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# Metal nanoparticles in water, a relevant toolbox for green catalysis

By *Audrey Denicourt-Nowicki*, Natalia Mordvinova, Alain Roucoux**

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## Abstract

This chapter describes recent advances in the synthesis of transition metal nanoparticles in neat water and their use as efficient, active and selective aqueous catalysts for various applications including hydrogenation, oxidation and carbon-carbon coupling reactions. This contribution reports different synthetic methodologies using the unique properties exerted by water and efficient capping agents to maintain stable the particles within the aqueous phase, such as water-soluble ligands, surfactants and polymers. In addition, catalytic reactions in water with nanoparticles contribute to the field of sustainable organic synthesis answering to the principles of green chemistry, sustainability, safety, and economic concerns. In the current context, nanocatalysis thus constitutes a relevant toolbox for a more eco-responsible chemistry at industrial level.

## Introduction

During the two last decades, nanometer-sized metallic species, finely dispersed in water, have attracted a great interest in the field of catalysis, and especially in green catalysis. These catalysts afford relevant, or even original in some cases, catalytic performances owing to their surface reactivity, combined with a potential recycling under adapted conditions such as biphasic catalysis [1-2]. They have been sucessfully applied in a wide range of catalytic reactions, including hydrogenation [3], carbon-carbon coupling reactions [4] and more scarcely in oxidation ones.

Synthetic processes, performed in water, remain of great interest due to intrinsic properties of this solvent (polarity, dielectric constant, high heat capacity, etc.), being inherently safer as well as available and inexpensive [5]. Moreover, the use of water allows a simple product extraction and an easy recycling of the catalyst. But water could also have influence on the catalytic performances, such as an acceleration of the reaction kinetics or selectivity [6-8]. Finally, the use of water for industrial scale-up seems to be a promising alternative to problematic or hazardous solvents [9].

In such a solvent, a bottom-up approach can be followed to prepare aqueous suspensions of metal nanoparticles, based on the reduction of commercially available transition metal salts in mild conditions and in the presence of a water-soluble protective agent in order to avoid their agglomeration. The last decade has evidenced an increasing interest for the development of relevant capping agents for the efficient stabilization of metal nanospecies within water, such as ligands possessing water-soluble functions (sulfonated phosphines, carbenes, etc.), surfactants or again polymers. The recent litterature reports many investigations to adapt organosoluble ligands dedicated to homogeneous catalysis into their water-soluble analogs by the introduction of hydrophilic functional polar moities [10-11]. The choice of the capping agents and the metal ratio can be crucial not only for the stability of the obtained nanoparticles but also for their catalytic performances since it can influence the reactivity and selectivity achieved in the targeted reaction.

In this non-exhaustive chapter, we will report some pertinent advances in catalytic applications involving aqueous suspensions of metal nanoparticles for hydrogenation, oxidation and carbon-carbon coupling reactions.

## 1. Protection by ligands

Ligands, which covalently bind at the particle's surface, constitute valuable protective agents for metal nanospecies since they can modulate both their electronic and steric environment, potentially inducing promising surface reactivities. Stabilization can generally be achieved by various ligands such as thiols, amines, carboxylic acids, phosphines, or more recently *N*-heterocyclic carbenes (NHCs). Most of them are used in organic solvents but in a few cases, the nanoparticle transfer from an organic medium to water was demonstrated feasible using a phase transfer agent. Among the water-soluble ligands recently used, phosphorous or nitrogenated ligands, as well as *N*-heterocyclic carbenes, were found to be

promising candidates for various catalytic applications, including hydrogenation and carbon-carbon coupling reactions (Table 1).

***Table 1.*** *Overview of recent catalytic applications with ligand-stabilized metal nanoparticles in neat water*

| Type of ligands | Examples of ligands | Metal | Reaction | References |
|---|---|---|---|---|
| Phosphorous | Phosphaadamantane, alkyl sulfonated phosphines | Ru, Pt | Hydrogenation of unsaturated substrates (olefins, arenes) | [12], [13] |
| | Tricyclohexylphosphine | Pd | Suzuki-Miyaura reaction | [20] |
| Nitrogenated | NTPA, CyDTA, EDTA… | Pd | Hydrogenation of polyunsaturated methyl esters | [15] |
| | Ammonium-functionalized bidentate nitrogen-containing ligands | Pd | Suzuki-Miyaura reaction | [19] |
| Carbonaceous | *N*-heterocyclic carbenes Sulfonated carbenes | Au, Pd | Hydrogenation of olefins | [17], [18] |
| | Imidazole-containing ligands | Pd | Suzuki-Miyaura reaction | [20] |

## 1.1. Hydrogenation reactions

### 1.1.1 Phosphorous ligands

Although the reduction of metal salts is the common approach to prepare nanospecies directly in water, the team of Philippot used organometallic complexes to prepare ruthenium and platinum nanoparticles (NPs) with 1,3,5-triaza-7-phosphaadamantane (PTA) as stabilizing agent, which allowed their easy dispersion in water (Figure 1) [12]. The obtained NPs display low size dispersity and very small mean diameters of 1.4 nm and 1.1 nm, respectively for ruthenium and platinum species. The authors evidenced the strong coordination of the ligand at the particle's surface with dodecanethiol exchange experiments followed by NMR spectroscopy. The aqueous colloidal suspensions proved active for hydrogenation of simple olefins (octene, dodecene) and arenes (toluene, *m*-methylanisole) under mild conditions (20°C, 1 to 10 bar $H_2$).

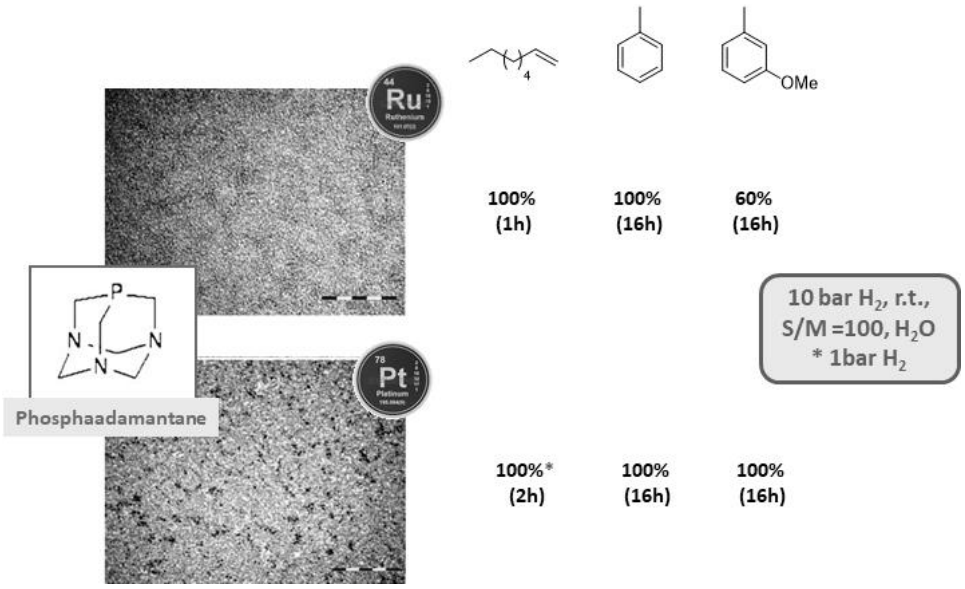



**Figure 1**. 1,3,5-triaza-7-phosphaadamantane-protected ruthenium and platinum NPs for hydrogenation of olefins and arenes (Adapted from ref. [12])

The same team also reported the organometallic synthesis of ruthenium nanoparticles stabilized by water-soluble alkyl sulfonated diphosphines as ligands (Figure 2) [13]. Sulfonated diphosphines with different numbers of carbon atoms (n) between the two phosphorous atoms (1,4-bis[(di-m-sulfonatophenyl) phosphino]-butane (or dppb-TS) for n=4, -propane (dppp-TS) for n= 3, and -ethane (dppe-TS) for n=2) were used. The obtained ruthenium NPs with small diameters in the range 1.2-1.5 nm depending on the [L]/[Ru] ratio and stable for some months, were investigated in the reduction of unsaturated substrates (tetradecene, styrene and acetophenone) in biphasic liquid–liquid conditions. In a first set of experiments, a comparison of the three catalysts obtained according to the ligand used was performed for styrene hydrogenation, showing a decrease in the following order: dppb-TS>dppp-TS>dppe-TS. This reactivity was explained by a higher flexibility, thus providing a suitable dynamic coordination mode at the particle's surface in solution. The best nanocatalyst, Ru-dppb-TS NPs, was also extended to the reduction of more lipophilic tetradecene and acetophenone. Compared to styrene, longer reaction times were needed for tetradecene under atmospheric hydrogen pressure, owing to its low water-solubility which limits the accessibility of the reducible C=C double bond to the active sites at the metal surface. In the case of acetophenone, a complete conversion was achieved in 20 h with interesting selectivities into phenylethan-1-ol (84%) and cyclohexylethan-1-ol (15%).

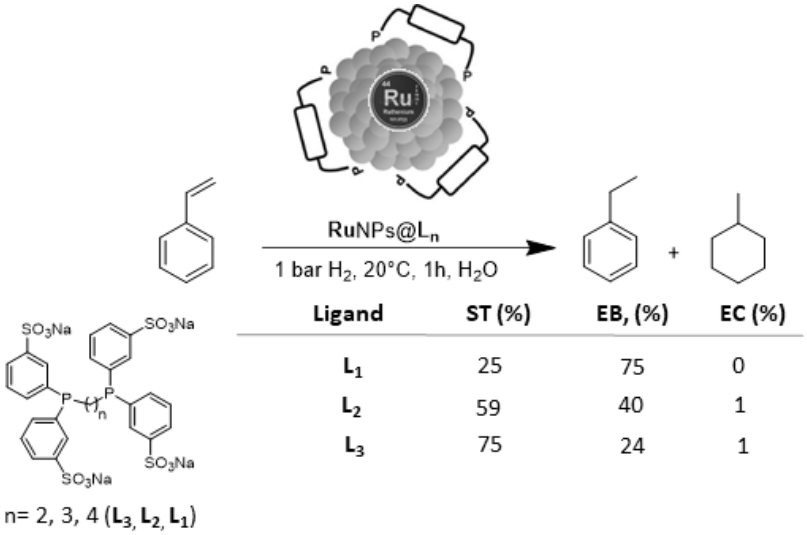



**Figure 2**. Diphosphine-coated Ru NPs. Comparison in styrene hydrogenation (Adapted from ref. [13])

More sophistically, ruthenium nanoparticles stabilized by a mixture of a sulfonated phosphine and a randomly methylated cyclodextrin proved to be active in the reduction of some unsaturated substrates such as styrene, acetophenone or *m*-methylanisole [14]. These systems showed an increased performance as the result of a shuttle effect of the cyclodextrin, as known in homogeneous catalysis.

