Ionic liquids in catalysis: molecular and nanometric metal systems

Gustavo Chacón[a,b], Jérôme Durand[c], Isabelle Favier[a], Emmanuelle Teuma[a], Montserrat Gómez[a*]

[a] Laboratoire Hétérochimie Fondamentale et Appliquée, UMR CNRS 5069, Université de Toulouse 3 – Paul Sabatier, 118 route de Narbonne, 31062 Toulouse cedex 9, France

[b] Current address: Institute of Chemistry, Laboratory of Molecular Catalysis UFRGS, Av. Bento Gonçalves, 9500, 91501-970 P.O. Box 15003, Porto Alegre, RS, Brazil.

[c] Laboratoire de Chimie de Coordination, UPR CNRS 8241 composante ENSIACET, Université de Toulouse, 4 allée Emile Monso-CS 44362, 31030 Toulouse cedex 4, France

gomez@chimie.ups-tlse.fr

Keywords: *ionic liquids, catalysis, organometallic complexes, metallic nanoparticles, supported ionic liquid phase.*

Abstract: The catalyst immobilisation in a liquid phase represents an attractive mean to preserve high reaction rates and selectivities, also leading to an easy recycling. To attain this goal, organic products should be extracted in a simple way from the catalytic phase giving metal-free compounds; for this reason, ionic liquids exhibiting high affinity for metallic species and low affinity for low polar compounds, turn into a promising medium for the synthesis of fine chemicals. In the present Accounts, we illustrate this approach through our research involving both types of catalysts, molecular organometallic compounds and metallic nanoparticles, dispersed in an ionic liquid phase.

_____

Introduction

Ionic liquids (ILs), more particularly imidazolium-based ILs (ImILs), are the most widespread molten salts applied for catalytic purposes [1]. ImILs display supramolecular arrangements with polar and non-polar domains [2], which can permit the confinement of different kind of species, including metallic nanoclusters. ILs have been also used in combination with solid supports, e.g. for chromatography, membranes and catalysis (Supported Ionic Liquid Phase Catalysis, SILPC) purposes [3]. As expected, IL-support interactions induce changes in physico-chemical and structural properties of the ILs involved [4,5]. A deep study of thin films of ImILs supported on silica and γ-alumina amorphous solids by different techniques (TGA, DSC, XRD, solid NMR), revealed a noteworthy effect on the IL structure depending on the support nature. Therefore for the composite $ImILs@Al_2O_3$, a supramolecular assembly loss of the IL could be evidenced, while for the analogous $ImILs@SiO_2$ material, the ions interact with the silica giving a clear thermostability diminution of the IL [5].

In this Accounts, an overview of our experience in the application of ILs in catalysis, using both homogeneous (molecular

(pre)catalysts) and heterogeneous (metallic nanoparticles) systems, is analysed. The role of the ILs will be highlighted through different applications. A special mention will be devoted to the recycling of the catalytic phase. In a first time, we will focus on molecular catalysts applied in stereoselective transformations (section 1), followed by the applications of palladium nanoparticles (PdNPs) in hydrogenation and C-C couplings including tandem and sequential one-pot processes (section 2), to conclude by the SILPC approach (immobilization of ImILs on multi-walled carbon nanotubes (MWCNT)), which can preserve the advantages of both homogeneous and heterogeneous catalysis (section 3).

1. Molecular-based catalytic systems: applications in stereoselective processes

In the last years, ILs found interesting applications in homogeneous enantioselective processes (including organocatalysts, enzymes and metallic complexes), in many cases improving activity (reaction rate) and stereoselectivity in relation to the use of conventional organic solvents [6]. What is even more important, the catalyst can be efficiently immobilised in the IL phase, permitting a straightforward catalyst recycling and avoiding the metal leaching. These aspects could be in particular found in Mo-catalysed alkene epoxidations and Pd-catalysed allylic substitutions, as following described.

1.1. Chiral dioxomolybdenum complexes applied in alkenes epoxidation

Molybdenum represents a crucial metal for nearly all living organisms, involved in catalysed redox transformations [7]. However its catalytic properties in synthesis have been less developed in comparison with their transition metals congeners, in particular in stereoselective processes [8]. In this frame, Mo-catalysed epoxidation of olefins has received a particular attention since the hydroperoxide processes developed by Halcon and Arco in the 1960's (with a current market quota of approximatively 20%), based on the use of t-butyl hydroperoxide (TBHP as oxidant) [9]; the concomitant t-butyl alcohol produced together with the desired epoxide is transformed and applied in the production of octane enhancers [10]. Although many contributions have been reported mainly involving (di)oxomolybdenum(VI) complexes, just a few of them, since the first report published in 2004 by A.A. Valente *et al.* [11], have been applied in ImILs [12]. To the best of our knowledge, only two types of chiral catalysts found applications in stereoselective processes, both of them coming from the dioxomolybdenum moiety and bearing chiral oxazolines: bidentate [13] (complexes **1-2**, Fig. 1), tridentate [13] (complex **3**, Fig. 1) and tetradentate [14] ligands (complex **4**, Fig. 1).
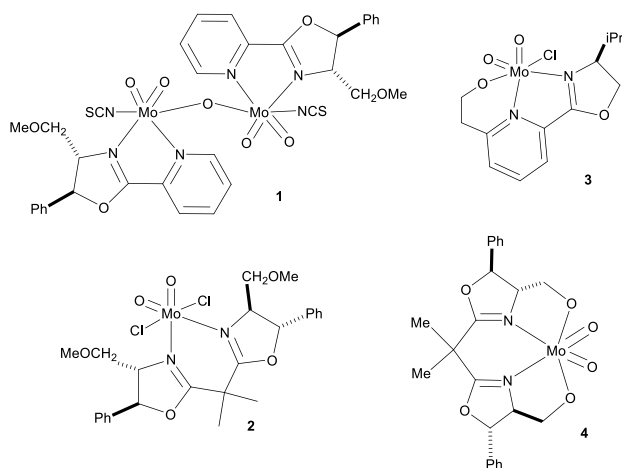
Figure 1. Dioxomolybdenum(VI) complexes containing chiral oxazoline-based ligands applied in stereoselective olefin epoxidation in ionic liquids (see [13] for **1-3**; see [14] for **4**).

