calo et al., 2009) Protocols introducing improved methods of the Ullmann reaction for recyclable systems, use ILs as reaction media.(Pachon et al., 2006; Calo et al., 2009) Rothenberg, for instance, presented a Pd-NPs catalysed Ullmann reaction based on electroreductive coupling of haloarenes in IL at room temperature (Scheme 9). (Pachon et al., 2006)

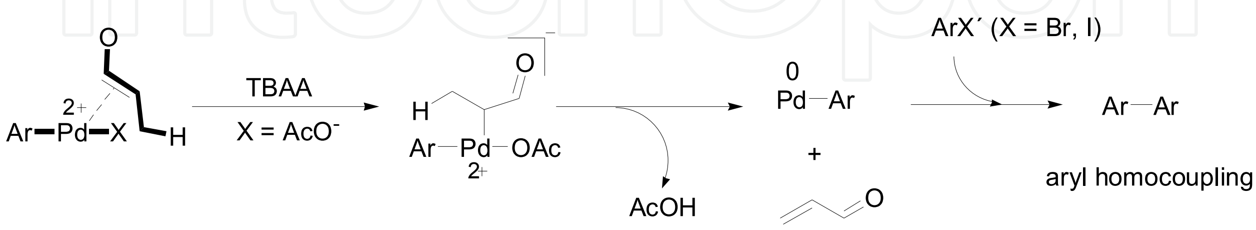
The Pd-NPs (2.5 ± 0.5 nm) were released in an electrochemical cell (Pd-anode and Pt-cathode). Here electron-transfer was crucial for closing the catalytic cycle. This system already gives remarkable yields with aryl bromides and iodides as substrates, simply by applying an electric current in water. To improve the electric conductivity and the



Scheme 9. Ullmann-typed aryl halide coupling with Pd nanocatalysts in IL under electroreductive conditions at 25 °C (top). Proposed catalytic cycle for the electroreductive Pd-NPs catalysed coupling of aryl halides (Pd^+ ions are depicted in dark grey). Noteworthy, the present model includes two single electron transfers from the same cluster, but in general interaction between different clusters is most likely to occur (bottom). Adapted with permission from reference (Pachon et al., 2006) (Copyright Wiley-VCH Verlag GmbH & Co. KGaA).

stabilisation of the Pd-NPs, 1-methyl-3-*n*-octylimidazolium tetrafluoroborate ($OMI.BF_4$) IL was introduced as recyclable solvent. Reaction monitoring at various electrode potentials revealed that a two-electron oxidation of H_2O closes the catalytic cycle by reformation of the Pd(0). Limitations of the system are given for functionalised aryl bromides and iodides with: R = H, NO_2, CH_3, NH_2, OCH_3, CN, CF_3, OH. The conversions vary extremely from 20 to 99% with reaction times from 8 to 24 h at 25 °C, using currents of 10 mA with 1.0–1.6 V. Noteworthy is that aryl chlorides do not undergo homocoupling under the described conditions. This set up is an unique example of electroreductive Pd-NPs catalysis in ILs. These insights into the kinetics suggest the formation of a phenyl radical anion during the reaction (Scheme 9). The advantage of this protocol is that simple electrons and water are the crucial elements for closing the catalytic cycle.(Pachon et al., 2006)

Another very mild approach for reductive homocoupling of aryl, vinyl and heteroaryl towards symmetrical biaryls uses aldehyde as reductant with Pd-NPs in TBAB and TBAA (entry 12, Table 1).(Calo et al., 2009) The IL here is crucial as it acts as base, reaction medium and it is a stabilising ligand for the Pd-NPs which serve as reservoir for active species. Bromo- and iodo arenes couple to biaryls in absence of other additives at temperatures between 40–90 °C with good conversions (70–90%). In this simple method the substrates and $Pd(OAc)_2$ are added to the IL, providing the catalytically active species directly in situ. One advantage of this approach is that the consumed reductant propanal is converted in presence of TBAA into acrolein (via the enolate ion), which can be simply separated by evaporation. Interestingly, the selectivity of the palladium species is tuneable in dependence of the IL-anion. With TBAB (X = Br) the pathway follows the Heck reaction (not shown) and with TBAA (X = AcO^-) the Ullmann reaction (Scheme 10).



Scheme 10. Pd-NPs catalysed Ullmann reaction in the presence of TBAA. Adapted with permission from reference.(Calo et al., 2009) (Copyright Wiley-VCH Verlag GmbH & Co. KGaA).

2.6 Recyclability of Pd-catalysts in C-C coupling reactions

In summary, convenient recyclable catalyst systems use simple tetraalkylammonium salts as well as imidazolium based ILs. Interestingly, such Pd-NPs in tetraalkylammonium salts or imidazolium ILs are capable to catalyse a whole range of cross-coupling reactions for several recycles in batch reactions of the previously discussed C-C coupling reactions, in particular: Heck, Suzuki, Stille, Sonogashira, and Ullmann reactions. (For references see Table 1 and the citations in the previous segments).

No*	Reaction	IL	Ar-X (X =)	Educt/ Pd	Conv. [%]	Runs
1	Heck	TBAB/TBAA	I, Br, Cl	67 (285)	10-99 (97-99)	n. d. (10)
2		TBAB, TBAA	Cl	67	25-98	n. d.
3		TBAB, BMP.NTf_2	I	200	6-98	5
4		(BCN)MI.NTf_2	I	100	16-99	4
5		BMI.PF_6	I	1000	100	n. d.
6	Suzuki	TBAB, THeptAB	Br, Cl	40	15-99	4
7		TOAB	Br	50	100	n. d.
8	Stille	BPy.NTf_2, (BCN)Py.NTf_2	I	20	44-65 (yield)	9
9		THeptAB	Br, Cl	40	27-98	5
10		(BCN)MI.BF_4	I	20	48-85	4
11	Sonogashira	BMI.PF_6	I	10	57 (yield)	n. d.
12	Ullmann	TBAA	Br	33	81-92	n. d.

BMP: 1-*n*-butyl-1-methylpyrrolidinium, BPy: 1-*n*-butylpyridinium, THeptA: tetraheptylammonium, TOA = tetraoctylammonium. *References: 1. (Calo et al., 2003; Calo et al., 2004) 2. (Calo et al., 2009). 3. (Forsyth et al., 2005). 4. (Fei et al., 2007). 5. (Cassol et al., 2005). 6. (Calo et al., 2005). 7. (Reetz et al., 1996) 8. (Zhao et al., 2004). 9. (Calo et al., 2005). 10. (Chiappe et al., 2006). 11. (Corma et al., 2005). 12. (Calo et al., 2009).

Table 1. Examples for Pd-NPs Catalysed Carbon-Carbon Cross-Coupling Reactions in ILs.