### 1.1.2 Nitrogenated ligands

In 2014, Papadogianakis *et al.* investigated the use of nitrogen-containing ligands as protective agents, considering their great advantages such as lower prices, higher hydrophilicity and stability, compared to phosphorous analogs [15]. Thus, water-soluble palladium NPs protected by nitrogenated ligands, were synthesized *in situ* during the aqueous/organic selective hydrogenation of renewable methyl esters of soybean oil into their monounsaturated analogs and compared to Pd/TPPTS reference system (Figure 3). Oustandingly high catalytic activities (TOF = 59,000 - 68,000 $h^{-1}$) and high selectivities into C18:1 esters up to 80% were achieved when using palladium dichloride precursor ($PdCl_2$) with nitrogenated ligands such as diethylenetriaminepentakis(methylphosphonic) acid (DTPPA), bathocuproine disulfonic acid disodium salt (BCDS), nitrolis(methylphosphonic) acid (NTPA). A recycling experiment at 120 °C showed that the palladium(0) NPs are stable and active, even at this temperature, thus making this system promising to obtain upgraded biodiesel fuel.

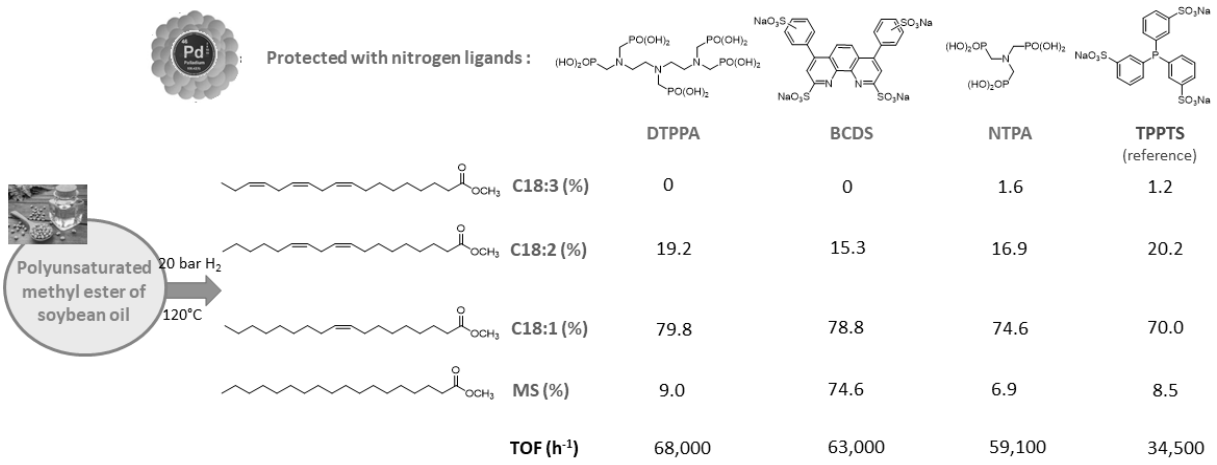



**Figure 3.** Hydrogenation of polyunsaturated methyl esters of soybean oil with Pd NPs. Nitrogen ligands *vs.* phosphorous one as protective agents (Adapted from ref. [15])

DTPPA: diethylenetriamine pentakis(methylphosphonic) acid, BCDS: bathocuproine disulfonic acid disodium salt, NPTA: nitrolis(methylphosphonic)acid, TPPTS : Trisodium 3,3',3-phosphinetriyltribenzenesulfonate

### 1.1.3 Carbon ligands

*N*-heterocyclic carbenes (NHCs) have recently found great interest as protective agents of metal nanospecies owing to their strong σ–donor effect and their easy modification with various functional groups, thus giving rise to tunable metal surfaces [16].

Glorius and coworkers developed the synthesis of palladium and gold NPs in water through a ligand exchange method. For that purpose they used a library of negatively charged NHCs possessing various functional groups, such as sulfonates or carboxylates (Figure 4) [17]. This approach consisted in displacing a weakly binding thioether (*i.e.* didodecylsulfide) with the charged NHC in a biphasic hexane/ DMF media and then redispersing the particles in water. The ligand exchange was followed by NMR experiments and the negative zeta potential values. The so-obtained NHC-decorated palladium showed relevant catalytic activities in the hydrogenation of various olefins (styrene, 1-decene, 3-methyl-2-cyclohexenone and citronellol). Among the reaction media, water seems the most promising, leading to reduction of all compounds with good yields (TON up to 2500 and TOF up to 2000 $h^{-1}$) under mild reaction conditions and low metal loadings. These catalysts were also used for the hydrogenation of more complex substrates. The γ,δ-olefin bond of sorbinaldehyde was reduced with a high degree of selectivity (> 98%). Pulegone and (+)- carvone were also hydrogenated with a complete conversion and a 1:1 diastereoisomeric ratio.

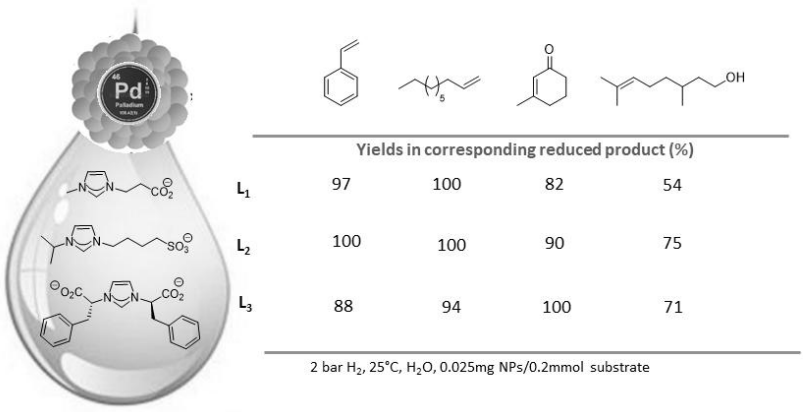



**Figure 4.** Water-soluble Pd NPs stabilized with sulfonated NHC ligands as relevant catalysts for hydrogenation of olefins (Adapted from ref. [17])

In a similar approach, Chaudret and coworkers used sulfonated NHC ligands for the synthesis of stable water-soluble palladium nanospecies through three different approaches (thermal decomposition, reduction under $^{13}CO$ atmosphere, and reduction with $H_2$) [18]. According to the method, particles with various shapes and sizes, ranging from 1.5 to 7 nm, were obtained and compared in the chemoselective hydrogenation of styrene (Figure 5). Best catalytic results were achieved with Pd@$L_4$ catalyst prepared by thermal decomposition of dimethyl palladium complexes, affording a 97% conversion after 3 h without precipitation of metal Pd. This catalyst could be recycled up to ten times without significant loss of the catalytic activity.

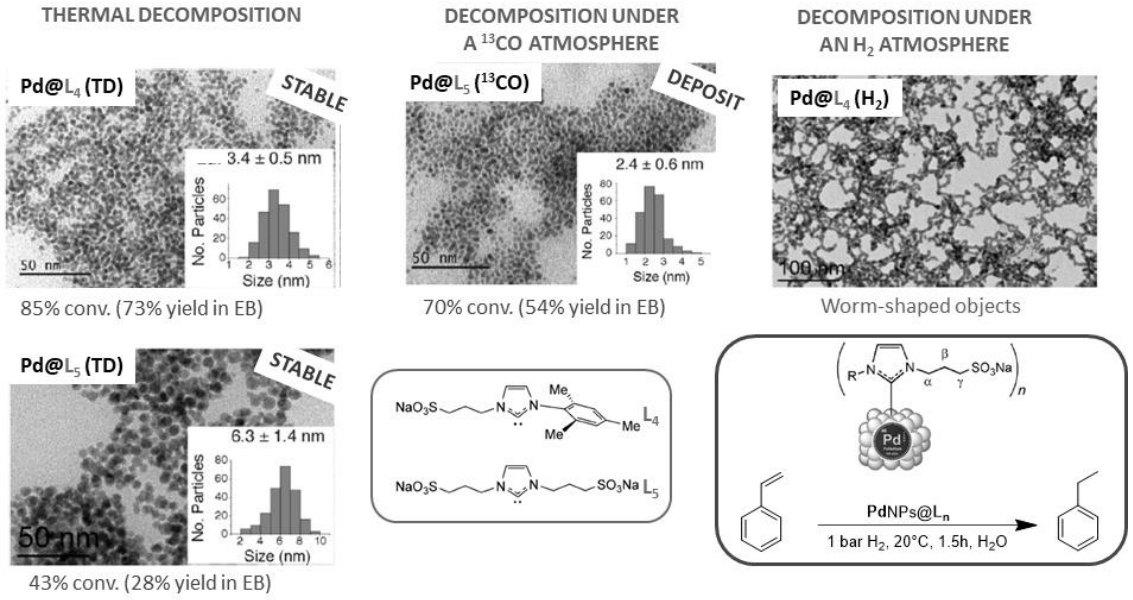



**Figure 5.** Comparison of sulfonated NHCs-stabilized Pd NPs prepared by various methods. Investigation in styrene hydrogenation (Adapted from ref. [18])

### 1.2 Suzuki-Miyaura coupling reactions

#### 1.2.1 Nitrogenated ligands

Wang and coworkers reported the easy synthesis of an ammonium-functionalized bidentate imidazole-based ligand (1-[*N*,*N'*,*N''*-trimethyl-(4-butyl)ammonium]-2-(2-pyridyl) imidazole chloride) and its corresponding palladium complex, as a catalyst precursor or a mere reservoir of Pd(0) for carbon-carbon coupling reactions (Figure 6, Catalyst 1) [19]. After catalytic reaction between bromoacetophenone and phenylboronic acid at 120°C, palladium nanospecies with size diameters of about 3 nm were observed. The obtained catalysts were highly efficient for the Suzuki-Miyaura reaction of substituted aryl chlorides and bromides with phenylboronic acid derivatives at 120°C in water, with yields ranging from 60 to 100% according to the substituents on the susbtrates.

#### 1.2.2 Carbonaceous and Phosphorous ligands

Lee et *al.* prepared a robust and highly electron rich zwitterionic complex, based on a dichloropalladium(II) complex, possessing a tricyclohexylphosphine and an imidazolium-based carbon donor as ligands [20]. The *in situ* formed nanoparticles were investigated for the Suzuki-Miyaura coupling reaction in water with a large scope of substrates, such as aryl-bromides or chlorides and sterically hindered arylboronic acid derivatives (Figure 6, Catalyst 2). The use of *n*-tetrabutylammonium bromide (TBAB) was required as co-protective agent of particles in water, as well as phase transfer agent for substrate's solubility. Moreover, this ammonium improves the catalyst's durability with a possible reuse over several runs, with similar catalytic performances (yields up to 100%). The authors observed a transfer of the particles in the liquid TBAB layer after the fourth run. However, one drawback of this system remains the high metal loading (2 mol%).