Dioxomolybdenum(VI) complexes containing chiral oxazolines were applied in the epoxidation of styrene-based substrates and optically pure limonene. In contrast with the negligible asymmetric inductions observed for styrenes epoxidation [12e], significant diastereoselectivity could be achieved for both limonene enantiomers [14], leading to the exclusive formation of trans-1,2-(R)-limonene epoxide with the bimetallic complex **1** in the pyrrolidinium-based IL [BMP][NTf$_2$] (Scheme 1); but no stereoselectivity was observed using imidazolium derivatives [13]. In toluene, a high diastereoselectivity was achieved (trans/cis = 80/20) but associated to a low chemoselectivity (26% of formation of diol) [15].

A multinuclear NMR study, including ^{95}Mo NMR [16], evidenced the formation of Mo-carbene species in ImILs, which triggered the decoordination of the chiral ligand leading to a stereoselectivity loss.
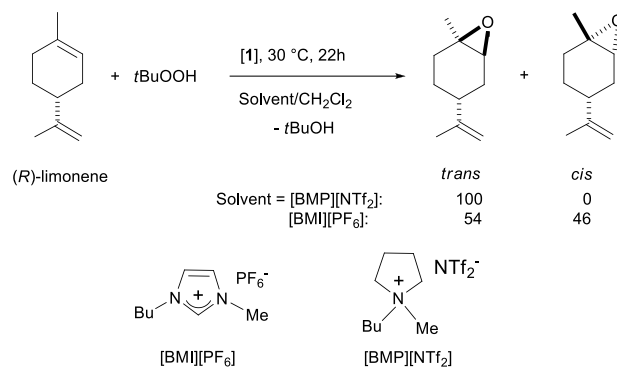

Scheme 1. Mo-catalysed diastereoselective (*R*)-limonene epoxidation in ILs (for structure of catalyst **1**, see Figure 1).

## 1.2. Chiral palladium complexes applied in asymmetric allylic substitutions

Pd-catalysed asymmetric allylic substitutions using soft nucleophiles, represent a powerful tool to form C-C and C-heteroatom bonds with excellent stereo-control [17,18]. Although this transformation is versatile, compatible with a broad range of functions and useful for the synthesis of target compounds (drugs, natural products…), only few catalytic systems can be recycled, preserving both the activity and the enantioselectivity. The immobilization of chiral palladium organometallic complexes in an ionic liquid phase was firstly reported by Toma in the 2000's, for the asymmetric allylic alkylation of the benchmark reaction (rac-(E)-1,3-diphenyl-3-acetoxyprop-1-ene with dimethylmalonate as nucleophile) in [BMI][PF$_6$] using chiral ferrocenylphosphine ligands (ee up to 90%)

[19,20]. In this frame, we were interested in the application of monodentate chiral P-heterocyclic ligands in Pd-catalysed C-C bond formation processes in [BMI][PF$_6$]. Unfortunately very low asymmetric induction was achieved (ee = 10%), even in conventional organic solvents [21]. Then we decided to use optically pure bidentate diphosphites derived from carbohydrate skeletons in asymmetric allylic alkylation, amination and phosphination reactions in [BMP][NTf$_2$] and [BMI][PF$_6$] [22] (Scheme 2). Both ILs gave high activity and excellent enantioselectivity (ee = 95%) for the alkylation, in contrast to the loss of activity and stereoselectivity observed using BINAP as chiral ligand [23]. However for the amination, the best activity together with a high asymmetric induction (ee = 96%) was observed using the pyrrolidium-based IL [BMP][NTf$_2$]; this fact is probably due to the hydrogen bond formation between the imidazolium ion and benzylamine leading to a lesser nucleophilic behaviour of the amine in [BMI][PF$_6$] than in [BMP][NTf$_2$] [24]. What is more important, the catalytic phase could be reused up to 9 times without loss of activity and maintaining the enantioselectivity more than 10 times. The Pd load on the isolated organic products was less than 0.1 ppm (determined by ICP-MS). The allylic phosphination led to moderate activities and high chemoselectivity, but unfortunately low enantioselectivity (ee up to 15%), similarly to that observed using dichloromethane instead of neat ionic liquid.
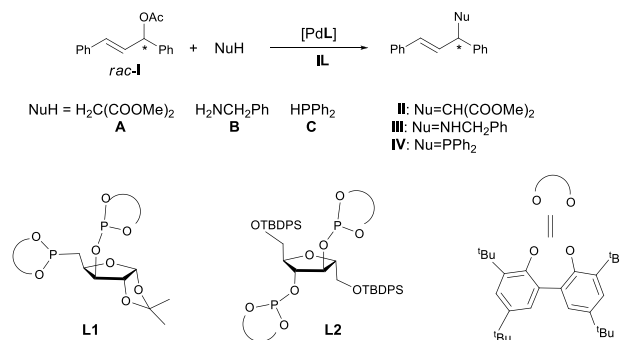
Scheme 2. Pd-catalysed asymmetric allylic substitutions in ionic liquids (IL = . [BMP][NTf$_2$] and [BMI][PF$_6$]), using chiral diphosphites (**L1**, **L2**).

Adapted chiral ligands, imidazolium-tagged chiral diamidophosphites, were also used in Pd-catalysed enantioselective allylic transformations, obtaining high asymmetric inductions, including for sulfonylation processes (ee = 72%) [25]. The catalytic phase was recycled up to six times.
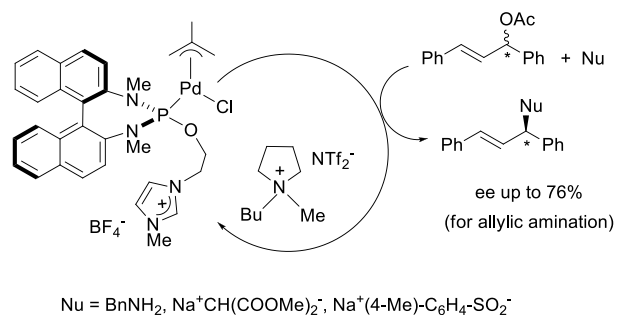
Figure 2. Pd-catalysed asymmetric allylic substitutions in ionic liquids, using imidazolium-tagged chiral diamidophosphites.