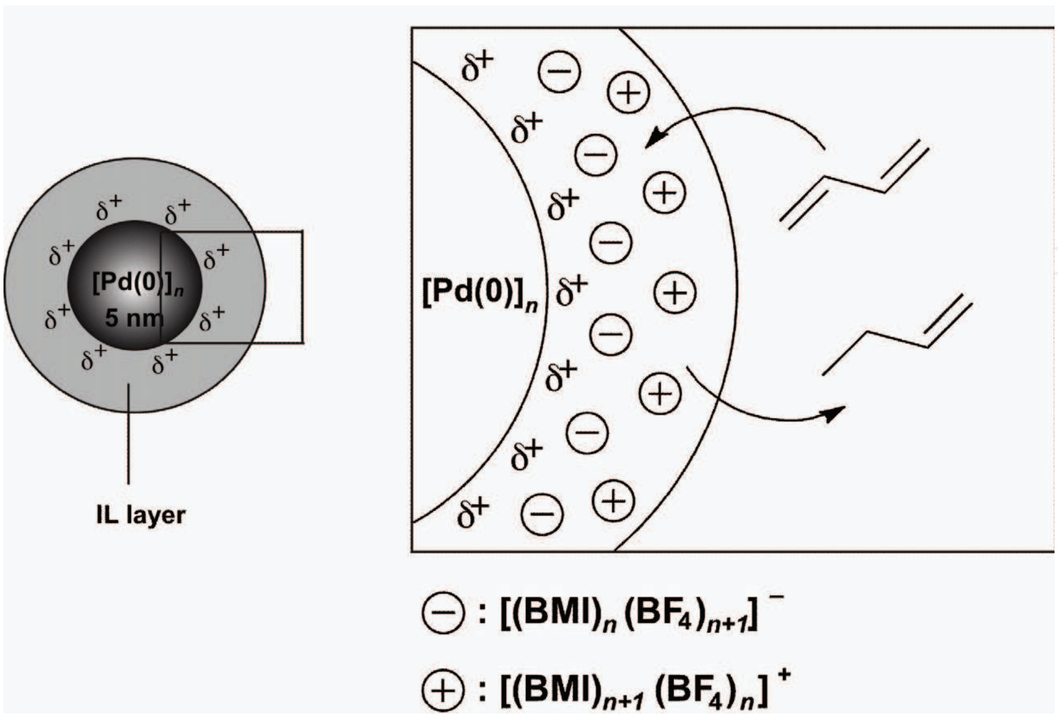


Fig. 3. Hydrogenation of 1,3-butadiene catalysed by metal Pd-NPs in IL. Reprinted with permission from reference (Dupont & Scholten, 2010) (Copyright The Royal Society of Chemistry).

3. Hydrogenation reactions catalysed by Pd-NPs in ILs

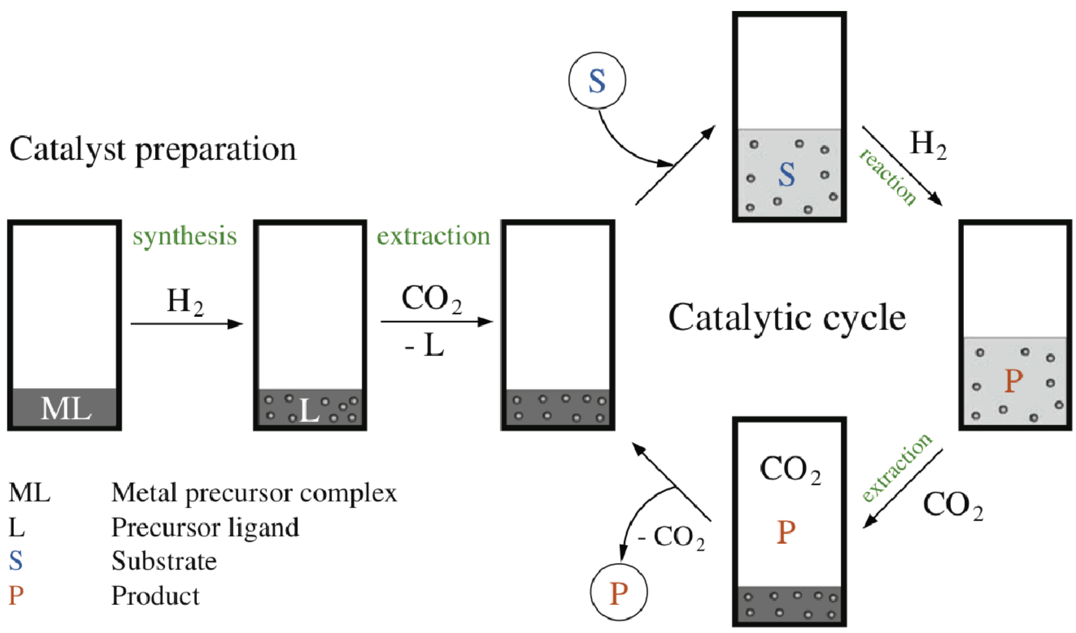
There is no doubt that hydrogenation reactions of unsaturated compounds are under the most extensively studied processes in catalysis.(Young et al., 1947; Brown & Brown, 1962; Harmon et al., 1969; Ohkuma et al., 1995; Lu et al., 2008) In this context, the preparation and stabilisation of metal NPs becomes a suitable alternative for the classical homogeneous and heterogeneous systems.(Crooks et al., 2001; Thomas et al., 2003; Astruc et al., 2005; Yan et al., 2010) Particularly, metal NPs prepared in ILs proved to be an outstanding recyclable catalytic-phase for the hydrogenation of different substrates exhibiting high catalytic activities.(Migowski & Dupont, 2007; Dupont & Scholten, 2010) In this section it selected works on the use of Pd(0)-NPs immobilised in ILs as catalyst-phase employed in hydrogenation reactions are briefly discussed (see Table 2).

Stable metal Pd-NPs could be synthesised directly in ILs as unique stabiliser agents or in the presence of additional ligands that, in general, improves the stability and catalytic activity of these nanomaterials.(Prechtl et al., 2010) By use of imidazolium-based ILs as sole stabilising agent, Pd(0)-NPs (4.9 ± 0.8 nm) were generated in BMI.PF_6 (or BMI.BF_4) from the reduction of $Pd(acac)_2$ (acac = acetylacetonate) by molecular hydrogen (4 atm, constant pressure) at 75 °C.(Umpierre et al., 2005) These NPs dispersed in IL were tested as catalyst on the selective hydrogenation of 1,3-butadiene to butenes. Once that the substrate 1,3-butadiene is at least four times more soluble in BMI.BF_4 than butenes, selectivities up to 97% in butenes was achieved at 40 °C and 4 atm of hydrogen (Figure 3). Moreover, 1-butene was the major product obtaining up to 72% of selectivity at 99% of 1,3-butadiene conversion (entry 1, Table 2). These selectivities in butenes could be explained due to the significant difference in solubility of the 1,3-butadiene and butenes, where the products were extracted from the IL layer by the substrate avoiding the subsequent hydrogenation step. Notably, there is no isomerisation of butenes during reaction, suggesting that the Pd(0)-NPs possess pronounced surface-like properties. After the catalytic reactions aggregation of the NPs could be observed, in certain cases.