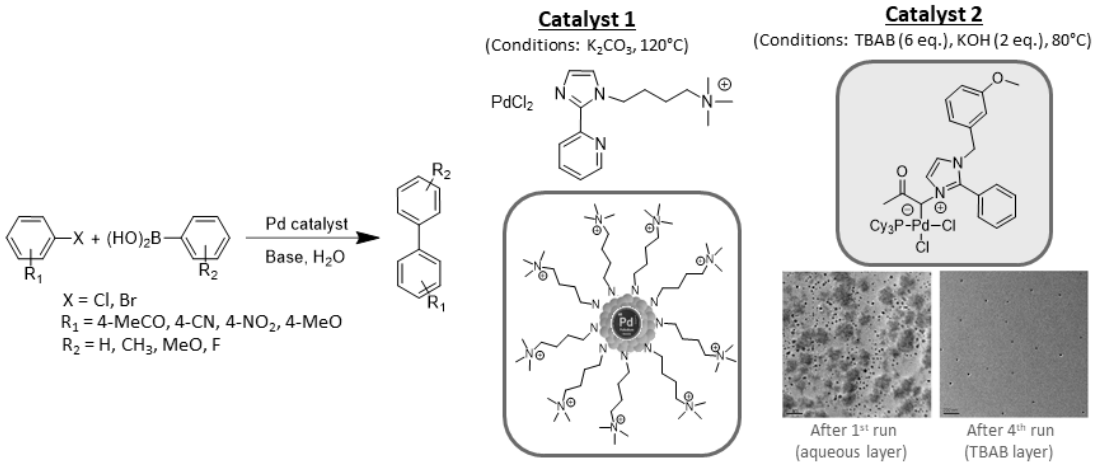



**Figure 6**. Water-soluble Pd NPs for Suzuki-Miyaura coupling reaction (Adapted from ref. [19] & [20])

## 2. Stabilization by surfactants

Surfactants are well-suited protective agents to stabilize metal nanospecies in water, affording rather strong electrosteric interactions with the particle's surface that avoid their aggregation. Among them, ammonium type surfactants, that possess a highly hydrophilic hydroxylated polar head combined with a sufficiently lipophilic chain, proved to be relevant particle stabilizers, due to the formation of an electrosteric double layer around the metal cores (Figure 7) [21-22].

For that purpose, the group of Roucoux has developed a library of easily accessible *N*,*N*-dimethyl-*N*-alkyl-*N*-(2-hydroxyethyl)ammonium salts (HEA salts) with various alkyl chain lengths (up to 18 carbon atoms), possessing mono- or poly-hydroxylated polar heads (HEA, HPA, HBA, THEA) and different counter-anions $X^-$ with X= Br, Cl, I, F, $CH_3SO_3$, $BF_4$, $HCO_3$ and $CF_3SO_3$ (Figure 7) [21, 23]. These surfactants were efficiently used as protective agents for nanoparticles of diverse metals (rhodium, palladium, ruthenium, iridium, gold, platinum, etc.). These aqueous suspensions of metal NPs were usually synthesized by chemical reduction of the corresponding chloride metal salts with sodium borohydride in dilute aqueous suspensions of quaternary hydroxylated ammonium salts and were investigated in various polyphasic catalytic reactions, including hydrogenation and oxidation reactions.

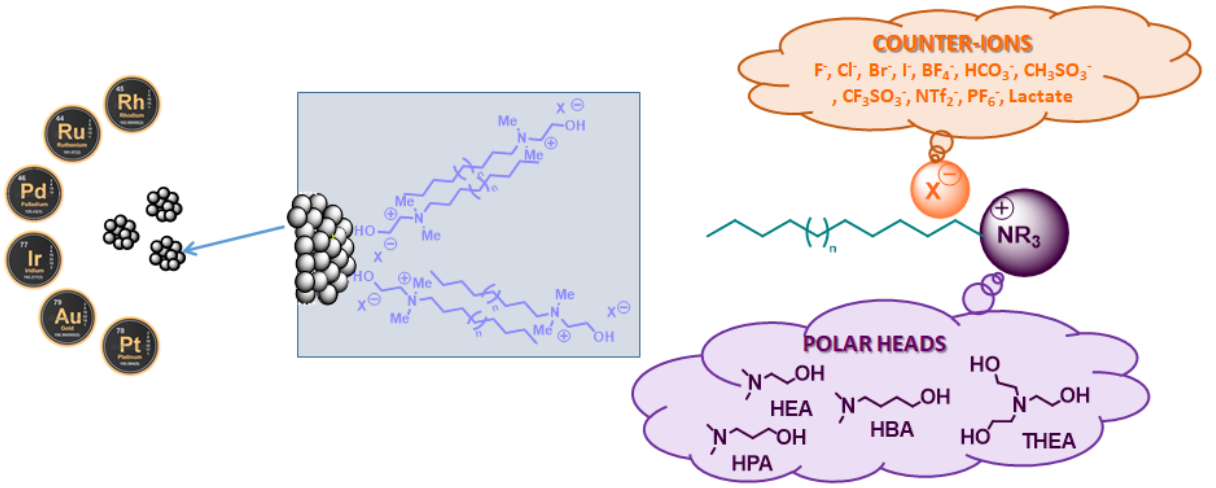



**Figure 7**. *N*-(hydroxyalkyl)-*N*-alkylammonium salts as efficient bilayer protective agents of various metal nanoparticles in water

### 2.1 Hydrogenation reactions

A systematic study on the influence of the surfactant features, including the length of the lipophilic chain [24], the nature of the counter-ion [22, 25] and the polar head [26-27], on the stability and activity of the obtained nanocatalysts was performed in arene hydrogenation

in neat water under mild conditions. Some of the relevant catalytic performances are gathered in Figure 8. First, among the noble metals investigated, rhodium nanospecies proved to be the most active [23], while ruthenium and iridium ones required higher pressure conditions [28-29]. Concerning the lipophilic chain of the surfactant, only 16- or 18 carbon-containing chains afforded efficient stabilization of the particles within the aqueous phase, compared to C12 and C14 ones, with a higher catalytic performances of C16 for anisole hydrogenation [24]. The influence of the counter-ion of the HEA16 surfactants on the rhodium NPs features (surface tension, morphology and size of the nanospecies) was also studied [22]. These compounds were easily synthesized by an one-step ion exchange reaction, starting from HEA16Cl salt. According to the weak stabilization at the metal surface, fluorinated ions (such as fluoride $F^-$, tetrafluoroborate $BF_4^-$ or triflate $CF_3SO_3^-$) gave rise to worm-like rhodium(0) particles, whereas spherical colloids were observed with chloride ($Cl^-$) and hydrogenocarbonate ($HCO_3^-$) ions being stronger protective agents. The spherical particles arising from $HCO_3^-$ anion provided higher catalytic activity compared to the $CF_3SO_3^-$ one. This can be explained by the different nanoparticle sizes and morphologies (spherical or dendrites respectively) exposing different active sites. Rhodium NPs coated with HEA16$CF_3SO_3$ and HEA16$BF_4$, afforded lowest activities, considering their extended dendrite morphology where higher energy facets possess lower density. Best results in terms of catalytic performances were achieved with rhodium particles stabilized with HEA16Cl, which also allowed an efficient catalyst recycling. The influence of the polar hydroxylated head of the surfactant on physico-chemical and catalytic properties was also investigated [26-27]. Based on a cetylammonium chloride salt as common skeleton, two novel surfactants bearing either a longer polar chain (HPA16Cl for *N*,*N*-dimethyl-*N*-cetyl-*N*–(3-hydroxy propyl)ammonium chloride) or a trishydroxylated head (THEA16Cl for *N*-cetyl-*N*-tris–(2-hydroxyethyl)ammonium chloride) were used to prepare rhodium(0) particles and compared to the usual HEA16Cl stabilizer in terms of geometry, steric hindrance, surface area per molecule and dynamic sizes. In the anisole hydrogenation at room temperature (r.t.) and 1 bar $H_2$, the catalytic activity was found to be influenced by the nature of the polar head, in the following order: THEA16Cl > HEA16Cl > HPA16Cl. This tendency was attributed to the larger hydrodynamic diameter of rhodium(0) species stabilized by the more longer hydroxypropyl head group (HPA), which can decrease the substrate's accessibility onto the metallic surface.