## 2. Palladium nanoparticles based catalytic systems

Palladium nanoparticles (PdNPs) stabilised by polymers, dendrimers or ligands were successfully applied as catalytic systems to promote C-C coupling reactions. In general,

metallic nanoparticles used as catalytic precursors either act as a reservoir of molecular species or display a surface-like reactivity depending on the reaction conditions [26].

2.1. Ligand-free systems

Dupont and co-workers described the synthesis of ligand-free PdNPs starting from a well-defined palladacycle in dichloromethane. Further dispersion of the obtained nanoparticles in [BMI][PF$_6$] led to an efficient catalyst for the Heck-Mizoroki cross-coupling reaction and suggested that they were actually acting as a source of molecular palladium complexes [27]. Direct synthesis in [BMI][PF$_6$] of PdNPs was carried out starting from various molecular precursors, following the procedure reported using organic solvents, that is decomposition of the complex under a dihydrogen atmosphere [28]. In that case, the ionic liquid was not only the solvent but also provided electrostatic stabilisation of the particles. Therefore, we could observe different organisations in solution by TEM analyses, depending on the nature of the Pd precursor. The particles generated from [PdCl$_2$(cod)] (cod = 1,5-cyclooctadiene) led to the most active system in the Suzuki-Miyaura coupling between bromobenzene and boronic acid, recycling the catalytic phase up to 7 times without any significant loss of activity neither metal leaching (less than 5 ppm in the final product) (Figure 3). All observations and tests using other catalytic precursors were more in

agreement with a colloidal nature of the catalytic species [29].
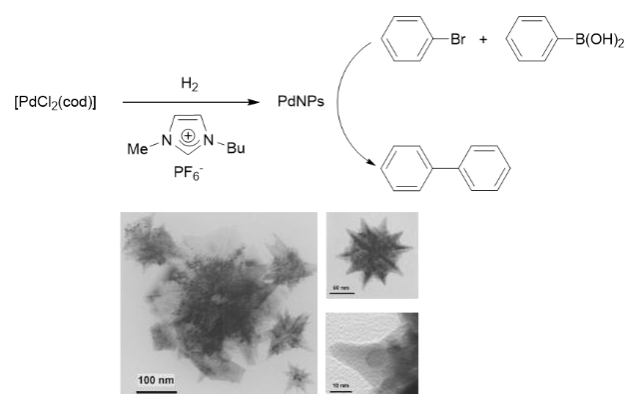
Figure 3. Schematic representation of the synthesis of PdNPs in [BMI][PF$_6$] and their applications in Pd-catalysed Suzuki-Miyaura coupling (top). TEM images of PdNPs from [PdCl$_2$(cod)] dispersed in [BMI][PF$_6$] (bottom).

Multinuclear diffusion ordered spectroscopy (DOSY) applied to PdNPs dispersed in ILs allowed gaining insights into the assembling of the particles in solution and the species in interaction with their surface [30]. These systems, consisting of PdNPs stabilised in various ILs, were also efficiently used as sole catalytic precursor for the sequential Heck-Mizoroki coupling and hydrogenation process. When [BMI][PF$_6$] was used, an orange solution was obtained at the end of the cross-coupling reaction, due to the formation of Pd-NHC molecular species [31]. The latter compounds could not be reduced under dihydrogen pressure and consequently the system becomes inactive for the further hydrogenation step which requires Pd^0 species. The use of a basic anion for the ionic liquid employed, [EMI][HP(O)$_2$OMe], allowed the development of an efficient catalytic system

for the two consecutive steps of the reaction (Scheme 3) [32].

The dual behaviour of such nanoparticles was thus established by evidencing their capability to act both as a heterogeneous catalyst and as a reservoir of active molecular species.
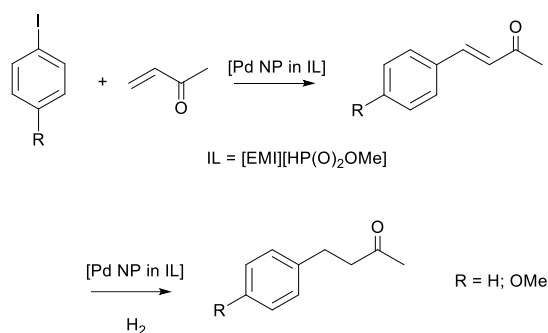
Scheme 3. Sequential Heck-Mizoroki coupling/hydrogenation process catalysed by PdNPs in a basic ionic liquid.

2.2. Ligands as co-stabilisers

During the formation and growth of metallic nanoparticles (MNPs), crystal structures constituted by a large surface area ratio and volume are favoured by kinetic and thermodynamic concerns. With the aim to control these effects, the use of stabilisers during synthesis of MNPs is a widely applied strategy, in particular in catalysis [33]. Accordingly, the use of phosphine-based ligands as stabilizers has been extensively employed due to their coordinating and easily tuning properties, which often lead to an increase of catalytic activity and/or selectivity [34].

2.2.1 Mono-phosphines

We were interested in the synthesis of PdNPs which were prepared in both, an organic

solvent (THF) and ILs ([BMI][PF$_6$] and [EMI][HP(O)$_2$OMe]) by decomposition of molecular precursors [Pd(ma)(nbd)] (ma = maleic anhydride; nbd = norbornadiene) and [Pd$_2$(dba)$_3$] (dba = dibenzylidenacetone) under hydrogen atmosphere, and in the presence of functionalized monophosphines (**L3-L6**) (Scheme 4) [35].
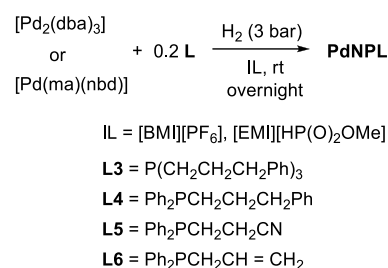
Scheme 4. Synthesis of PdNPs stabilised by monophosphines **L3**-**L6** in ImILs.