A "green" method based on the combination of IL and supercritical carbon dioxide was employed as an efficient metal NPs preparation route and product separation.(Jutz et al., 2009) This procedure consists of the removal of the residual ligands after NPs synthesis by the supercritical CO_2 as well as of the extraction of the products at the end of the hydrogenation reaction (Scheme 11). Indeed, Pd-NPs could be prepared in imidazolium ($BMI.PF_6$ and BMI.OTf) or in quaternary ammonium (THAB; THA = tetrahexylammonium) salts by the reduction of $Pd(acac)_2$ with molecular hydrogen. The Pd-NPs synthesised in THAB presented a mean diameter of 3.5 ± 0.6 nm, while the particles in $BMI.PF_6$ or BMI.OTf exhibited considerable agglomeration reaching sizes of 10-30 nm. These nanocatalysts immobilised in ILs were able to catalyse the hydrogenation of acetophenone with good selectivities in 1-phenylethanol (entries 2 and 3, Table 2). The NPs prepared in THAB showed no significant activity for acetophenone hydrogenation. In particular, Pd-NPs in $BMI.PF_6$ proved to be the best catalytic system without loss in its activity after recharges.

When compared to the NPs generated in IL as unique stabiliser agent, a functionalised imidazolium IL, namely 2,3-dimethyl-1-[3-*N*,*N*-*bis*(2-pyridyl)-propylamido]imidazolium hexafluorophosphate ($BM_2DPA.PF_6$), was shown to be used as protective ligand to support the synthesis of more stable Pd-NPs in $BM_2I.PF_6$ (BM_2I = 1-*n*-butyl-2,3-dimethylimidazolium).(Hu et al., 2009) Indeed, the functionalised IL displayed an important role in enhancing the stabilisation of NPs. The precursor $Pd(OAc)_2$ could be reduced by molecular hydrogen in $BM_2I.PF_6$ with the presence of $BM_2DPA.PF_6$ producing Pd-NPs (5-6 nm). Notably, the isolation of the NPs and re-dispersion in the IL showed a remarkably effect on the catalytic activity in hydrogenation experiments. In fact, when isolated and re-dispersed in IL, the Pd-NPs provide higher substrate conversions in the catalytic insights by comparison with those non-isolated NPs (entries 4 and 5, Table 2). This can be related to the fact that, when in excess (non-isolated NPs), the ligand could block the active sites of the NP dropping considerably the catalyst's activity. Notably, using 2-cyclohexen-1-one as standard substrate, the system could be re-used efficiently for seven runs (entry 6, Table 2).

Similarly, the use of phenantroline (Phen) as additional ligand on the synthesis of Pd-NPs in $BMI.PF_6$ was also demonstrated.(Huang et al., 2003) Protected and well-dispersed NPs (2-5 nm) was obtained from the reduction of $Pd(OAc)_2$ by hydrogen in the IL with the presence of phenantroline. Insights into the catalytic process showed that these ligand-protected Pd-NPs in ILs were very active catalysts for the hydrogenation of olefins, achieving total conversions in the most cases (entries 7 and 8, Table 2). The importance of the additional ligand was proved when cyclohexene hydrogenation was carried out with Pd-NPs prepared only in IL. After the first reaction, a Pd black precipitation occured in the IL and, in the second cycle a drastic decrease in activity was observed. However, using the Phen-protected Pd-NPs in IL, no significant loss in activity was detected for at least 10 recycles during cyclohexene hydrogenation.

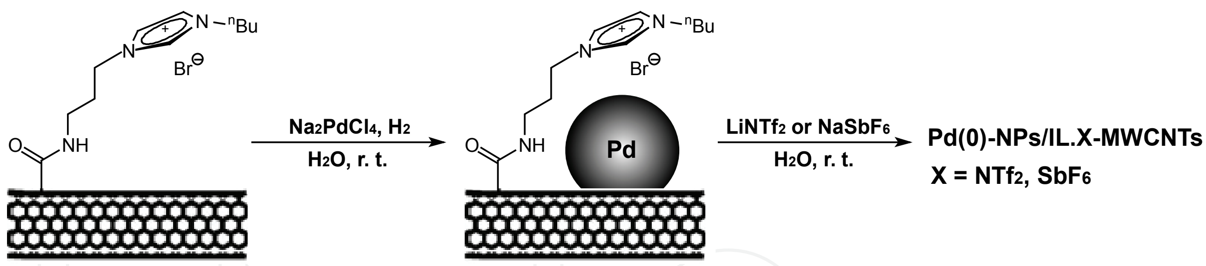


Scheme 11. "Green" method developed to generate metal NPs in ILs and their use as catalyst during hydrogenation reactions. Reprinted with permission from reference (Jutz et al., 2009) (Copyright Elsevier).

In the same context, palladium metal NPs (3 nm) were synthesised from the ethanolic reduction of $PdCl_2$ in the presence of poly(*N*-vinyl-2-pyrrolidone) (PVP) as stabilising ligand.(Mu et al., 2004) Then, these PVP-stabilised NPs were immobilised in BMI.PF_6 and employed as efficient catalyst-phase in olefin hydrogenation under mild conditions (entry 9, Table 2).

As an appropriate capping agent, TBAB was employed for the generation of Pd-NPs.(Le Bras et al., 2004) From a mixture containing a [Pd(II)] precursor, TBAB and tributylamine at 120 °C, metal NPs with mean diameters of 4.1 and 7.5 nm can be prepared using $Pd(OAc)_2$ and $PdCl_2$, respectively. Since the catalytic reactions were performed at room temperature, it was necessary to dissolve the NPs mixture in an organic solvent or in IL. In order to verify the potential recyclability of these systems, BMI.PF_6 was chosen as suitable solvent. The stabilised Pd-NPs (4.1 nm) dispersed in IL present good efficiency and selectivity in hydrogenation of unsaturated compounds (entries 10 and 11, Table 2), even on the recycling tests during five successive reactions with different substrates.

A simple and efficient deposition of Pd-NPs onto an IL functionalised multi-walled carbon nanotubes (IL-MWCNT) support was reported as a proper method to stabilise metal NPs.(Chun et al., 2008) The reduction of an aqueous solution of Na_2PdCl_4 and the IL.Br-MWCNT (bearing a bromide anion) by hydrogen under mild conditions afforded deposited metal Pd-NPs (10 nm) on IL.Br-MWCNTs (Scheme 12). Moreover, the direct exchange of the bromide anion from the system Pd-NPs/IL.Br-MWCNTs to NTf_2 or SbF_6 in water can tune the solubility properties of these materials in other solvents. Interestingly, in a mixture containing an IL and another organic solvent (MeOH or *i*-PrOH), these systems dissolve preferentially in the IL phase. Notably, the Pd-NPs/IL.X-MWCNTs (X = Br, NTf_2, SbF_6) were applied firstly as catalyst on the *trans*-stilbene hydrogenation in MeOH, reaching high TOFs values. In addition, the catalyst containing SbF_6 as anion showed the best results compared to those obtained bearing Br or NTf_2 anion. Thus, Pd-NPs/IL.SbF_6-MWCNTs was



Scheme 12. Synthesis of supported metal Pd-NPs in functionalised IL-MWCNTs. Adapted with permission from reference (Chun et al., 2008) (Copyright The Royal Society of Chemistry).