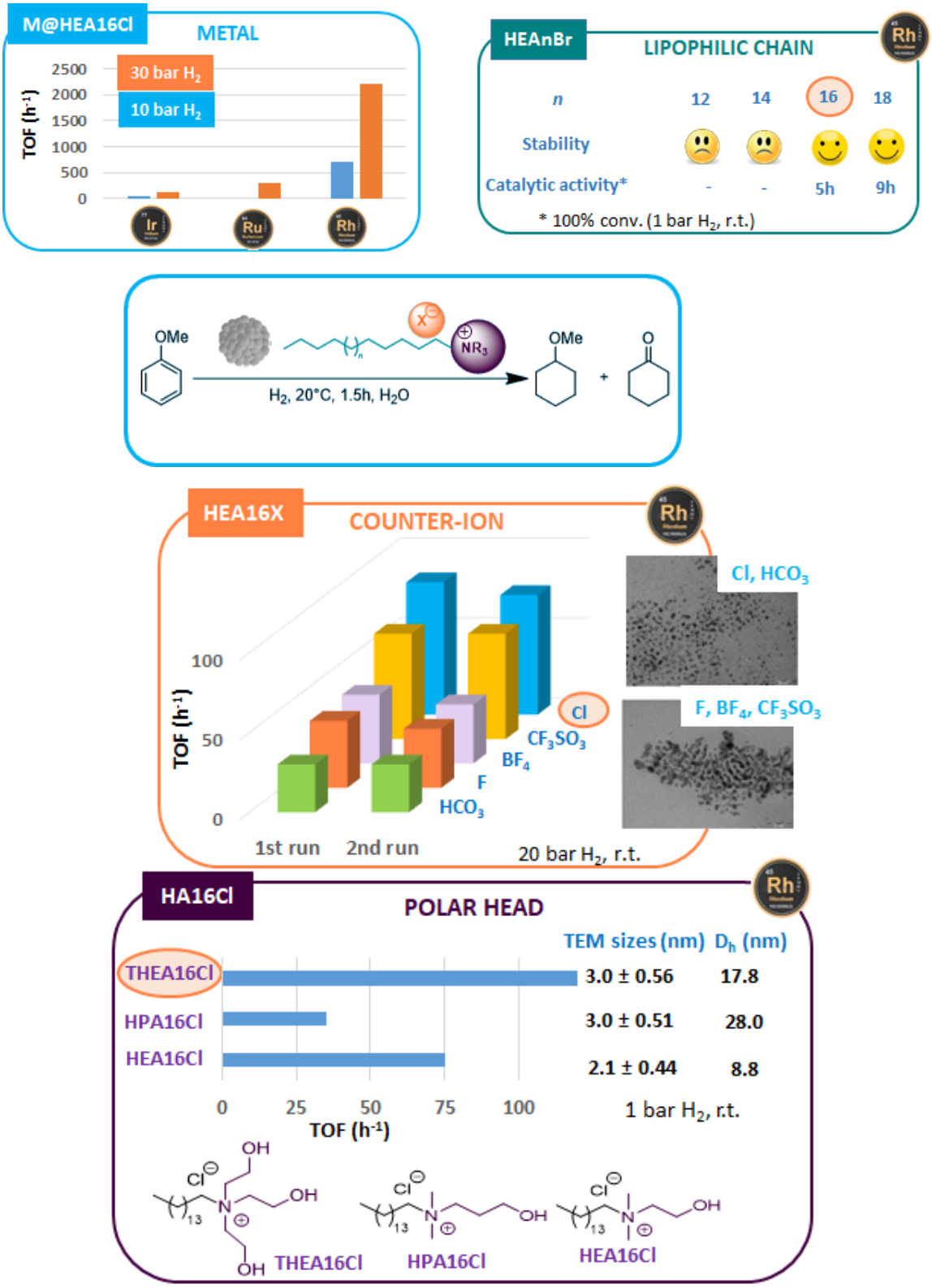
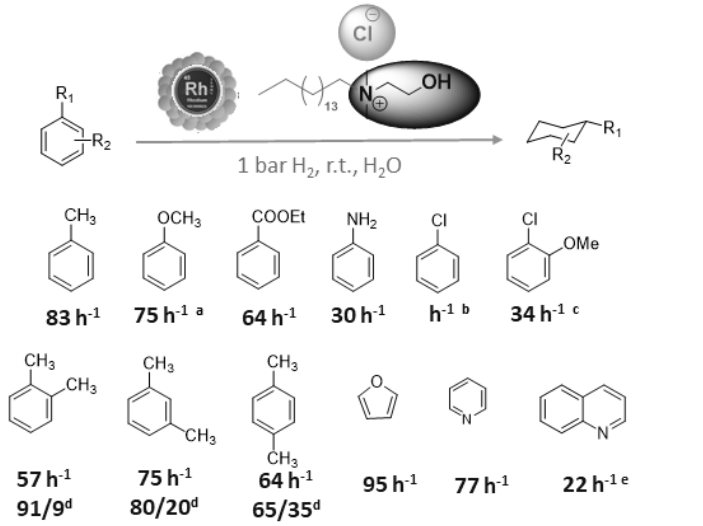



**Figure 8.** Optimization of the surfactant features in the reduction of anisole with noble NPs

HEA: HydroxyEthylAmmonium, HA: HydroxyAmmonium, THEA: TrisHydroxyEthylAmmonium, HPA: HydroxyPropylAmmonium

Based on this optimization work, the Rh@HEA16Cl catalyst was evaluated in the hydrogenation of various arenes, including alkylated, functionalized and disubstituted ones [26], oxygen or nitrogen-containing heteroaromatics [30], and halogenoarenes [31] under mild biphasic conditions, with outstanding turnover catalytic activities (TOF $h^{-1}$ values). An overview of the results obtained is presented in Figure 9.




[a] With 30% cyclohexanone formed, [b] Cyclohexane obtained, [c] 53% methylcyclohexane and 47% cyclohexane; [d] Cis major isomer, [e] 1,2,3,4-tetrahydroquinoline

**Figure 9.** Turnover catalytic activities (TOF $h^{-1}$ values) in the reduction of various arenes catalyzed by Rh@HEA16Cl

Concerning disubstituted arenes such as xylene isomers, the selectivity is in favour of the thermodynamically less stable *cis*-product, as generally observed in heterogeneous catalysis [32-33], owing to a "continuous" coordination of the substrate at the metal surface and consequently the addition of the dihydrogen *via* only one face of the substrate [34-35]. In the case of halogenoarenes, such as chlorobenzene or chloroanisole, a concomittant dehalogenation occurred within the reduction of the aromatic ring with rhodium(0) nanoparticles [31]. This rhodium-catalyzed tandem process is particularly relevant for the removal of toxic and persistent halogeno-anisole or phenol derivatives present in the industrial effluents or polluted groundwater. In many cases, the catalyst could be reused by a simple extraction of the organic phase with an appropriate solvent (alkanes or ether) over several runs, with similar catalytic performances. In case of catalyst's aggregation, the colloidal suspensions could be easily heterogenized onto inorganic supports such as silica or titanium dioxide [36-37], as well as in mesoporous materials [38] or non-functionalized magnetic supports ($\gamma$-$Fe_2O_3$) [39-40]. Finally, it can be underlined that host-guest inclusion complexes between hydroxylated ammonium surfactants and cyclodextrins were successfully

used to protect ruthenium or rhodium NPs [41], providing interesting catalysts for arene hydrogenations.

The use of effective catalytically active nanospecies for asymmetric reactions is a challenging research area [42]. Based on their methodology, namely the use of hydroxylated ammonium salts as nanoparticle stabilizers, the group of Roucoux has followed two main approaches for the asymmetric hydrogenation of ethylpyruvate in neat water. On one hand, they synthesized a library of water-soluble ammonium salts based on an optically active skeleton derived from *N*-methylephedrine or *N*-methylprolinol, associated with various counter-ions ($Br^-$, $HCO_3^-$, (*S*)- or (*R*)-lactate) (Figure 10) [43-44]. Aqueous suspensions of rhodium NPs, prepared by the usual approach, with a size diameter between 1.75 and 3 nm, were evaluated in the reduction of ethylpyruvate at r.t., under 40 bar of $H_2$. A promising asymmetric induction up to 13% was achieved, using optically active NMeEph12X salts with a dodecyl lipophilic chain, in combination with bromide or (S)-(–)-lactate ion. These nanocatalysts proved also efficient for the reduction of *m*-methylanisole, a challenging transformation to access optically enriched cyclohexyl derivatives. High *cis* selectivity was achieved, but with no asymmetric induction. On the other hand, colloidal suspensions of platinum were prepared by chemical reduction of $H_2PtCl_6$ with dihydrogen in the presence of the usual HEA16Cl surfactant, followed by the adsorption of the optically pure cinchonidine onto the metal surface. The so-obtained catalyst, stabilized with the ammonium surfactant and modified with the *cinchona* salt, proved to efficiently transform ethylpyruvate in (*R*)-ethyllactate with a complete conversion and up to 55% enantiomeric excess, under 40 bar of $H_2$ in only 13 min [45]. Moreover, the catalyst was easily recycled and reused with no loss of the catalytic performances, leading upon time to a high order superstructure. Unfortunately, the use of randomly methylated cyclodextrins grafted with chiral amino-acid moities, alone or combined with optically active ammonium surfactants, as stabilizers for ruthenium nanoparticles did not allow to achieve asymmetric induction [46-47].

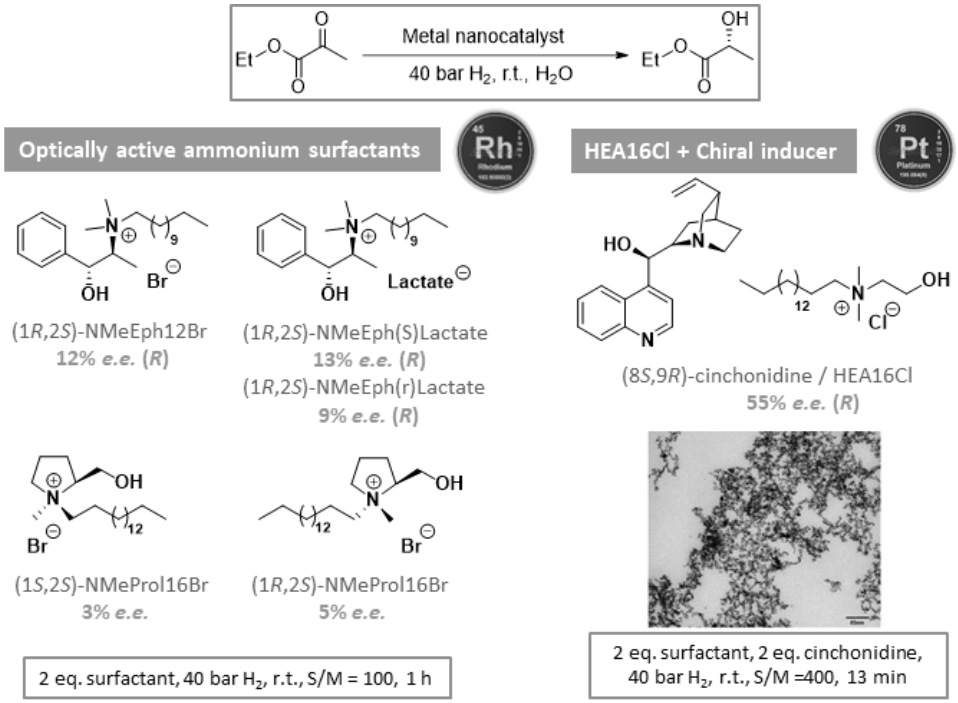



**Figure 10.** Optically active aqueous suspensions of metal nanoparticles – Towards asymmetric hydrogenation of ethylpyruvate

### 2.2 Oxidation reactions

More recently, these ammonium surfactants bearing a hydroxylated polar head were used as protective agents of ruthenium nanospecies for oxidation of terpenic olefins in water [48]. The aqueous suspensions of Ru(0) species were prepared starting from ruthenium chloride ($RuCl_3.3H_2O$). A systematic study was carried out, using hydroxyethylammonium (HEA) derivatives with various counter-ions (Cl, Br, $BF_4$), a trishydroxyethyl ammonium (THEA) surfactant, two *N*-oxide (NO12 and NO16) compounds and the commercially available CTABr surfactant and PVP polymer for comparison purpose (Figure 11). The obtained ruthenium colloids (*ca.* 2 nm) proved to be active and selective in the oxidation of α-pinene in the presence of *tert*-butylhydroperoxide, in neat water and at r.t. As product of great interest for fine chemistry, verbenone was obtained as major product with a yield up to 41%, in the presence of Ru@HEA16Cl catalyst. This catalytic system was extended to valencene, affording the corresponding nootkatone with a 60% isolated yield in water, at room temperature. This result is quite similar to the one achieved with a Cu-Al-Ox catalyst in acetonitrile at 80°C [49]. This oxyfunctionalized molecule constitutes an important flavoring constituent due its citrusy, woody, peely and grapefruitlike aroma profile [50], and a natural insect repellent [51].