Only phosphines containing alkyl-phenyl substituents, **L3** and **L4**, gave spherical and well-dispersed PdNPs (mean diameter: 2.6 nm); in contrast, ligands **L5** and **L6** led exclusively to the formation of agglomerates. These results agree with those observed using 4-(3-phenylpropyl)pyridine as stabiliser: Pd and Ru nanoparticles were efficiently synthesized in both THF and ImILs, proving the coordination of the phenyl group at the metallic surface (see below, Figure 8) [36,37]. **PdNPL3** and **PdNPL4** were active in C-C cross-couplings and hydrogenations, but in both types of processes metal leaching was observed.

2.2.2 Thioether-phosphines

It is well known that soft metals present a high affinity towards sulphur, giving strong

sulphur-metal bonds, which can turn into a poisoning effect [38]. That is why, when metallic nanoparticles are involved in catalysis, sulphur compounds such as CS_2 or thiols are commonly used in order to discriminate between homogeneous and heterogeneous reactivity (in other words, to elucidate if MNPs present a surface-like reactivity or act as reservoir of molecular species) [39]. But in some cases sulphur compounds could enhance the catalytic activity, inducing charge depletion at the metallic surface as observed for gold nanoparticles stabilised by a polymer (poly(glycidyl)methacrylate), modified by poly(allylamine) hydrochloride) in the presence of alkylthiolate ligands, applied in the reduction of 4-nitrophenol using $NaBH_4$ as reducing agent [40]. Sulphur-based compounds can also help to the immobilisation of MNPs on modified supports by sulphur functions, which avoid the leaching of molecular species, as observed in the case of PdNPs supported on modified silica, which were applied in Suzuki-Miyaura couplings and hydrogenations [41]. In this context, we were interested in the study of thioether-phosphines as stabilisers with the aim to modulate the catalytic reactivity of PdNPs, which were prepared in both, an organic solvent (THF) and ImILs (see Figure 4 for ligands structure) [42-44]. When PdNPs were prepared in THF, the nature of the substituents on the sulphur atom played an important role on the stabilisation of the PdNPs. Actually in the case of R = phenyl (**L7**), the NPs

were better dispersed than in the case of the decyl group (**L8**), where only agglomerates were observed. In addition, both ligands, **L7** and **L8**, were modified during the synthesis of PdNPs, observing by-products formation coming from C-S and C-P bond activations. This ligand degradation reached up 30% for both thioether-phosphines. The corresponding species formed could be identified by different techniques (GC-MS, ^{31}P NMR, XPS) (Figure 4) [42]. It is important to underline that in contrast to the C-S bond activation [45], the cleavage of C(aryl)-P bonds promoted by MNPs was not previously reported.
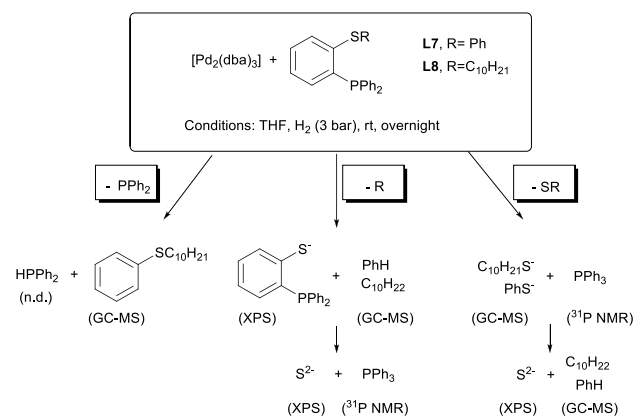

Figure 4. Schematic representation for the C-S and C-P bond activations observed during the synthesis of PdNPs. In brackets, the techniques permitting the identification of the formed species.

With the aim to weaken the direct interaction of thioether-phosphines with the metallic clusters and consequently to avoid their degradation, we decided to synthesise PdNPs in ILs (Scheme 5) [43,44].
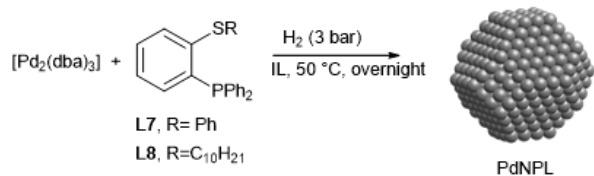
Scheme 5. Synthesis of PdNPs in the presence of thioether-phosphines in ImILs.

Smaller particles were obtained in the presence of **L7** and **L8**, giving **L7** better dispersion than **L8** as observed in the case of PdNPs prepared in THF (Figure 5). PdNPs were bigger in the IL than in THF (2.9 vs 1.6 nm), which is probably due to the role of the IL as stabiliser. However in IL medium, the ligand degradation was less significant (no more than 6%), what means that the IL prevents the C-P and C-S bond activation induced by palladium clusters.
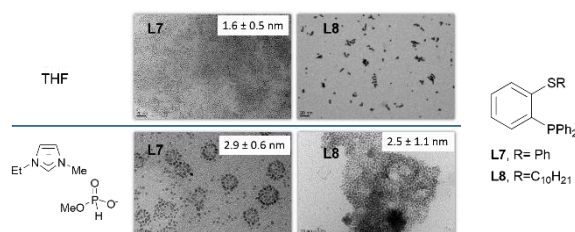
**Figure 5**. TEM images of PdNPs prepared in [EMI][HP(O)$_2$OMe].

We tested these PdNPs in the Heck-Mizoroki cross-coupling reaction (Table 1).

Table 1. Pd-catalysed Heck-Mizoroki cross-coupling reaction using preformed PdNPs as catalytic precursors.
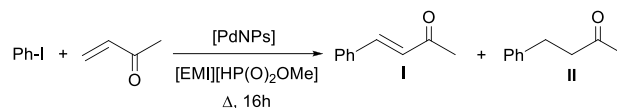
Entry	Catalyst	T (°C)	Conv. (%)	Selectivity I/II
1	PdNPs	120	100	100/0
2	**PdNPL7**	90	61	60/40
		120	100	80/20
		150	100	20/80
3	**PdNPL8**	90	71	50/50
		120	100	78/22

In contrast to ligand-free PdNPs for those only the cross-coupling product was formed (entry 1, Table 1) [32], when PdNPs were stabilised by a thioether ligand, 4-phenyl-butan-2-one **II** was also generated (entries 2-3, Table 1). Conversion and selectivity in the Heck product **I** increased between 90 and 120 °C, but the reduced compound **II** was the major product at 150 °C (entry 2, Table 1). These results indicated that the anion plays a role of reducing agent. This behaviour could be evidenced treating the compound **I** at high temperature in the absence of dihydrogen, obtaining up to 94% of product **II** (Scheme 6).
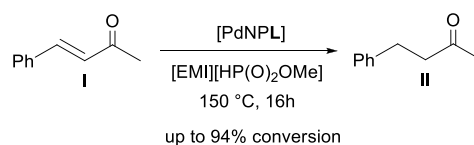

Scheme 6. Pd-catalysed reduction of the Heck-coupling product **I** into **II** promoted by [EMI][HP(O)$_2$OMe] (L = thioether-phosphine ligands).