No*	Solvent	Substrate	Product	T (°C)	t (h)	Conv. (%)	Runs
1	BMI.BF_4	1,3-butadiene[a]	1-butene	40	6	99[b]	n.d.
2	BMI.PF_6	acetophenone[c]	1-phenylethanol	25	4	98[d]	6
3	BMI.OTf	acetophenone[e]	1-phenylethanol	25	4	33[f]	n.d
4	$BM_2I.PF_6$/ IL-ligand	cinnamaldehyde[g]	aldehyde + alcohol	35	2	75[h]	n.d.
5	$BM_2I.PF_6$/ IL-ligand	cinnamaldehyde[i]	aldehyde	35	2	36[j]	n.d.
6	$BM_2I.PF_6$/ IL-ligand	2-cyclohexen-1-one	cyclohexanone	35	3	100	7
7	BMI.PF_6/ Phen-ligand	cyclohexene[k]	cyclohexane	40	5	100	10
8	BMI.PF_6/ Phen-ligand	1,3-cyclohexadiene[k]	cyclohexene (cyclohexane)	40	2 (7)	95 (100)[l]	n.d.
9	BMI.PF_6/ PVP-ligand	cyclohexene[m]	cyclohexane	40	1	100	n.d.
10	BMI.PF_6[n]	benzylpropenoate[o]	benzyl propanoate	25	20	97[p]	n.d.
11	BMI.PF_6[n]	1-benzyloxy-2-allylbenzene[o]	1-benzyloxy-2-propylbenzene	25	22	98[p]	n.d.
12	BMI.SbF_6 + *i*-PrOH[q]	olefins[r]	alkanes	20	0.08-0.17	100	50

a) Substrate/catalyst (S/C molar ratio) = 1063 and 4 atm of H_2 (constant pressure); b) Selectivity of 72% in 1-butene; c) S/C = 78 and 50 atm of H_2; d) Selectivity of 90% in 1-phenylethanol; e) S/C = 177 and 50 atm of H_2; f) Quantitative selectivity in 1-phenylethanol; g) S/C = 250 and 15 atm of H_2 (isolated and re-dispersed NPs); h) 65% in 3-phenyl propionaldehyde and 10% in 3-phenyl-propan-1-ol; i) S/C = 250 and 15 atm of H_2 (non-isolated NPs); j) Only 3-phenyl propionaldehyde was observed; k) S/C = 500 and 1 atm of H_2 (constant pressure); l) Only cyclohexene was observed at 2 h, but cyclohexane was the product after 7 h of reaction; m) S/C = 250 and 1 atm of H_2; n) The NPs were prepared in TBAB and then isolated and re-dispersed in BMI.PF_6 for catalytic insights; o) S/C = 100 and a balloon filled with H_2 was used; p) Yield of product; q) NPs supported in functionalised IL-MWCNTs were dispersed in BMI.SbF_6/*i*-PrOH (1/4, v/v) for hydrogenation insights; r) S/C = 100 and 1 atm of H_2 (balloon).

*References: 1. (Umpierre et al., 2005). 2. (Jutz et al., 2009). 3. (Jutz et al., 2009). 4. (Hu et al., 2009). 5. (Hu et al., 2009). 6. (Hu et al., 2009). 7. (Huang et al., 2003). 8. (Huang et al., 2003). 9. (Mu et al., 2004). 10. (Le Bras et al., 2004). 11. (Le Bras et al., 2004). 12. (Chun et al., 2008).

Table 2. Selected hydrogenation reactions of unsaturated compounds catalysed by metal Pd-NPs in ILs. (For references, see in the table caption)

chosen as catalyst to test the potential for recyclability during hydrogenation of several olefins under biphasic conditions (*i*-PrOH/BMI.SbF_6). In fact, this catalytic system could be recycled up to 50 times without loss in activity, indicating to be a robust recyclable catalyst immobilised in the IL phase (entry 12, Table 2).

4. Summary

The summarised contributions about carbon-carbon cross-coupling and hydrogenation reactions with Pd-NPs in ILs show interesting activity and are attractive as recyclable catalyst systems. In both reaction types, the ILs prevented the formation of bulk metal via agglomeration of the NPs. In case of the C-C coupling reactions, the Pd-NPs acted as reservoir for catalytically active molecular Pd species. For hydrogenation reactions, the surface of nanoparticles is catalytically active for heterogeneous reactions. The choice of cations, anions, functional groups and additive bases can influence the Pd-NPs´ reactivity, stability and reaction pathways. Moreover, the choice of palladium precursors for the generation of Pd-NPs most likely plays a minor role, as plethora palladium complexes and palladium salts are known as suitable “pre-catalysts” for the discussed reactions. It is expected that further Pd-catalysed coupling reactions will be more deeply investigated with Pd-NPs in ILs. Additional mechanistic studies might reveal that homogeneous catalytic systems involve NPs as reservoir for molecular species in several reaction types.

5. Acknowledgements

This work is financially supported by the Ministry of Innovation of NRW (MIWFT), Alexander-von-Humboldt Foundation and CNPq.

6. References

Astruc, D. (2007). "Palladium nanoparticles as efficient green homogeneous and heterogeneous carbon-carbon coupling precatalysts: A unifying view." *Inorganic Chemistry* 46(6) 2007: 1884-1894 [0020-1669].

Astruc, D.; Lu, F. & Aranzaes, J. R. (2005). "Nanoparticles as recyclable catalysts: The frontier between homogeneous and heterogeneous catalysis." *Angewandte Chemie-International Edition* 44(48) 2005: 7852-7872.

Bedford, R. B. (2003). "Palladacyclic catalysts in c-c and c-heteroatom bond-forming reactions." *Chemical Communications*(15) 2003: 1787-1796 [1359-7345].

Beletskaya, I. P. & Cheprakov, A. V. (2000). "The heck reaction as a sharpening stone of palladium catalysis." *Chemical Reviews* 100(8) 2000: 3009-3066 [0009-2665].

Bernardi, F.; Scholten, J. D.; Fecher, G. H.; Dupont, J. & Morais, J. (2009). "Probing the chemical interaction between iridium nanoparticles and ionic liquid by xps analysis." *Chemical Physics Letters* 479(1-3) 2009: 113-116 [0009-2614].

Bonnemann, H.; Brijoux, W.; Brinkmann, R.; Dinjus, E.; Joussen, T. & Korall, B. (1991). "Formation of colloidal transition-metals in organic phases and their application in catalysis." *Angewandte Chemie-International Edition in English* 30(10) 1991: 1312-1314 [0570-0833].

Bonnemann, H.; Brijoux, W. & Joussen, T. (1990). "The preparation of finely divided metal and alloy powders." *Angewandte Chemie-International Edition in English* 29(3) 1990: 273-275 [0570-0833].

Brown, H. C. & Brown, C. A. (1962). "New convenient technique for hydrogenation of unsaturated compounds." *Journal Of The American Chemical Society* 84(8) 1962: 1495.

Calo, V.; Nacci, A. & Monopoli, A. (2004). "Regio- and stereo-selective carbon-carbon bond formation in ionic liquids." *Journal Of Molecular Catalysis A-Chemical* 214(1) 2004: 45-56.