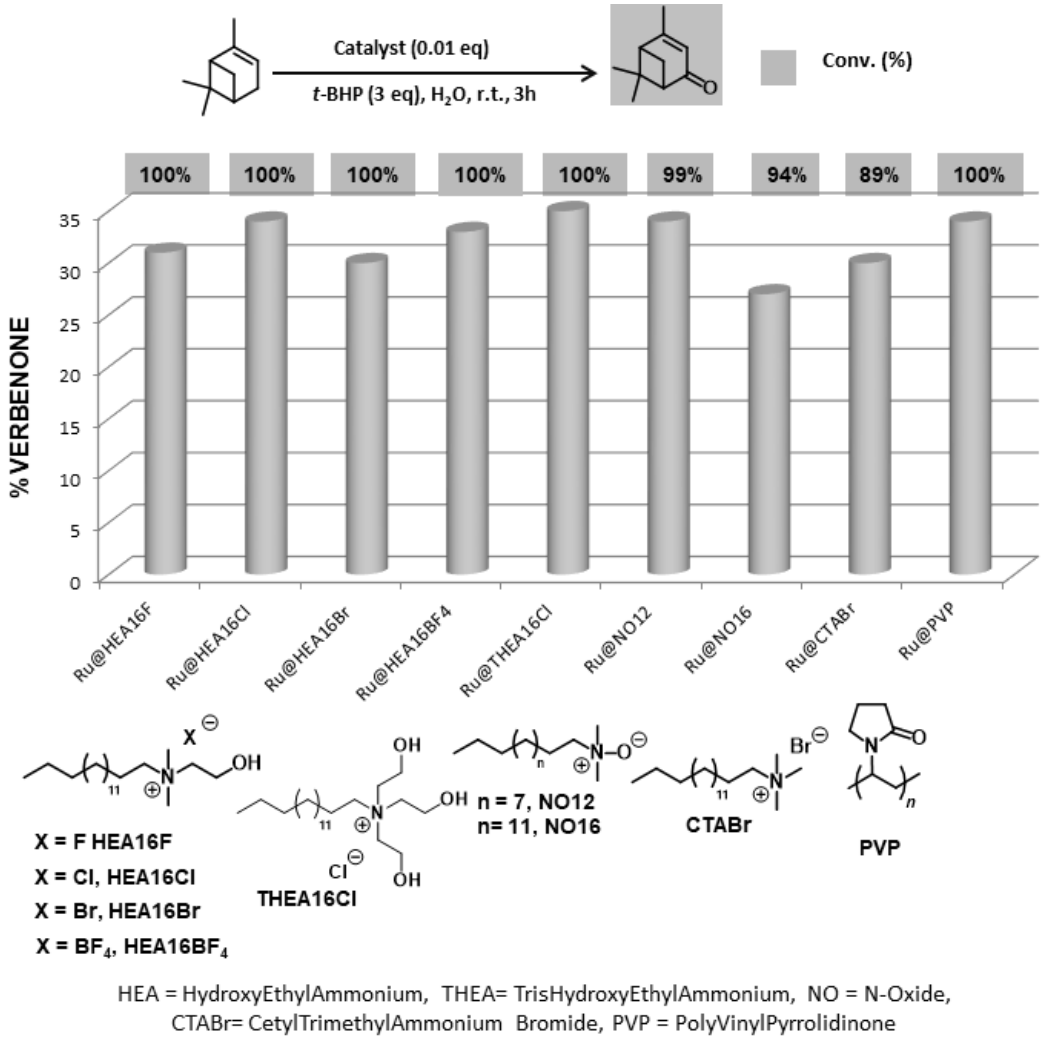



**Figure 11.** Ammonium surfactant-stabilized Ru NPs for oxidation of α-pinene **1** in neat water (Adapted from ref. [48])

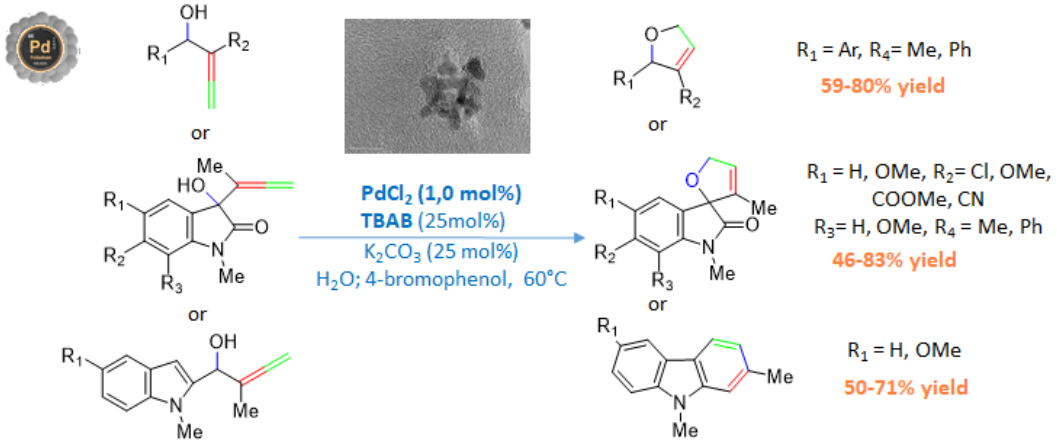
### 2.3 Other reactions

In an original way, tetrabutylammonium (TBAB)-coated palladium nanospecies were proved active for the chemoselective cyclization reaction of a large scope of α-allenol derivatives in water, leading to dihydrofurans and carbazoles as promising synthons for fine chemistry. The catalytic performances obtained with pre-generated particles were higher than those achieved with palladium precursor ($PdCl_2$) or *in situ* generated nanoparticles, combined with an efficient durability over several runs (Figure 12a) [52]. However, the addition of bromophenol as a co-stabilizing agent seems unavoidable.

Sodium laurate-protected rhodium NPs, possessing a mean size of 5.2 nm, were synthesized *in situ* from the dimethylamine-borane reduction [53]. These catalysts were found highly effective and durable in the hydrolysis of ammonia-borane at r.t. and even at low

catalyst concentration, with a total turnover number (TTO) of 80000 mol $H_2$/mol Rh and a turnover frequency (TOF) of 200 mol $H_2$/mol Rh min (Figure 12b).

(a) TBAB@Pd nanoparticles as catalyst for the cyclization of α-allenols




(b) Sodium laurate@Rh nanoparticles for hydrolysis of ammonia-borane

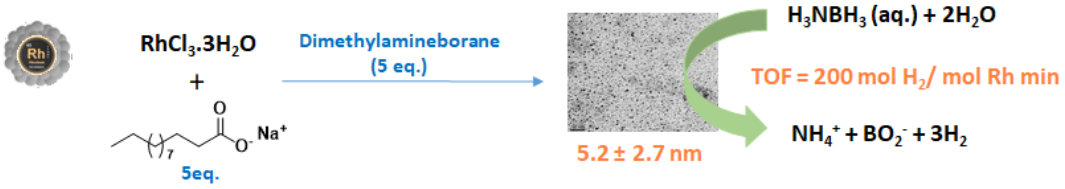
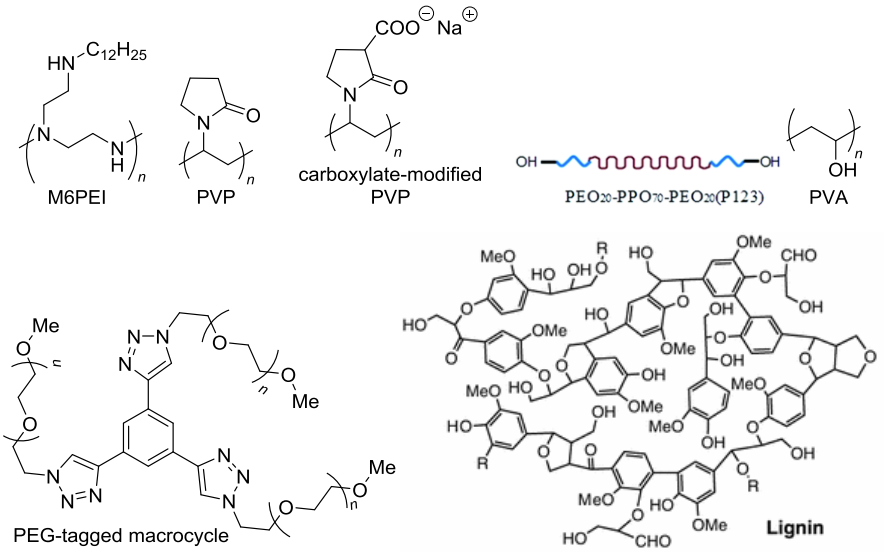



**Figure 12.** Surfactant-stabilized metal nanoparticles in other catalytic applications

## 3. Stabilization by polymers

Water-soluble polymers also constitute a suitable library of stabilizing agents for metal nanoparticles, providing a steric protection in water. The nanocatalysts obtained can be applied in various catalytic reactions including hydrogenation, carbon-carbon coupling and oxidation reactions (Table 2).

**Table 2.** Overview of recent catalytic applications with polymer-stabilized metal nanoparticles in neat water




| Reactions | Polymers | Metal | References |
|---|---|---|---|
| Hydrogenation of olefins | Polyethyleneimine (M6PEI), pluronic block P123 copolymer (P123), Dendrimers, cucurbit[6]uril | Pd, Ru, Pt | [58], [59], [60], [61] |
| Hydrogenation of arenes | PVP, carboxylate-modified PVP, cucurbit[6]uril | Rh | [54], [55], [56] |
| Hydrogenation of nitroarenes | PVA, cucurbit[6]uril | Pd | [57], [61] |
| Hydrogenation of epoxides | cucurbit[6]uril | Pd | [61] |
| Hydrogenation of CO | PVP, cucurbit[6]uril | Rh, Pd | [54], [61] |
| C-C coupling reactions | PEG, cucurbit[6] | Pd | [62] |
| Stille Reaction | Dendrimers | Ni | [66] |
| Tsuji-Trost allylation | PVP | Pd | [64] |
| Oxidation | PVP | Au-Pt-Ag | [67], [68] |

### 3.1 Hydrogenation reactions

Polyvinylpyrrolidone (PVP)-stabilized metallic nanoparticles are among the most used nanocatalysts, demonstrating excellent activities and stabilities particularly in hydrogenation reactions, as gathered in Figure 13. In fact, well-defined PVP-protected rhodium(0) nanospecies, with a mean size diameter of 2.2 nm, were synthesized by the decomposition under hydrogen of the organometallic $[Rh(\eta^3\text{-}C_3H_5)_3]$ complex in THF in the presence of PVP [54]. This nanocatalyst afforded excellent activity and selectivity in the hydrogenation of aromatics possessing electron-donating or -withdrawing substituents, in water under mild conditions (r.t., 1 bar $H_2$), with conversions from 74 to 100%. Selectivities superior to 97%

were achieved for substrates presenting another reducible function (*i.e.* oxo group), except for acetophenone with the major formation of 1-phenylethanol. The Rh@PVP catalyst was also active for the reduction of levulinic acid and its corresponding methyl ester, leading to the quantitative production of γ-valerolactone, a value-added platform chemical for flavor and biofuel industries, under moderate reaction conditions (120°C, 20 bar $H_2$).