3. Supported Ionic Liquid Phases on Multi-walled Carbon Nanotubes

Multi-walled carbon nanotubes (MWCNTs) can be used as support for the preparation of SILPC materials (Supported Ionic Liquid Phase Catalysts) because of their inherent advantageous properties, such as good mechanical strength, high chemical stability, and a large surface area-to-volume ratio [46].

We were interested in the functionalization of MWCNTs in order to support an ionic liquid phase containing the catalyst (IL = [BMI][PF$_6$]), both organometallic complexes and metallic nanoparticles. Therefore, rhodium-based SILPCs were prepared by immobilisation of a rhodium complex, [Rh(nbd)(PPh$_3$)$_2$][PF$_6$] on functionalised MWCNTs [4]. MWCNTs without external functionalisation (CNT0) were prepared by C-CVD (Catalytic Chemical Vapour Deposition) [47]. Their treatment with nitric acid led to the formation of CNT1 containing hydrophilic groups (CO, COOH), quinines and phenol on the surface. CNT1 was successively treated with thionyl chloride, imidazole, butyl bromide and potassium hexafluorophosphate, leading to the CNT2 material (Figure 6).
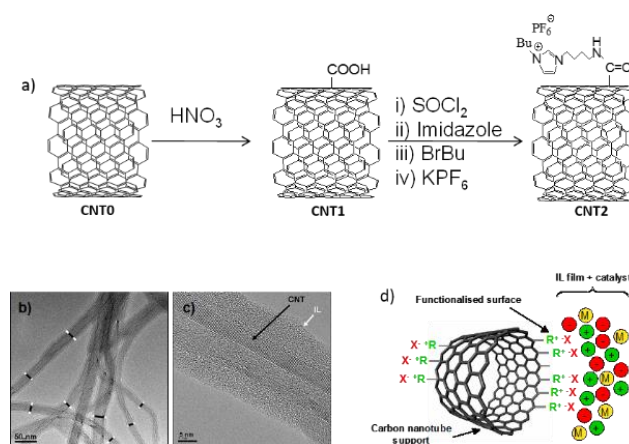
Figure 6. a) Schematic surface functionalisation of MWCNTs with imidazolium-based groups; b) TEM image of CNT2b-SIL (55%) (white bar means the IL film on the surface; black bar, MWCNT); c) HR-TEM micrograph of CNT2b-SIL (55% w/w on IL); d) schematic representation of SILPC on MWCNTs.

Tuning the amount of imidazole led to the formation of different supports: CNT2a, CNT2b and CNT2c, which are an increasing imidazolium concentration. The dispersibility of MWCNTs in [BMI][PF$_6$] was clearly improved upon surface functionalization, following the trend: CNT2 > CNT1 >> CNT0. TGA analyses indicated that the [BMI][PF$_6$] film decomposes between 340 °C and 360 °C, in contrast to 425 °C for pure IL. CNT2a and CNT2b were obtained as powders, whereas CNT2c, with the highest concentration of ionic groups at the surface, was a gel. The catalytic activity of SILPC containing the rhodium complex was evaluated for the hydrogenation of 1-hexene at 40 °C under 25 bar of hydrogen; only CNT2 based systems gave full conversion, without IL nor Rh leaching. The best catalyst was constituted by Rh/CNT2a-SIL (55% w/w on IL), permitting the recycling of the

material (up to five times). This catalyst was much more active and selective (hydrogenation versus olefin isomerisation) than the corresponding SILPCs prepared on oxide supports (such as SiO_2, Al_2O_3, TiO_2, ZrO_2, MgO or ZnO) or activated carbon instead of functionalised MWCNTs (Figure 7).
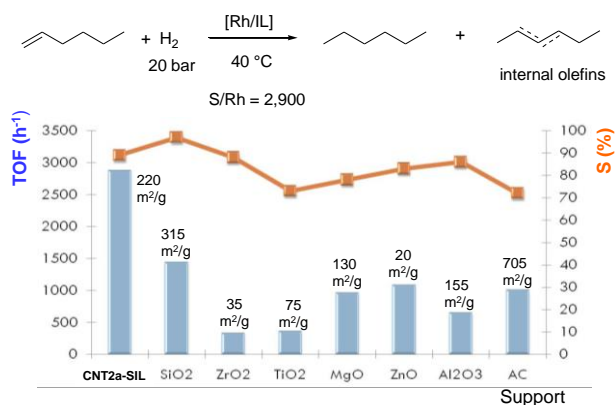
Figure 7. 1-Hexene hydrogenation catalysed by different materials constituted by a liquid phase of Rh in [BMI][PF_6] supported on different materials (figures on the blue columns stand for BET specific surface area). The orange line indicates the selectivity percentage towards the hydrogenation product.