Calo, V.; Nacci, A. & Monopoli, A. (2006). "Effects of ionic liquids on pd-catalysed carbon-carbon bond formation." *European Journal Of Organic Chemistry*(17) 2006: 3791-3802.

Calo, V.; Nacci, A.; Monopoli, A. & Cotugno, P. (2009). "Heck reactions with palladium nanoparticles in ionic liquids: Coupling of aryl chlorides with deactivated olefins." *Angewandte Chemie-International Edition* 48(33) 2009: 6101-6103 [1433-7851].

Calo, V.; Nacci, A.; Monopoli, A. & Cotugno, P. (2009). "Palladium-nanoparticle-catalysed ullmann reactions in ionic liquids with aldehydes as the reductants: Scope and mechanism." *Chemistry-a European Journal* 15(5) 2009: 1272-1279 [0947-6539].

Calo, V.; Nacci, A.; Monopoli, A.; Damascelli, A.; Ieva, E. & Cioffi, N. (2007). "Palladium-nanoparticles catalyzed hydrodehalogenation of aryl chlorides in ionic liquids." *Journal Of Organometallic Chemistry* 692 2007: 4397-4401.

Calo, V.; Nacci, A.; Monopoli, A.; Detomaso, A. & Iliade, P. (2003). "Pd nanoparticle catalyzed heck arylation of 1,1-disubstituted alkenes in ionic liquids. Study on factors affecting the regioselectivity of the coupling process." *Organometallics* 22(21) 2003: 4193-4197 [0276-7333].

Calo, V.; Nacci, A.; Monopoli, A.; Fornaro, A.; Sabbatini, L.; Cioffi, N. & Ditaranto, N. (2004). "Heck reaction catalyzed by nanosized palladium on chitosan in ionic liquids." *Organometallics* 23(22) 2004: 5154-5158 [0276-7333].

Calo, V.; Nacci, A.; Monopoli, A.; Ieva, E. & Cioffi, N. (2005). "Copper bronze catalyzed heck reaction in ionic liquids." *Organic Letters* 7(4) 2005: 617-620.

Calo, V.; Nacci, A.; Monopoli, A.; Laera, S. & Cioffi, N. (2003). "Pd nanoparticles catalyzed stereospecific synthesis of beta-aryl cinnamic esters in ionic liquids." *Journal of Organic Chemistry* 68(7) 2003: 2929-2933 [0022-3263].

Calo, V.; Nacci, A.; Monopoli, A. & Montingelli, F. (2005). "Pd nanoparticles as efficient catalysts for suzuki and stille coupling reactions of aryl halides in ionic liquids." *Journal of Organic Chemistry* 70(15) 2005: 6040-6044 [0022-3263].

Cassol, C. C.; Umpierre, A. P.; Ebeling, G.; Ferrera, B.; Chiaro, S. S. X. & Dupont, J. (2007). "On the extraction of aromatic compounds from hydrocarbons by imidazolium ionic liquids." *International Journal Of Molecular Sciences* 8(7) 2007: 593-605.

Cassol, C. C.; Umpierre, A. P.; Machado, G.; Wolke, S. I. & Dupont, J. (2005). "The role of pd nanoparticles in ionic liquid in the heck reaction." *Journal Of The American Chemical Society* 127(10) 2005: 3298-3299 [0002-7863].

Chiappe, C.; Pieraccini, D.; Zhao, D. B.; Fei, Z. F. & Dyson, P. J. (2006). "Remarkable anion and cation effects on stille reactions in functionalised ionic liquids." *Advanced Synthesis & Catalysis* 348(1-2) 2006: 68-74 [1615-4150].

Chun, Y. S.; Shin, J. Y.; Song, C. E. & Lee, S. G. (2008). "Palladium nanoparticles supported onto ionic carbon nanotubes as robust recyclable catalysts in an ionic liquid." *Chemical Communications*(8) 2008: 942-944.

Consorti, C. S.; Flores, F. R. & Dupont, J. (2005). "Kinetics and mechanistic aspects of the heck reaction promoted by a cn-palladacycle." *Journal Of The American Chemical Society* 127(34) 2005: 12054-12065 [0002-7863].

Corma, A.; Garcia, H. & Leyva, A. (2005). "Catalytic activity of palladium supported on single wall carbon nanotubes compared to palladium supported on activated carbon study of the heck and suzuki couplings, aerobic alcohol oxidation and selective hydrogenation." *Journal of Molecular Catalysis a-Chemical* 230 2005: 97-105 [1381-1169].

Corma, A.; Garcia, H. & Leyva, A. (2005). "Comparison between polyethylenglycol and imidazolium ionic liquids as solvents for developing a homogeneous and reusable palladium catalytic system for the suzuki and sonogashira coupling." *Tetrahedron* 61(41) 2005: 9848-9854.

Crooks, R. M.; Zhao, M. Q.; Sun, L.; Chechik, V. & Yeung, L. K. (2001). "Dendrimer-encapsulated metal nanoparticles: Synthesis, characterization, and applications to catalysis." *Accounts of Chemical Research* 34(3) 2001: 181-190.

Cui, Y. G.; Biondi, I.; Chaubey, M.; Yang, X.; Fei, Z. F.; Scopelliti, R.; Hartinger, C. G.; Li, Y. D.; Chiappe, C. & Dyson, P. J. (2010). "Nitrile-functionalized pyrrolidinium ionic liquids as solvents for cross-coupling reactions involving in situ generated nanoparticle catalyst reservoirs." *Physical Chemistry Chemical Physics* 12(8) 2010: 1834-1841 [1463-9076].

de Vries, A. H. M.; Mulders, J.; Mommers, J. H. M.; Henderickx, H. J. W. & de Vries, J. G. (2003). "Homeopathic ligand-free palladium as a catalyst in the heck reaction. A comparison with a palladacycle." *Organic Letters* 5(18) 2003: 3285-3288 [1523-7060].

de Vries, A. H. M.; Mulders, J.; Willans, C. E.; Schmieder-van de Vondervoort, L.; Parlevliet, F. J. & de Vries, J. G. (2003). "Heck reactions with homeopathic palladium." *Abstracts of Papers of the American Chemical Society* 225 2003: 60-ORGN [0065-7727].

de Vries, A. H. M.; Parlevliet, F. J.; Schmieder-van de Vondervoort, L.; Mommers, J. H. M.; Henderickx, H. J. W.; Walet, M. A. M. & de Vries, J. G. (2002). "A practical recycle of a ligand-free palladium catalyst for heck reactions." *Advanced Synthesis & Catalysis* 344(9) 2002: 996-1002 [1615-4150].

Deshmukh, R. R.; Rajagopal, R. & Srinivasan, K. V. (2001). "Ultrasound promoted c-c bond formation: Heck reaction at ambient conditions in room temperature ionic liquids." *Chemical Communications*(17) 2001: 1544-1545 [1359-7345].

Dieguez, M.; Pamies, O.; Mata, Y.; Teuma, E.; Gomez, M.; Ribaudo, F. & van Leeuwen, P. (2008). "Palladium nanoparticles in allylic alkylations and heck reactions: The molecular nature of the catalyst studied in a membrane reactor." *Advanced Synthesis & Catalysis* 350(16) 2008: 2583-2598.