In a similar approach, Dyson and coworkers developed a carboxylate-modified PVP which allows an increased stability of the rhodium colloids, compared to their PVP-coated analogs, due to the weak coordination of the carboxylate group at the metal surface. This additional electrostatic stabilization with the formation of a protective electrical double layer was assessed by an increase in the zeta potential value from -20 mV for PVP to -64 mV for the modified one [55]. This catalyst was active in the hydrogenation of various functionalized arenes under 20 bar of $H_2$ and at 60°C, with an improved thermal and catalytic stability upon recycling, compared to PVP system for which a loss of activity was observed after the fifth run.

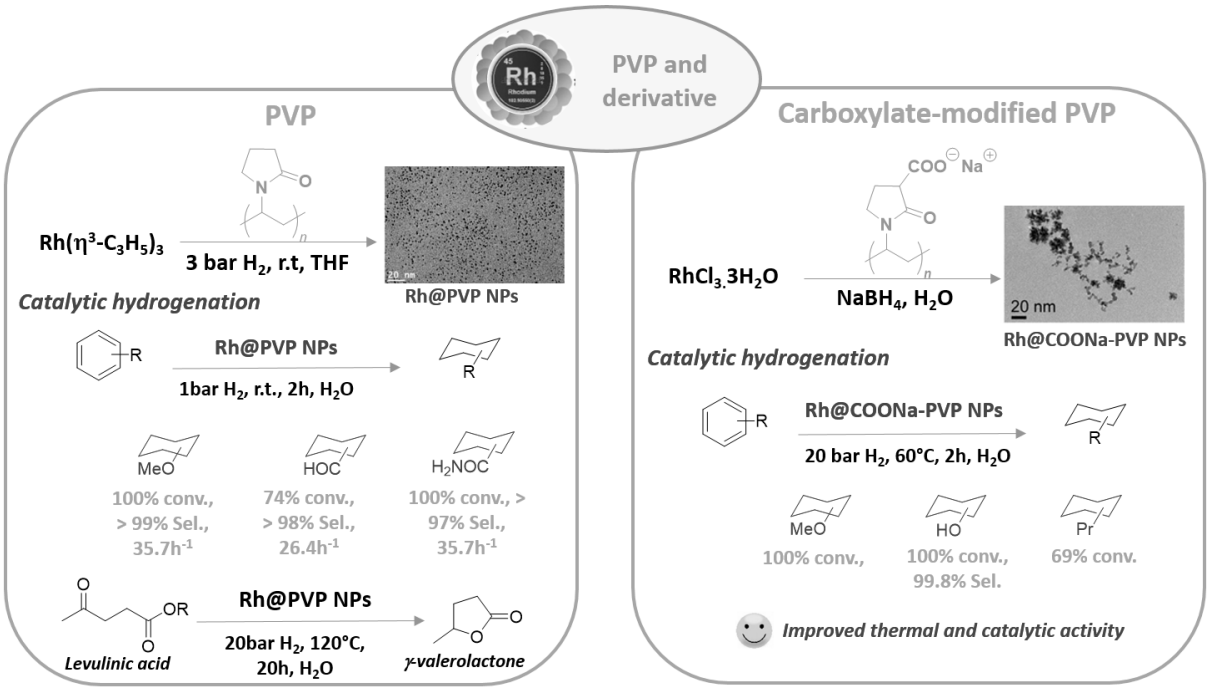



**Figure 13.** PVP and carboxylate-modified PVP-coated Rh NPs for arene hydrogenation

This team also studied the influence of water-soluble phosphines on the chemoselectivity in the hydrogenation of phenylacetone, catalyzed by PVP-coated rhodium nanospecies (Figure 14) [56]. After optimization, a relevant chemoselectivity towards the reduction of the aromatic ring was increased from 70% (with no ligand) to 92% with **Pc**

probably owing to site blocking effects as well as to the hydrophobicity of this ligand, which avoids the approach of the carbonyl group.

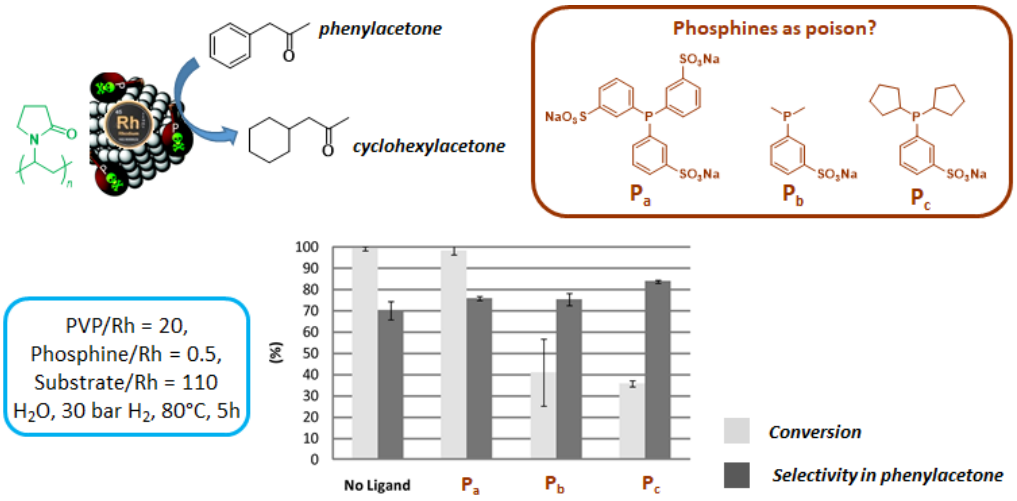



**Figure 14.** Influence of various phosphines on PVP-coated Rh NPs on the chemoselectivity in phenylacetone hydrogenation (Adapted from ref. [56])

Very recently, palladium nanoparticles confined in polyvinylalcohol (PVA) were synthesized by reduction of palladium acetate under dihydrogen, with a mean size of *ca.* 4.8 nm [57]. They proved active for the selective reduction of nitrobenzene into aniline with a 99.3% conversion in 3 h, under 20 bar of $H_2$ and at 45°C, with a high substrate/metal ratio of 500 (Figure 15). Moreover, this catalytic system could be easily recycled without any reactivation treatments, therefore with a decrease in the catalytic activity.

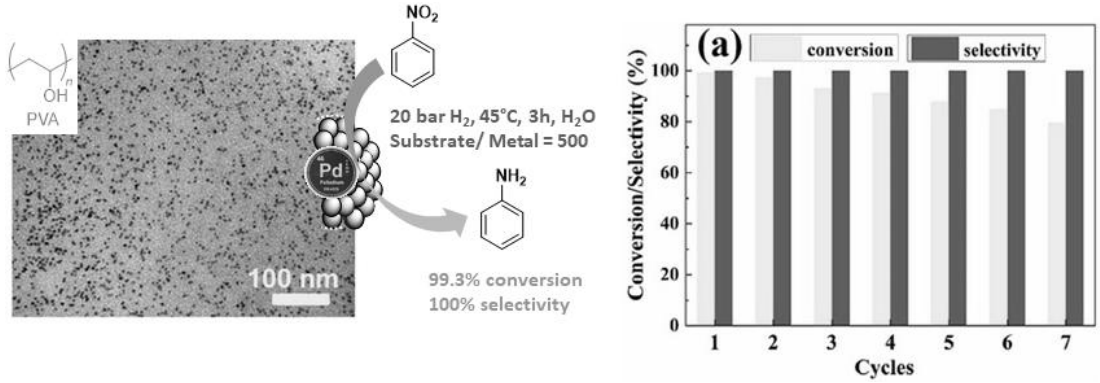



**Figure 15.** PVA-protected palladium colloids for the selective hydrogenation of nitrobenzene (Adapted from ref. [57])

Cheap and non-toxic polyoxoethylene-polyoxopropylene-polyoxoethylene triblock copolymer (P123) was used as protective agent of ruthenium NPs in water [58]. Optimization studies showed that P123 with a molecular weight of 5800 gave the best compromise between

efficient stability within aqueous phase and relevant catalytic performances in the hydrogenation of α-pinene into *cis*-pinane with a complete conversion (99.9%) and a 98.9% selectivity (Figure 16). This catalyst could be efficiently recycled by a biphasic approach over eight runs, before a drop of the conversion.

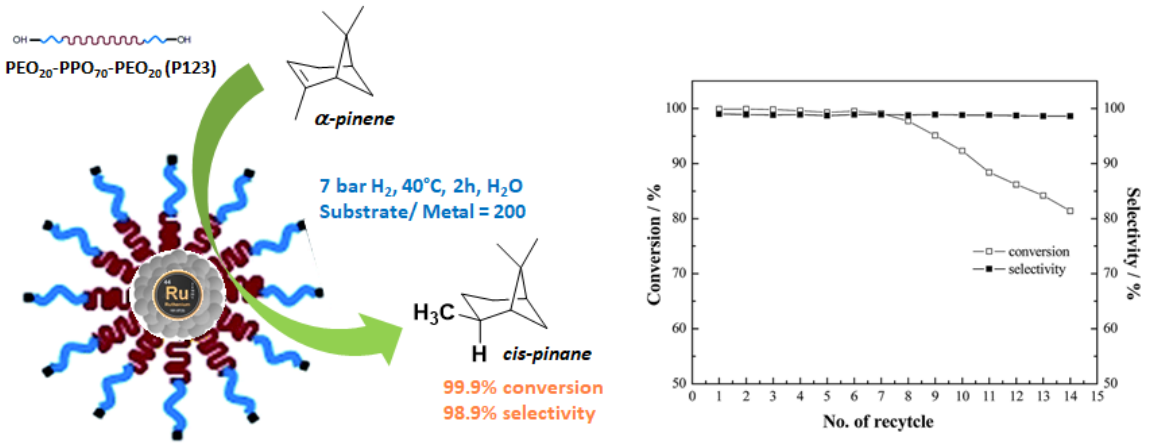



**Fig. 16.** P123-protected ruthenium(0) NPs for the reduction of α-pinene into cis-rich pinane(Adapted from ref. [58])

In 2016, supramolecular self-assemblies of polyethyleneimine (M6PEI) amphiphilic polymer with the previously described hydroxyethylammonium (HEA16Cl) surfactant were used as stabilizers for aqueous palladium NPs [59]. The size of the metal cores and the hydrodynamic diameter of the nanospecies were determined respectively by Transmission Electron Microscopy (TEM), as well as Small Angle X-rays Scattering (SAXS) and Dynamic Light Scattering (DLS), as shown in Figure 17. The catalytic performances of these Pd NPs were investigated in the biphasic hydrogenation of alkenes (*i.e.*, cyclooctene) and α,β-unsaturated ketones (*i.e.*, 5-methylhex-3-en-2-one) under mild conditions (r.t., 1 bar $H_2$). A comparison study was performed in order to determine the influence of various mixtures HEACl-M6PEI with those of M6PEI or HEA salts alone as references. This study showed that the specific activity (SA), determined on the basis of an optimized time for complete conversion, increases in the following order : M6PEI <Mix 3 < Mix 2 < Mix 1 < HEA16Cl (Figure 17). Although best catalytic performances were obtained with Pd@HEA16Cl catalyst owing to a better access of the substrates to the particle surface according to a dynamic behaviour due to surfactant fluxional exchanges, these self-assemblies of an ammonium salt within a polyethyleneimine provided high stability and relevant catalytic activities.