Functionalised MWCNTs were also employed to efficiently immobilize PdNPs [37]. PdNPs were prepared by decomposition of [$Pd_2(dba)_3$] under hydrogen atmosphere and in the presence of 4-(3-phenylpropyl)pyridine (**L9**) acting as stabiliser improving the dispersion of NPs, in two imidazolium-based ILs (Figure 8). With [BMI][PF_6], well-dispersed NPs were obtained with a large particle size distribution (4.3 ± 1.3 nm); using [EMI][$HP(O)_2OMe$], a quite narrow particle size distribution (4.5 ± 0.8 nm) could be obtained.
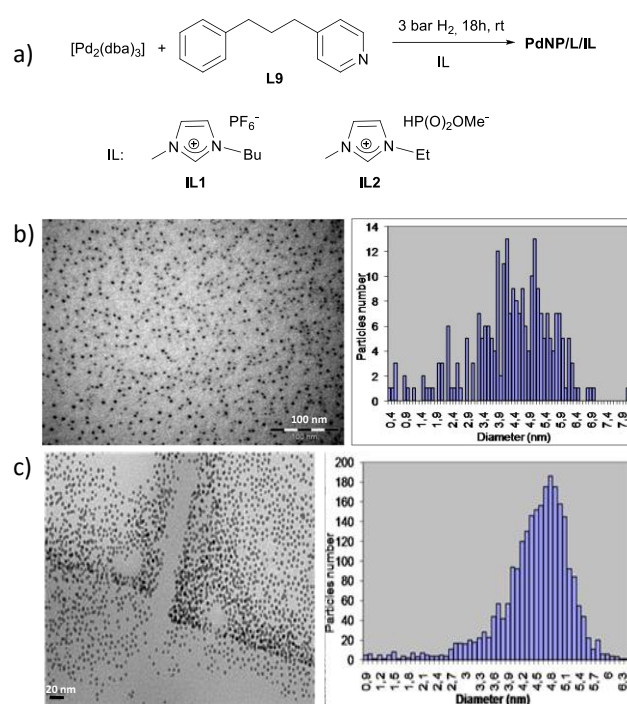
Figure 8. a) Synthesis of palladium nanoparticles in an IL in the presence of the ligand **L9**; b) and c) TEM images with the corresponding size distribution diagram for PdNP/L9/IL1 (4.3 ± 1.3 nm) and PdNP/L9/IL2 (4.5 ± 0.8 nm) respectively.

Then, the functionalised MWCNTs containing at the surface imidazolium ionic functionalities (CNT2a) [4], were added to a solution of preformed PdNPs in [BMI][PF_6] (IL1) or [EMI][$HP(O)_2OMe$] (IL2), giving PdNP-L9-IL1/CNT2a and PdNP-L9-IL2/CNT2a catalytic materials [37]. For comparative purposes, preformed PdNP in [BMI][PF_6] with and without ligand, were also supported on silica, forming PdNP-IL1/SiO_2 and PdNP-L9-IL1/SiO_2. These materials were used as catalysts in Heck-Mizoroki coupling, hydrogenation, and in the corresponding Heck coupling/hydrogenation sequential process (Scheme 7). In the hydrogenation of benzylidenacetone, no

significant influence of the ligand was found; PdNP-IL1/SiO$_2$ and PdNP-L9-IL1/SiO$_2$ exhibited similar catalytic behaviour, probably due to the electrostatic stabilization of PdNPs by the ImIL, as proved from DOSY NMR experiments [30].

solvent = N-methyl-pyrrolidone; [BMI][PF$_6$]; [EMI][HP(O)$_2$OMe]
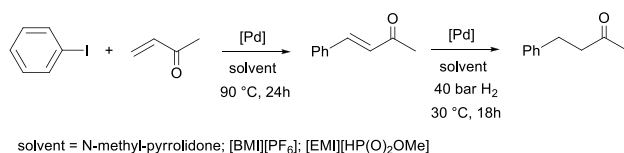
Scheme 7. Sequential Heck coupling/hydrogenation process catalysed by PdNPs supported on functionalised MWCNTs.

The catalytic system with the functionalised MWCNTs, PdNP-L9-IL1/CNT2a, showed a higher catalytic activity than that obtained with PdNP-L9-IL1/SiO$_2$, even with a lower palladium content; the open structure of the carbon nanotubes can favour the mass transfer phenomenon. The activity found with PdNP-L9-IL2/CNT2a was lower than that observed using the analogous catalytic system in [BMI][PF$_6$]. The PdNP-L9-IL1/CNT2a catalyst was reused four times without significant loss of activity. The coupling between iodobenzene and methylvinylketone was studied in the presence of PdNP-L9-IL2/CNT2a; [EMI][HP(O)$_2$OMe] was chosen as IL to avoid the addition of an external base (due to the basicity of the anion methylhydrogenphosphonate). A conversion of 96% was achieved using [EMI][HP(O)$_2$OMe] as solvent with the PdNP-L9-IL2/CNT2a catalyst. The system supported on silica, PdNP-L9-IL2/SiO$_2$ was less efficient than that supported on CNT2a.

With the aim to demonstrate the dual homogeneous and heterogeneous behaviour of MNPs, we applied these SILP catalysts as the sole catalytic precursor for a Heck coupling/hydrogenation sequential process. The most appropriate system, PdNP-L9-IL2/CNT2a, with [EMI][HP(O)$_2$OMe] as solvent, under mild conditions, led to both coupling products, 4-phenyl-3-buten-2-one and 4-phenyl-butan-2-one (hydrogenated product of 4-phenyl-3-buten-2-one, see Scheme 7) in a ca. 50:50 ratio (96% of iodobenzene conversion), without byproducts formation. This catalytic material was reused up to three times. In this sequential process, the generation of molecular palladium carbene species was prevented because no exogenous base was required. Then the molecular species formed during the Heck coupling gave PdNPs under hydrogenation conditions, permitting the further hydrogenation of the coupling product 4-phenyl-3-buten-2-one.

Outlook

In summary, this personal Accounts evidences the interest of ionic liquids in catalysis, mostly due to their negligible vapour pressure, thermal stability and diversity of structures, permitting a convenient way to immobilize catalysts, both molecular- and nanoparticles-based systems. Metal-free organic products were extracted by biphasic systems (addition of an

immiscible solvent with the IL used), without need of further purifications. The approach related to supported ionic liquid catalytic phase has proved its efficiency and potential applications. Engineering strategies, such as those involving polymer membranes modified with poly(ionic liquids), appear as highly valuable means to design continuous production [48].

Acknowledgements

References

[1]   For selected contributions, see: a) I. Favier, D. Madec, M. Gómez in *Metallic nanoparticles in ionic liquids. Applications in Catalysis,* Chapter 5 in *Nanomaterials in catalysis,* Eds. P. Serp and K. Philippot, Wiley-VCH, Weinheim (Germany), **2013**, pp 203-249*; b)* Q. Zhang, S. Zhang, Y. Deng, *Green Chem.* **2011**, 13, 2619; c) J. Dupont, J.D. Scholten, *Chem. Soc. Rev.* **2010**, 39, 1780; d) H. Olivier-Bourbigou, L. Magna, D. Morvan, *Appl. Catal. A-Gen.* **2010**, 373, 1; e) M. Antonietti, D. Kuang, B. Smarsly, Y. Zhou, *Angew. Chem. Int. Ed.* **2004**, 43, 4988.