Dubbaka, S. R.; Zhao, D. B.; Fei, Z. F.; Volla, C. M. R.; Dyson, P. J. & Vogel, P. (2006). "Palladium-catalyzed desulfitative mizoroki-heek coupling reactions of sulfonyl chlorides with olefins in a nitrile-functionalized ionic liquid." *Synlett*(18) 2006: 3155-3157.

Dupont, J. (2004). "On the solid, liquid and solution structural organization of imidazolium ionic liquids." *Journal of the Brazilian Chemical Society* 15(3) 2004: 341-350 [0103-5053].

Dupont, J.; Consorti, C. S. & Spencer, J. (2005). "The potential of palladacycles: More than just precatalysts." *Chemical Reviews* 105(6) 2005: 2527-2571.

Dupont, J.; de Souza, R. F. & Suarez, P. A. Z. (2002). "Ionic liquid (molten salt) phase organometallic catalysis." *Chemical Reviews* 102(10) 2002: 3667-3691 [0009-2665].

Dupont, J.; Fonseca, G. S.; Umpierre, A. P.; Fichtner, P. F. P. & Teixeira, S. R. (2002). "Transition-metal nanoparticles in imidazolium ionic liquids: Recycable catalysts for biphasic hydrogenation reactions." *Journal Of The American Chemical Society* 124(16) 2002: 4228-4229.

Dupont, J. & Scholten, J. D. (2010). "On the structural and surface properties of transition-metal nanoparticles in ionic liquids." *Chemical Society Reviews* 39 2010: 1780-1804.

Dupont, J. & Spencer, J. (2004). "On the noninnocent nature of 1,3-dialkylimidazolium ionic liquids." *Angewandte Chemie-International Edition* 43(40) 2004: 5296-5297 [1433-7851].

Dupont, J. & Suarez, P. A. Z. (2006). "Physico-chemical processes in imidazolium ionic liquids." *Physical Chemistry Chemical Physics* 8(21) 2006: 2441-2452.

Durand, J.; Teuma, E.; Malbosc, F.; Kihn, Y. & Gomez, M. (2008). "Palladium nanoparticles immobilized in ionic liquid: An outstanding catalyst for the suzuki c-c coupling." *Catalysis Communications* 9(2) 2008: 273-275 [1566-7367].

Fei, Z. F.; Zhao, D. B.; Pieraccini, D.; Ang, W. H.; Geldbach, T. J.; Scopelliti, R.; Chiappe, C. & Dyson, P. J. (2007). "Development of nitrile-functionalized ionic liquids for c-c coupling reactions: Implication of carbene and nanoparticle catalysts." *Organometallics* 26(7) 2007: 1588-1598 [0276-7333].

Fernandez, F.; Cordero, B.; Durand, J.; Muller, G.; Malbosc, F.; Kihn, Y.; Teuma, E. & Gomez, M. (2007). "Palladium catalyzed suzuki c-c couplings in an ionic liquid: Nanoparticles responsible for the catalytic activity." *Dalton Transactions* 2007: 5572-5581 [1477-9226].

Forsyth, S. A.; Gunaratne, H. Q. N.; Hardacre, C.; McKeown, A.; Rooney, D. W. & Seddon, K. R. (2005). "Utilisation of ionic liquid solvents for the synthesis of lily-of-the-valley fragrance {beta-lilial (r); 3-(4-t-butylphenyl)-2-methylpropanal}." *Journal Of Molecular Catalysis A-Chemical* 231(1-2) 2005: 61-66.

Gao, S. Y.; Zhang, H. J.; Wang, X. M.; Mai, W. P.; Peng, C. Y. & Ge, L. H. (2005). "Palladium nanowires stabilized by thiol-functionalized ionic liquid: Seed-mediated synthesis and heterogeneous catalyst for sonogashira coupling reaction." *Nanotechnology* 16(8) 2005: 1234-1237 [0957-4484].

Gelesky, M. A.; Scheeren, C. W.; Foppa, L.; Pavan, F. A.; Dias, S. L. P. & Dupont, J. (2009). "Metal nanoparticle/ionic liquid/cellulose: New catalytically active membrane materials for hydrogenation reactions." *Biomacromolecules* 10(7) 2009: 1888-1893.

Gopidas, K. R.; Whitesell, J. K. & Fox, M. A. (2003). "Synthesis, characterization, and catalytic applications of a palladium-nanoparticle-cored dendrimer." *Nano Letters* 3(12) 2003: 1757-1760 [1530-6984].

Gozzo, F. C.; Santos, L. S.; Augusti, R.; Consorti, C. S.; Dupont, J. & Eberlin, M. N. (2004). "Gaseous supramolecules of imidazolium ionic liquids: "magic" numbers and intrinsic strengths of hydrogen bonds." *Chemistry-A European Journal* 10(23) 2004: 6187-6193 [0947-6539].

Gu, Y. L. & Li, G. X. (2009). "Ionic liquids-based catalysis with solids: State of the art." *Advanced Synthesis & Catalysis* 351(6) 2009: 817-847.

Hardacre, C.; Holbrey, J. D.; McMath, S. E. J.; Bowron, D. T. & Soper, A. K. (2003). "Structure of molten 1,3-dimethylimidazolium chloride using neutron diffraction." *Journal of Chemical Physics* 118(1) 2003: 273-278 [0021-9606].

Harmon, R. E.; Parsons, J. L.; Cooke, D. W.; Gupta, S. K. & Schoolen.J (1969). "Homogeneous catalytic hydrogenation of unsaturated organic compounds." *Journal Of Organic Chemistry* 34(11) 1969: 3684-3685.

Hu, Y.; Yang, H. M.; Zhang, Y. C.; Hou, Z. S.; Wang, X. R.; Qiao, Y. X.; Li, H.; Feng, B. & Huang, Q. F. (2009). "The functionalized ionic liquid-stabilized palladium nanoparticles catalyzed selective hydrogenation in ionic liquid." *Catalysis Communications* 10(14) 2009: 1903-1907.

Hu, Y.; Yu, Y. Y.; Hou, Z. S.; Li, H.; Zhao, X. G. & Feng, B. (2008). "Biphasic hydrogenation of olefins by functionalized ionic liquid-stabilized palladium nanoparticles." *Advanced Synthesis & Catalysis* 350(13) 2008: 2077-2085.

Huang, J.; Jiang, T.; Han, B. X.; Gao, H. X.; Chang, Y. H.; Zhao, G. Y. & Wu, W. Z. (2003). "Hydrogenation of olefins using ligand-stabilized palladium nanoparticles in an ionic liquid." *Chemical Communications*(14) 2003: 1654-1655.

Jutz, F.; Andanson, J. M. & Baiker, A. (2009). "A green pathway for hydrogenations on ionic liquid-stabilized nanoparticles." *Journal Of Catalysis* 268(2) 2009: 356-366.

Kim, N.; Kwon, M. S.; Park, C. M. & Park, J. (2004). "One-pot synthesis of recyclable palladium catalysts for hydrogenations and carbon-carbon coupling reactions." *Tetrahedron Letters* 45(38) 2004: 7057-7059 [0040-4039].