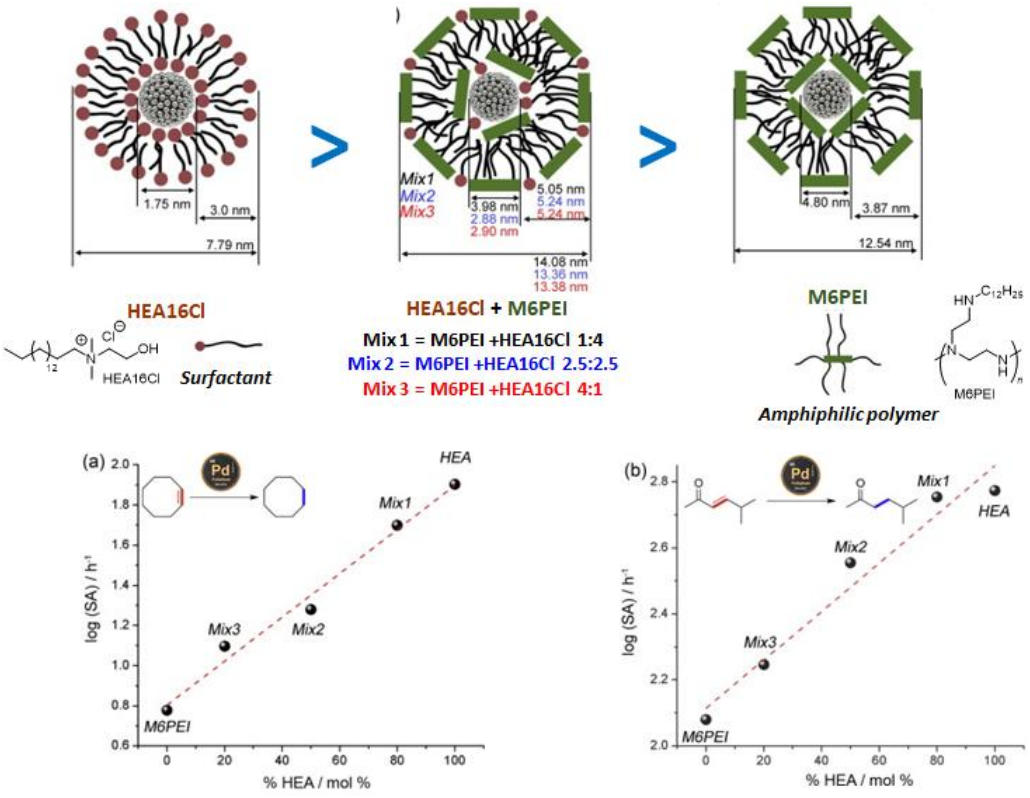



**Figure 17.** M6PEI/HEA16Cl self-assemblies-stabilized Pd(0) colloids. Correlation of specific activity (SA) for the reduction of cyclooctene (a) and 5-methyl-hex-3-en-2-one (b) and HEA16Cl amount (Adapted from ref. [59])

Platinum nanospecies, coated by a glycol-dendrimer bearing modified xylose branches, were also active for the hydrogenation of the olefinic bond of α,β-unsaturated ketones, such as isophorone and (*R*)-(+)-pulegone in water, under 1 bar $H_2$, at r.t. under long reaction times (Figure 18) [60]. For comparison, the Pd@HEA16Cl nanocatalyst, previously described, afforded the corresponding saturated ketones with a 90% conversion in less than one hour

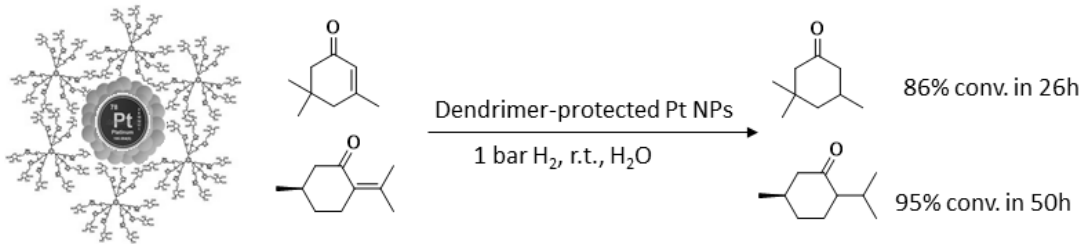



**Figure 18.** Glycodendrimer-stabilized Pt nanoparticles as catalyst for hydrogenation of olefins (Adapted from ref. [60])

Cucurbit[6]uril (CB[6]), a macrocycle in which six glycoluril units are joined with twelve methylene bridges, was reported to stabilize metal NPs, either by forming a passive layer or acting as a protecting agent [61]. A CB[6] material loaded with 3 nm-sized palladium nanospecies (Pd content: 2.5% wt) was obtained by an impregnation method of the $PdCl_2$ precursor on the support, followed by a reduction step. This catalyst showed remarkable conversion, selectivity (> 99%) and high turnover frequency (up to 205,882 $h^{-1}$), for the chemoselective hydrogenation of various reducible groups, including epoxides, olefins, carbonyls, nitriles, azo, imines and nitroarenes (Figure 19). The durability of the catalyst was successfully studied on several runs (> 10 times) with any significant loss in conversion nor selectivity.

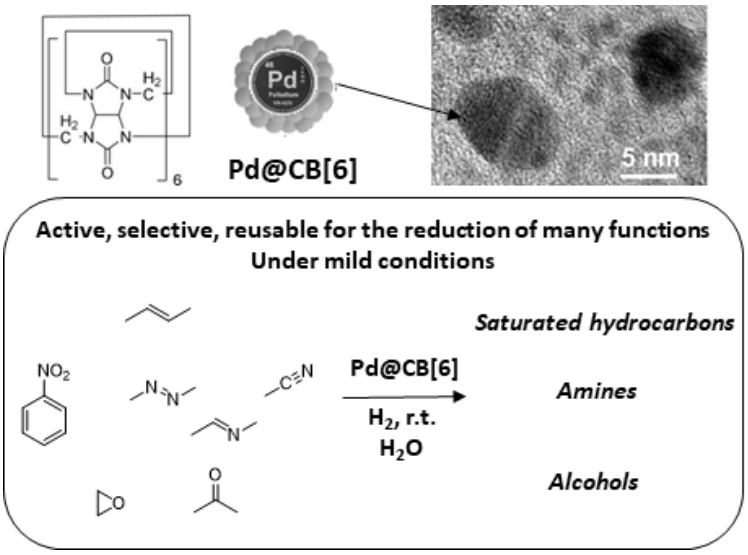



**Figure 19.** Cucurbit[6]uril-coated Pd NPs for hydrogenations (Adapted from ref. [61])

### 3.2 Carbon-Carbon coupling reactions

Carbon–carbon coupling reactions using as catalysts palladium nanospecies constitute key reactions of organic chemistry.

PEG-coated palladium NPs, easily prepared from a Fischer carben complex, proved effective for a wide range of carbon-carbon coupling reactions such as Suzuki, Heck, copper-free Sonagashira and Stille reactions with good catalytic activities (Figure 20) [62].

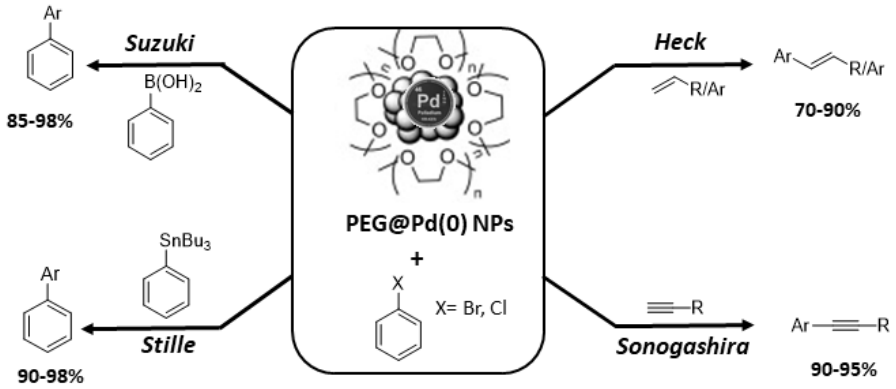



**Figure 20.** PEG@Pd NPs, efficient catalyst for carbon-carbon couplings (Adapted from ref. [62])

Nearly at the same time, the team of Pleixats reported the use of a PEG-tagged compound, possessing three long polyoxyethylenated chains and potentially coordinating triazole moieties, as protective agent for palladium nanospecies [63]. The so-obtained nanoparticles showed pertinent activities in the Suzuki coupling reactions of aryl iodides, as well as the more challenging bromides, with a large scope of aryl and heteroaryl substrates (Figure 21).