[2]   J. Dupont, *J. Braz. Chem. Soc.* **2004**, 15, 341.

[3]   a) A.P. De los Ríos, F.J. Hernández-Fernández, F. Tomás-Alonso, J.M. Palacios, D. Gómez, M. Rubio, G. Víllora, *J. Membr. Sci.* **2007**, 300, 88; b) C.P. Mehnert, *Chem. Eur. J.* **2005**, 11, 50.

[4]   L. Rodriguez-Pérez, E. Teuma, A. Falqui, M. Gómez, P. Serp, *Chem. Commun.* **2008**, 4201.

[5]   a) L. Rodriguez-Pérez, Y. Coppel, I. Favier, E. Teuma, P. Serp, M. Gómez, *Dalton Trans.* **2010**, 39, 7565; b) F. Jiang, C. Li, H. Fu, C. Wang, X. Guo, Z. Jiang, G. Wu, S. Chen, *J. Phys. Chem. C* **2015**, 119, 22724.

[6]   For selected reviews, see: a) J. Durand, E. Teuma, M. Gómez, *C.R. Chimie* **2007**, 10, 152; b) M.H.G. Prechtl, J.D. Scholten, A.D.B. Neto, J. Dupont, *Curr. Org. Chem.* **2009**, 13, 1259; c) C. Van Doorslaer, J. Wahlen, P. Mertens, K. Binnemans, D. De Vos, *Dalton Trans.* **2010**, 39, 8377; d) Y. Qiao, A.D. Headley, *Catalysts* **2013**, 3, 709.

[7]   For a selected review, see: R.R. Mendel, F. Bittner, *Biochim. Biophys. Acta* **2006**, 1763, 621.

[8]   For an overview, see: J.A. Brito, B. Royo, M. Gómez, *Catal. Sci. Technol.* **2011**, 1, 1109 and references cited therein.

[9]   Industrial applications developed by Halcon and Arco companies: a) J. Kolar (Halcon), US 3.350.422, US3.351.635, **1967**; b) M.N. Sheng, Zajaczek (Arco), GB 1.136.923, **1968**, 1, 923.

[10]   M.G. Clerici, M. Ricci, G. Strukul, in *Formation of C-O bonds by oxidation,* Chapter 2 in *Metal-catalysis in industrial organic processes*, Ed. G.P. Chiusoli and P.M. Maitlis, RSC Publishing, Cambridge (UK), **2006**, pp 23-78.

[11]   A.A. Valente, Z. Petrovski, L.C. Branco, C.A.M. Afonso, M. Pillinger, A.D. Lopes, C.C. Romão, C.D. Nunes, I.S. Gonçalves, . *J. Mol. Catal. A: Chem.* **2004**, 218, 5.

[12]   For selected contributions, see: a) T.S.M. Oliveira, A.C. Gomes, A.D. Lopes, J.P. Lourenço, F.A. Almeida Paz, M. Pillinger, I.S. Gonçalves, *Dalton Trans.* **2015**, 44, 14139; b) S.S. Balula, S.M. Bruno, A.C. Gomes, A.A. Valente, M. Pillinger, I.S. Gonçalves, D.J. Macquarrie, J.H. Clark, *Inorg. Chim. Acta* **2012**, 387, 234; c) A. Günyar, D. Betz, M. Drees, E. Herdtweck, F.E. Kühn, *J. Mol. Catal. A: Chem.* **2010**, 331, 117; d) C. Bibal, J.C. Daran, S. Deroover, R. Poli, *Polyhedron* **2010**, 29, 639; e) M. Abrantes, F.A. Almeida Paz, A.A. Valente, C.C.L. Pereira, S. Gago, A.E. Rodrigues, J. Klinowski, M.

Pillinger, I.S. Gonçalves, *J. Organomet. Chem.* **2009**, 694, 1826.

[13]   J.A. Brito, S. Ladeira, E. Teuma, B. Royo, M. Gómez, *Appl. Catal. A-Gen.* **2011**, 398, 88.

[14]   P. Nieves, S. Gago, C.C.L. Pereira, S. Figueiredo, A. Lemos, A.D. Lopes, I.S. Gonçalves, M. Pillinger, C.M. Silva, A.A. Valente, *Catal. Lett.* **2009**, 132, 94.

[15]   J.A. Brito, M. Gómez, G. Muller, H. Teurel, J.-C. Clinet, E. Duñach, M.A. Maesto, *Eur. J. Inorg. Chem.* **2004**, 4278.

[16]   J.A. Brito, H. Teurel, S. Massou, M. Gómez, *Magn. Reson. Chem.* **2009**, 47, 573.

[17]   For earlier works, see: a) J. Tsuji, H. Takahashi, M. Morikawa, *Tetrahedron Lett.* **1965**, 4387; b) B.M. Trost, T.J. Fullerton, *J. Am. Chem. Soc.* **1973**, 95, 292; c) B.M. Trost, T.J. Dietsche, *J. Am. Chem. Soc.* **1973**, 95, 8200.

[18]   For some selected reviews, see: a) B.M. Trost, D.L. van Vranken, *Chem. Rev.* **1996**, 96, 395; b) B.M. Trost, M.L. Crawley, *Chem. Rev.* **2003**, 103, 2921; c) Z. Lu, S. Ma, *Angew. Chem. Int. Ed.* **2008**, 47, 258; d) M. Diéguez, O. Pàmies, *Acc. Chem. Res.* **2010**, 43, 312.

[19]   a) S. Toma, B. Gotov, I. Kmentová, E. Solcániová, *Green Chem.* **2000**, 2, 149; b) I. Kmentová, B. Gotov, E. Solcániová, S. Toma, *Green Chem.* **2002**, 4, 103.