Le Bras, J.; Mukherjee, D. K.; Gonzalez, S.; Tristany, M.; Ganchegui, B.; Moreno-Manas, M.; Pleixats, R.; Henin, F. & Muzart, J. (2004). "Palladium nanoparticles obtained from palladium salts and tributylamine in molten tetrabutylammonium bromide: Their use for hydrogenolysis-free hydrogenation of olefins." *New Journal of Chemistry* 28(12) 2004: 1550-1553.

Lebel, H.; Janes, M. K.; Charette, A. B. & Nolan, S. P. (2004). "Structure and reactivity of "unusual" n-heterocyclic carbene (nhc) palladium complexes synthesized from imidazolium salts." *Journal of the American Chemical Society* 126(16) 2004: 5046-5047 [0002-7863].

Liu, Y.; Wang, S. S.; Liu, W.; Wan, Q. X.; Wu, H. H. & Gao, G. H. (2009). "Transition-metal catalyzed carbon-carbon couplings mediated with functionalized ionic liquids, supported-ionic liquid phase, or ionic liquid media." *Current Organic Chemistry* 13(13) 2009: 1322-1346 [1385-2728].

Liu, Y. B.; Khemtong, C. & Hu, J. (2004). "Synthesis and catalytic activity of a poly(n,n-dialkylcarbodiimide)/palladium nanoparticle composite: A case in the suzuki coupling reaction using microwave and conventional heating." *Chemical Communications*(4) 2004: 398-399 [1359-7345].

Lu, W. J.; Chen, Y. W. & Hou, X. L. (2008). "Iridium-catalyzed highly enantioselective hydrogenation of the c=c bond of alpha, beta-unsaturated ketones." *Angewandte Chemie-International Edition* 47(52) 2008: 10133-10136.

Migowski, P. & Dupont, J. (2007). "Catalytic applications of metal nanoparticles in imidazolium ionic liquids." *Chemistry-a European Journal* 13(1) 2007: 32-39.

Moreno-Manas, M. & Pleixats, R. (2003). "Formation of carbon-carbon bonds under catalysis by transition-metal nanoparticles." *Accounts of Chemical Research* 36(8) 2003: 638-643 [0001-4842].

Mu, X. D.; Evans, D. G. & Kou, Y. A. (2004). "A general method for preparation of pvp-stabilized noble metal nanoparticles in room temperature ionic liquids." *Catalysis Letters* 97(3-4) 2004: 151-154.

Narayanan, R. & El-Sayed, M. A. (2003). "Effect of catalysis on the stability of metallic nanoparticles: Suzuki reaction catalyzed by pvp-palladium nanoparticles." *Journal of the American Chemical Society* 125(27) 2003: 8340-8347 [0002-7863].

Ohkuma, T.; Ooka, H.; Ikariya, T. & Noyori, R. (1995). "Preferential hydrogenation of aldehydes and ketones." *Journal Of The American Chemical Society* 117(41) 1995: 10417-10418.

Pachon, L. D.; Elsevier, C. J. & Rothenberg, G. (2006). "Electroreductive palladium-catalysed ullmann reactions in ionic liquids: Scope and mechanism." *Advanced Synthesis & Catalysis* 348(12-13) 2006: 1705-1710 [1615-4150].

Pathak, S.; Greci, M. T.; Kwong, R. C.; Mercado, K.; Prakash, G. K. S.; Olah, G. A. & Thompson, M. E. (2000). "Synthesis and applications of palladium-coated poly(vinylpyridine) nanospheres." *Chemistry of Materials* 12(7) 2000: 1985-1989 [0897-4756].

Phan, N. T. S.; Van Der Sluys, M. & Jones, C. W. (2006). "On the nature of the active species in palladium catalyzed mizoroki-heck and suzuki-miyaura couplings - homogeneous or heterogeneous catalysis, a critical review." *Advanced Synthesis & Catalysis* 348(6) 2006: 609-679 [1615-4150].

Pittelkow, M.; Moth-Poulsen, K.; Boas, U. & Christensen, J. B. (2003). "Poly(amidoamine)-dendrimer-stabilized pd(0) nanoparticles as a catalyst for the suzuki reaction." *Langmuir* 19(18) 2003: 7682-7684 [0743-7463].

Prechtl, M. H. G.; Scariot, M.; Scholten, J. D.; Machado, G.; Teixeira, S. R. & Dupont, J. (2008). "Nanoscale ru(0) particles: Arene hydrogenation catalysts in imidazolium ionic liquids." *Inorganic Chemistry* 47(19) 2008: 8995-9001.

Prechtl, M. H. G.; Scholten, J. D. & Dupont, J. (2009). "Tuning the selectivity of ruthenium nanoscale catalysts with functionalised ionic liquids: Hydrogenation of nitriles." *Journal Of Molecular Catalysis A-Chemical* 313(1-2) 2009: 74-78.

Prechtl, M. H. G.; Scholten, J. D. & Dupont, J. (2010). "Carbon-carbon cross coupling reactions in ionic liquids catalysed by palladium metal nanoparticles." *Molecules* 15(5) 2010: 3441-3461.

Ramarao, C.; Ley, S. V.; Smith, S. C.; Shirley, I. M. & DeAlmeida, N. (2002). "Encapsulation of palladium in polyurea microcapsules." *Chemical Communications*(10) 2002: 1132-1133 [1359-7345].

Redel, E.; Kramer, J.; Thomann, R. & Janiak, C. (2009). "Synthesis of co, rh and ir nanoparticles from metal carbonyls in ionic liquids and their use as biphasic liquid-liquid hydrogenation nanocatalysts for cyclohexene." *Journal Of Organometallic Chemistry* 694(7-8) 2009: 1069-1075.

Reetz, M. T.; Breinbauer, R. & Wanninger, K. (1996). "Suzuki and heck reactions catalyzed by preformed palladium clusters and palladium/nickel bimetallic clusters." *Tetrahedron Letters* 37(26) 1996: 4499-4502 [0040-4039].

Reetz, M. T. & de Vries, J. G. (2004). "Ligand-free heck reactions using low pd-loading." *Chemical Communications*(14) 2004: 1559-1563 [1359-7345].

Reetz, M. T. & Helbig, W. (1994). "Size-selective synthesis of nanostructured transition-metal clusters." *Journal of the American Chemical Society* 116(16) 1994: 7401-7402 [0002-7863].

Reetz, M. T. & Lohmer, G. (1996). "Propylene carbonate stabilized nanostructured palladium clusters as catalysts in heck reactions." *Chemical Communications*(16) 1996: 1921-1922 [1359-7345].

Reetz, M. T. & Quaiser, S. A. (1995). "A new method for the preparation of nanostructured metal-clusters." *Angewandte Chemie-International Edition in English* 34(20) 1995: 2240-2241 [0570-0833].

Reetz, M. T. & Westermann, E. (2000). "Phosphane-free palladium-catalyzed coupling reactions: The decisive role of pd nanoparticles." *Angewandte Chemie-International Edition* 39(1) 2000: 165-+ [1433-7851].