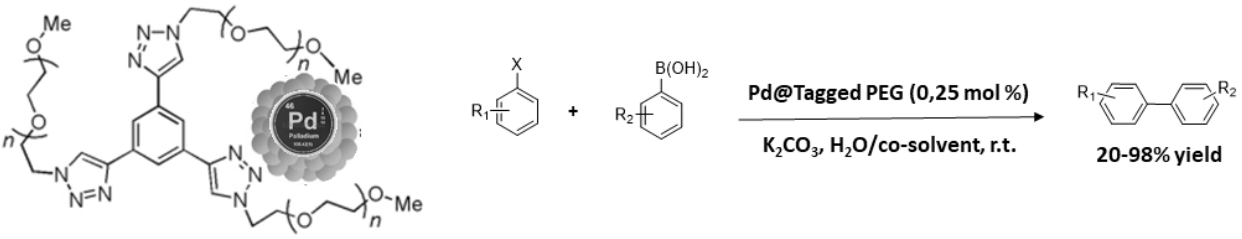



**Figure 21.** PEG-tagged capping agent of Pd NPs for Suzuki couplings (Adapted from ref. [63])

Polyvinylpyrrolidinone (PVP)-stabilized palladium NPs, obtained by a polyol reduction method under microwave, were successfully investigated in the Tsuji–Trost allylation of a series of ethyl acetoacetates with allyl methyl carbonates in water, with complete conversion in a few hours at a very low metal loading (Figure 22) [64]. The addition of triphenylphosphine was crucial to help the transfer of the nanospecies from aqueous media to the aqueous/organic interphase. Furthermore, this catalyst was also active in the allylation of lignin with a higher selectivity towards the aromatic OH groups (with conversion up to 82%).

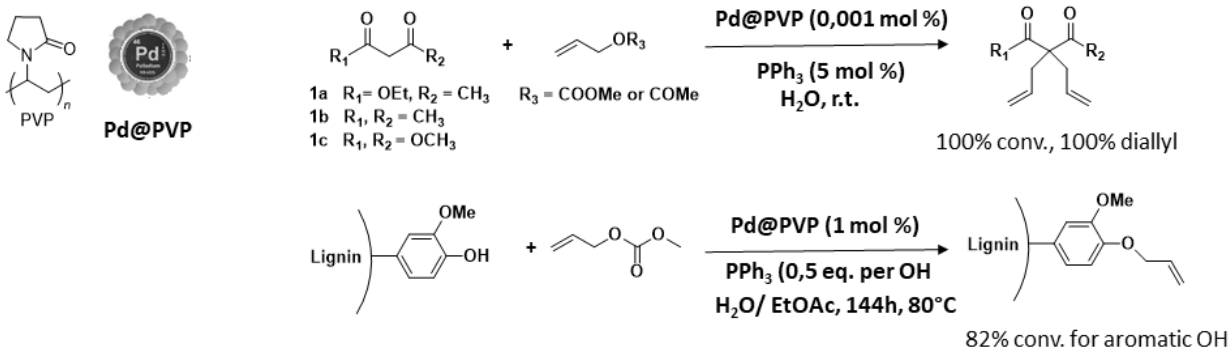
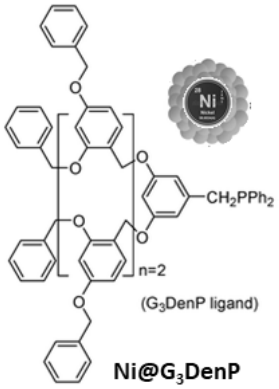
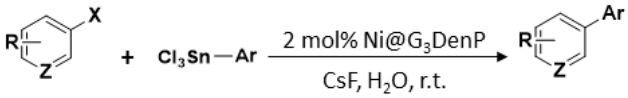



**Figure 22.** PVP-protected Pd NPs for Tsuji-Trost allylations (Adapted from ref. [64])

Dendrimer ($G_3$DenP)-coated nickel colloids, prepared by chemical reduction of the nickel dichloride with sodium borohydride, proved active and recyclable for the Stille coupling reaction in neat water, without co-catalyst [65]. This catalytic system was applied to a large scope of trichlorophenylstannanes with a series of bromo or chloro-arenes, leading to the formation of the corresponding biaryls with good to excellent yields (Figure 23).




| R | X/Z | Ar | t (h) | Yield (%) |
|---|---|---|---|---|
| *p*-COOMe | Br/C | Ph | 3 | 99 |
| *p*-$CH_3$ | Br/C | Ph | 4 | 97 |
| *p*-$NMe_2$ | Br/C | Ph | 4 | 98 |
| *p*-COOMe | Cl/C | Ph | 5 | 98 |
| H | 2-Br/N | Ph | 6 | 89 |
| o-$CH_3$ | Cl/C | Thiophene | 6 | 90 |

**Figure 23.** $G_3$DenP-capped Ni NPs for Stille coupling reactions (Adapted from ref. [65])

Stable aqueous dispersions of palladium NPs on cucurbit[6]uril (CB[6]) nanocapsules (PN), possessing 'disulfide loops', were synthesized through a two-step process and proved active with complete conversion in 1 to 2 h and reusable in carbon–carbon or carbon–nitrogen bond forming reactions in aqueous media (Figure 24) [66].

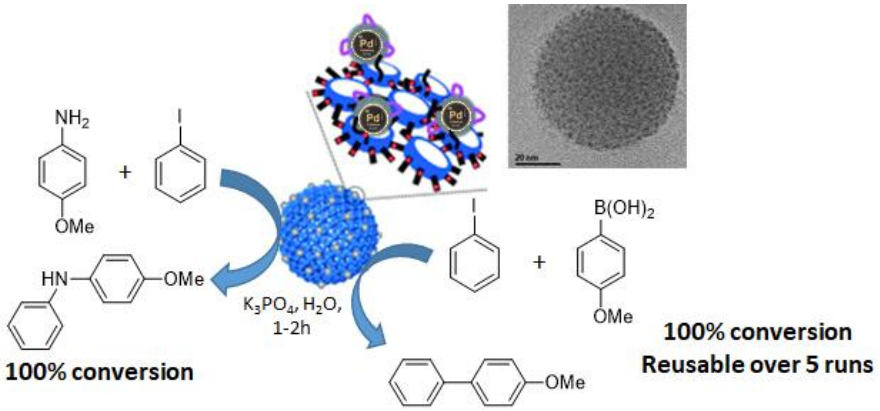



**Figure 24.** Pd@CB-PNs catalyzed C-C and C-N bond-forming reactions (Adapted from ref. [66])

### 3.3 Oxidation reactions

Bimetallic and trimetallic nanoparticles with various compositions and structures are particularly relevant in glucose oxidation, compared to their monometallic counterparts. Among the various bi- or trimetallic alloys (Au–Ag, Au–Cu, Au–Pt, Au–Pd, Au–Rh and Au-Pt-Ag) prepared by rapid injection at 0°C of $NaBH_4$ into the corresponding metallic ion solutions in the presence of PVP as a protective agent. The $Au_{70}$–$Pt_{80}$–$Ag_{10}$ trimetallic NPs (ca. 1.5 nm) showed a high and durable catalytic activity for the aerobic glucose oxidation (Figure 25) [67-68], which was 5 times higher than that of AuNPs and about 1.5 to 3 times higher than that of bimetallic alloys. The quite different catalytic performances observed for the trimetallic alloy were attributed to different factors, namely, the small particle size, long-term stability (due to thermodynamically stable alloyed structure) and the formation of negatively charged Au atoms (due to electron donation of Ag neighboring atoms) acting as catalytically active sites for the desired reaction.

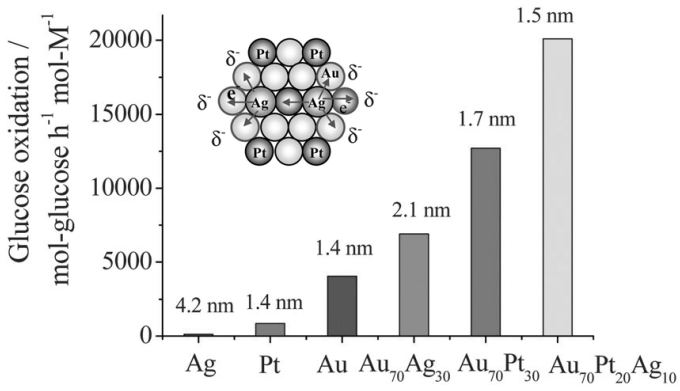



**Figure 25.** Comparison of various bi- or trimetallic alloys on the glucose oxidation (Adapted from ref. [67-68])

## Conclusions and perspectives

In the current context of the development of eco-responsible chemical processes, the synthesis of metallic nanoparticles, stabilized in neat water, presents a great interest. The development of water-soluble capping agents, such as ligands (as used in homogeneous catalysis), ammonium surfactants as well as polymers has already led to promising results. Mainly noble metal nanospecies were synthesized through a bottom approach under quite mild conditions in the presence of these stabilizers. As reported in this chapter, many nanocatalysts showed relevant catalytic performances (both in terms of activity and selectivity) for diverse applications, including hydrogenation of various unsaturated substrates (arenes, olefins and enones), oxidation processes as well as carbon-carbon coupling reactions (such as Suzuki, Sonogashira, Heck, Stille reactions, etc.). In most cases, the studied catalytic systems could be easily recycled through a biphasic approach.

This chapter evaluates different wet chemical methods for the production of metal nanoparticles. This classical approach is relatively simple, modular and scalable and leads to a set of interesting properties for target catalytic applications. Thus, during the two last decades, the scientific community has focused with success on the control over the nanostructures with well-defined composition, shapes and sizes as well as selective surface or controlled cristallographic phases.

Based on the diversity of synthetic methodologies and the induced kinetic properties, catalysis and nanomaterials have been inextricably linked to each other for a long time. While the synthesis of novel, highly efficient, poisoning-resistant, or low-cost catalysts to improve productivity and selectivity has evidenced as an economic priority, the environmental impact is a more recent concern. Consequently, the development of an ideally greener nanocatalyst, able to provide a large-scale production of fine chemicals intermediates, as well as its scalable and adaptable synthesis in order to always satisfy the growing industrial demand, still remains a great challenge.

Along with reducing the environmental impact of organic synthesis by atom economy, energy efficiency as well as waste prevention, the use of greener media remains a crucial parameter. Alternatives to usual organic solvents, such as 2-methyltetrahydrofuran, 1,3-dioxolane or polyethylene glycol or the use of renewable solvents such as 1,3-propanediol or glycerol have been investigated. Nevertheless, using water as a reaction medium seems to be an ideal solution due to its unique properties in terms of economy and environment. Water thus appears as a promising alternative to problematic or hazardous solvents by simplifying

operations, allowing mild reaction conditions and enabling easy extraction and purification work-up of products from the reaction medium.

If the use of water as reaction media for industrial scale-up is still underway, the growing interest of the industry for cleaner processes provides nice opportunities in order to combine nanoscience and catalysis with an emphasis on green chemistry concerns. Finally but not the least, the synthesis of nanometer-sized catalysts based on cheap, abundant first row transition metals is certainly of great interest in the drive towards low environmental footprint processes.

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