[20]   For selected reports concerning Pd-catalyzed allylation reactions in ILs constituted by Pd/non-chiral ligands catalytic systems, see: a) W. Chen, L. Xu, C. Chatterton, J. Xiao, *Chem. Commun.* **1999**, 1247; b) J. Ross, J. Xiao, *Chem. Eur. J.* **2003**, 9, 4900; c) L. Leclercq, I. Suisse, G. Nowogrocki, F. Agbossou-Niedercorn, *Green Chem.* **2007**, 9, 1097; d) M. Kawatsura, H. Nobuto, S. Hayashi, T. Hirakawa, D. Ikeda, T. Itoh, *Chem. Lett.* **2011**, 40, 953; e) P. Linciano, M. Pizzetti, A. Porcheddu, M. Taddei, *Synlett* **2013**, 24, 2249.

[21]   M.V. Escárcega-Bobadilla, E. Teuma, A.M. Masdeu-Bultó, M. Gómez, *Tetrahedron* **2011**, 67, 421.

[22]   I. Favier, A. Balanta Castillo, C. Godard, S. Castillón, C. Claver, M. Gómez, E. Teuma, *Chem. Commun.* **2011**, 47, 7869.

[23]   I. Guerrero-Rios, E. Martin, *Dalton Trans.* **2014**, 43, 7533.

[24]   L. Cammarata, S. G. Kazarian, P. A. Salter, T. Welton, *Phys. Chem. Chem. Phys.* **2001**, 3, 5192.

[25]   M. J. Bravo, I. Favier, N. Saffon, R. M. Ceder, G. Muller, M. Gómez, M. Rocamora, *Organometallics* **2014**, 33, 771.

[26]   J. Durand, E. Teuma, M. Gómez, *Eur. J. Inorg. Chem.* **2008**, 3577.

[27]   C. C. Cassol, A. P. Umpierre, G. Machado, S. I. Wolke, J. Dupont, *J. Am. Chem. Soc.* **2005**, 127, 3298.

[28]   For a selected review, see: C. Amiens, B. Chaudret, D. Ciuculescu-Pradines, V. Collière, K. Fajerwerg, P. Fau, M. Kahn, A. Maisonnat, K. Soulantica, K. Philippot, *New J. Chem.* **2013**, 37, 3374.

[29] J. Durand, E. Teuma, F. Malbosc, Y. Kihn, M. Gómez, *Catal. Commun.* **2008**, 9, 273.

[30]   J. Durand, F. Fernández, C. Barrière, E. Teuma, K. Gómez, G. González, M. Gómez, *Magn. Reson. Chem.* **2008**, 46, 739.

[31]   For a selected contribution, see: N. D. Clement, K. J. Cavell, C. Jones, C. J. Elsevier, *Angew. Chem. Int. Ed.* **2004**, 43, 1277.

[32]   S. Jansat, J. Durand, I. Favier, F. Malbosc, C. Pradel, E. Teuma, M. Gómez, *ChemCatChem* **2009**, 1, 244.

[33]   R. G. Finke, in *Metal Nanoparticles. Synthesis, Characterization and Applications*, Eds. D. Feldheim and C. Foss, CRC Press, Fort Collins, Colorado, **2002**, pp 17–54.

[34]   a) S. Jansat, M. Gómez, K. Philippot, G. Muller, E. Guiu, C. Claver, S. Castillón, B. Chaudret, *J. Am. Chem. Soc.* **2004**, 126, 1592; b) I. Favier, M. Gómez, G. Muller, M. R. Axet, S. Castillón, C. Claver, S. Jansat, B. Chaudret, K. Philippot, *Adv. Synth. Catal.* **2007**, 349, 2459.

[35]   G. Chacón, D. Madec, M. Gómez, *under submission*.

[36]   I. Favier, S. Massou, E. Teuma, K. Philippot, B. Chaudret, M. Gómez, *Chem. Commun*. **2008**, 3296.

[37]   L. Rodriguez-Pérez, C. Pradel, P. Serp, M. Gómez, E. Teuma, *ChemCatChem* **2011**, 3, 749.

[38]   X. Tiancun, A. Lidun, *Catal. Lett*. **1992**, 12, 287.

[39]   a) J. A Widegren, R. G. Finke, *J. Mol. Catal. A: Chemical* **2003**, 198, 317 ; b) C. M. Hagen, L. Vieille-Petit, G. Laurenczy, G. Süss-Fink, R. G. Finke, *Organometallics* **2005**, 24, 1819.

[40]   M. Li, G. Chen, S. Bhuyain, *Nanoscale* **2015**, 7, 2641.

[41]   Qazi, A. Sullivan, *Dalton Trans*. **2011**, 40, 10637.

[42]   A. M. López-Vinasco, I. Favier, C. Pradel, L. Huerta, I. Guerrero-Ríos, E. Teuma, M. Gómez, E. Martin, *Dalton Trans*. **2014**, 43, 9038.

[43]   E. Raluy, I. Favier, A. M. López-Vinasco, C. Pradel, E. Martin, D. Madec, E. Teuma, M. Gómez, *Phys. Chem. Chem. Phys*. **2011**, 13, 13579.

[44]   A. M. López-Vinasco, I. Guerrero-Ríos, I. Favier, C. Pradel, E. Teuma, M. Gómez, E. Martin, *Catal. Commun*. **2015**, 63, 56.

[45]   For a review related to C-S bond splitting promoted by transition metals, see: L. Wang, W. He, Z. Yu, *Chem. Soc. Rev*. **2013**, 42, 599.

[46]   a) C. Pavia, E. Ballerini, L.A. Bivona, F. Giacalone, C. Aprile, L. Vaccaro, M. Gruttadauria, *Adv. Synth Catal*. **2013**, 355, 2007; b) M.-A. J. Neouze, *Mater. Chem.* **2010**, 20, 9593; c) P. H. Z. Ribeiro, E. Y. Matsubara, J. M. Rosolen, P. M. Donate, R. Gunnella, *J. Mol. Catal. A: Chem*. **2015**, 410, 34.

[47]   M. Corrias, B. Caussat, A. Ayral, J. Durand, Y. Khin, P. Kalck, P. Serp, *Chem. Eng. Sci*. **2003**, 58, 4475.

[48]   Y. Gu, I. Favier, C Pradel, D. L. Gin, J.-F. Lahitte, R. D. Noble, M. Gómez, J.-C. Remigy, *J. Membr. Sci*. **2015**, 492, 331.