Reetz, M. T.; Westermann, E.; Lohmer, R. & Lohmer, G. (1998). "A highly active phosphine-free catalyst system for heck reactions of aryl bromides." *Tetrahedron Letters* 39(46) 1998: 8449-8452 [0040-4039].

Rocaboy, C. & Gladysz, J. A. (2003). "Thermomorphic fluorous imine and thioether palladacycles as precursors for highly active heck and suzuki catalysts; evidence for palladium nanoparticle pathways." *New Journal of Chemistry* 27(1) 2003: 39-49 [1144-0546].

Rossi, L. M. & Machado, G. (2009). "Ruthenium nanoparticles prepared from ruthenium dioxide precursor: Highly active catalyst for hydrogenation of arenes under mild conditions." *Journal Of Molecular Catalysis A-Chemical* 298(1-2) 2009: 69-73.

Rossi, L. M.; Silva, F. P.; Vono, L. L. R.; Kiyohara, P. K.; Duarte, E. L.; Itri, R.; Landers, R. & Machado, G. (2007). "Superparamagnetic nanoparticle-supported palladium: A highly stable magnetically recoverable and reusable catalyst for hydrogenation reactions." *Green Chemistry* 9(4) 2007: 379-385.

Scheeren, C. W.; Machado, G.; Dupont, J.; Fichtner, P. F. P. & Texeira, S. R. (2003). "Nanoscale pt(0) particles prepared in imidazolium room temperature ionic liquids: Synthesis from an organometallic precursor, characterization, and catalytic properties in hydrogenation reactions." *Inorganic Chemistry* 42(15) 2003: 4738-4742.

Scholten, J. D.; Ebeling, G. & Dupont, J. (2007). "On the involvement of nhc carbenes in catalytic reactions by iridium complexes, nanoparticle and bulk metal dispersed in imidazolium ionic liquids." *Dalton Transactions* 2007: 5554-5560 [1477-9226].

Silveira, E. T.; Umpierre, A. P.; Rossi, L. M.; Machado, G.; Morais, J.; Soares, G. V.; Baumvol, I. L. R.; Teixeira, S. R.; Fichtner, P. F. P. & Dupont, J. (2004). "The partial hydrogenation of benzene to cyclohexene by nanoscale ruthenium catalysts in imidazolium ionic liquids." *Chemistry-A European Journal* 10(15) 2004: 3734-3740.

Takahashi, Y.; Ito, T.; Sakai, S. & Ishii, Y. (1970). "A novel palladium(o) complex - bis(dibenzylideneacetone)palladium(o)." *Journal of the Chemical Society D-Chemical Communications*(17) 1970: 1065-&.

Thomas, J. M.; Johnson, B. F. G.; Raja, R.; Sankar, G. & Midgley, P. A. (2003). "High-performance nanocatalysts for single-step hydrogenations." *Accounts of Chemical Research* 36(1) 2003: 20-30.

Tromp, M.; Sietsma, J. R. A.; van Bokhoven, J. A.; van Strijdonck, G. P. F.; van Haaren, R. J.; van der Eerden, A. M. J.; van Leeuwen, P. & Koningsberger, D. C. (2003). "Deactivation processes of homogeneous pd catalysts using in situ time resolved spectroscopic techniques." *Chemical Communications*(1) 2003: 128-129 [1359-7345].

Tsuzuki, S.; Tokuda, H.; Hayamizu, K. & Watanabe, M. (2005). "Magnitude and directionality of interaction in ion pairs of ionic liquids: Relationship with ionic conductivity." *Journal of Physical Chemistry B* 109(34) 2005: 16474-16481 [1520-6106].

Umpierre, A. P.; Machado, G.; Fecher, G. H.; Morais, J. & Dupont, J. (2005). "Selective hydrogenation of 1,3-butadiene to 1-butene by pd(0) nanoparticles embedded in imidazolium ionic liquids." *Advanced Synthesis & Catalysis* 347(10) 2005: 1404-1412 [1615-4150].

Xu, L. J.; Chen, W. P. & Xiao, J. L. (2000). "Heck reaction in ionic liquids and the in situ identification of n-heterocyclic carbene complexes of palladium." *Organometallics* 19(6) 2000: 1123-1127 [0276-7333].

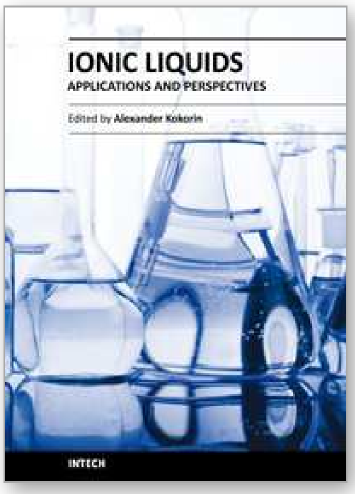
Yan, N.; Xiao, C. X. & Kou, Y. (2010). "Transition metal nanoparticle catalysis in green solvents." *Coordination Chemistry Reviews* 254(9-10) 2010: 1179-1218.

Yang, X.; Fei, Z. F.; Zhao, D. B.; Ang, W. H.; Li, Y. D. & Dyson, P. J. (2008). "Palladium nanoparticles stabilized by an ionic polymer and ionic liquid: A versatile system for c-c cross-coupling reactions." *Inorganic Chemistry* 47(8) 2008: 3292-3297.

Yin, L. X. & Liebscher, J. (2007). "Carbon-carbon coupling reactions catalyzed by heterogeneous palladium catalysts." *Chemical Reviews* 107(1) 2007: 133-173 [0009-2665].

Young, W. G.; Meier, R. L.; Vinograd, J.; Bollinger, H.; Kaplan, L. & Linden, S. L. (1947). "Investigations on the stereoisomerism of unsaturated compounds.8. The catalytic hydrogenation of butadiene." *Journal Of The American Chemical Society* 69(8) 1947: 2046-2050.

Zhao, D. B.; Fei, Z. F.; Geldbach, T. J.; Scopelliti, R. & Dyson, P. J. (2004). "Nitrile-functionalized pyridinium ionic liquids: Synthesis, characterization, and their application in carbon - carbon coupling reactions." *Journal of the American Chemical Society* 126(48) 2004: 15876-15882 [0002-7863].



Ionic Liquids: Applications and Perspectives

Edited by Prof. Alexander Kokorin

ISBN 978-953-307-248-7

Hard cover, 674 pages

Publisher InTech

Published online 21, February, 2011

Published in print edition February, 2011

This book is the second in the series of publications in this field by this publisher, and contains a number of latest research developments on ionic liquids (ILs). This promising new area has received a lot of attention during the last 20 years. Readers will find 30 chapters collected in 6 sections on recent applications of ILs in polymer sciences, material chemistry, catalysis, nanotechnology, biotechnology and electrochemical applications. The authors of each chapter are scientists and technologists from different countries with strong expertise in their respective fields. You will be able to perceive a trend analysis and examine recent developments in different areas of ILs chemistry and technologies. The book should help in systematization of knowledges in ILs science, creation of new approaches in this field and further promotion of ILs technologies for the future.