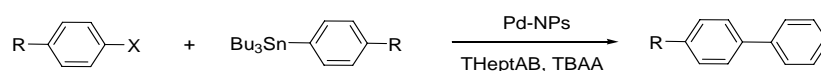


ILs are known for their quite low viscosity [76]. Additionally, it was shown that the ether functionalized ILs are also capable to control the activity of Pd nanoscale catalysts [77]. Alcohol-functionalised ILs can act as reducing agents as well as promising stabilisers for Pd-NPs [78].

Calo, Nacci and their coworkers have presented in recent years several contributions using palladium nanoscale catalysts dispersed in tetraalkylammonium ILs, with a focus on carbon-carbon cross-coupling reactions [57]. The Pd-NPs were generated by reducing Pd(OAc)₂ in molten TBAB with TBAA as base. The Pd-NPs are capable to catalyse reactions of aryl bromides and chlorides. The NPs-structure is described as “core-shell”, with a metal core (diameter: 3.3 nm) and a stabilising IL-layer composed of tetrabutylammonium cations and Br[−] and [PdBr₄]^{2−} species (Figure 2).

Among other palladium cross-coupling reactions, they reported the Stille reaction using their recyclable Pd-NPs/IL-systems for the coupling of aryl bromides and chlorides with tributylphenylstannane at temperatures between 90–130 °C (16 h) with relatively low catalyst-loadings based on 2.5 mol% Pd(OAc)₂ and 5 mol% TBAA in THeptAB (Scheme 6) [57]. Bromoarenes were coupled with almost quantitative conversions (97 %) and several chloroarenes with moderate to high conversions (27–98%).

Scheme 6. Cross-coupling of aryl halides with organostannanes catalysed by Pd-NPs in THeptAB at 90–130 °C (R = H, Me, CH₃CO, NO₂, MeO; X = Br, Cl).

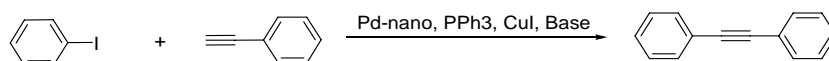


Sonogashira Reaction

In the last decade, the groups of Zhang and Corma reported two completely different approaches for the Sonogashira cross coupling reaction with palladium nanocatalysts in IL media [79,80]. Zhang and coworkers developed a method for the synthesis of Pd-nanowires in IL, and applied this material for the entitled reaction. Corma *et al.* used a palladacycle in IL under thermal decomposition conditions for the synthesis of Pd-NPs.

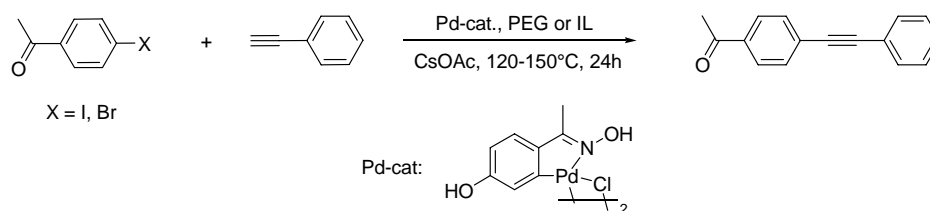
Zhang's group synthesised palladium nanowires in a thiol-functionalised IL (TFIL) applying the seed growth method [80]. The authors reduced H₂PdCl₄ with NaBH₄ in a solution of gold colloids (2.2 nm) as seeds in the TFIL, pointing out that the obtained Pd-nanowires (diameter: 2–4 nm) were only obtained with certain ratios and concentrations of gold and palladium precursors and TFIL. With lower/higher gold concentrations, the authors obtained core/shell nanostructures. The catalytic properties of these nanowires were then tested in the Sonogashira cross coupling, showing very high activity and stability with phenyl iodide and phenyl acetylene as test substrates for the coupling to diphenyl acetylene, in presence of CuI and PPh₃. Quantitative conversions were reached within 7–12 hours at 75 °C (Scheme 7). Interestingly, with the mentioned bimetallic core/shell-NPs (Au_{Core}Pd_{Shell}) a conversion of only 82% was obtained under similar conditions.

Scheme 7. Sonogashira reaction catalysed by Pd-nanowires [80].



Corma and coworkers paid attention to the development of a robust and recyclable multiphase catalyst system using the carbapalladacycle complex of 4-hydroxyacetophenone oxime (Scheme 8), which is known as a highly active palladium catalyst for C-C forming reactions in water [79]. Therefore, they studied the complex stability at elevated temperature in ILs and polyethyleneglycol (PEG). The carbapalladacycle decomposes in water, BMI.PF₆ and BMI.Cl yielding Pd-NPs in water and BMI.PF₆ (2–5 nm) and PdCl₄²⁻ in the latter. Contrarily, the palladacycle is stable upon heating in 1-*n*-butyl-2,3-dimethylimidazolium hexafluorophosphate (BM₂I.PF₆) and in PEG. The activity of the complex in PEG is higher than in ILs, which is assumed to be related to the stability of the complex. Moreover, the palladacycle decomposes in PEG during the reaction and the Pd-NPs (2–5 nm) are stabilised by PEG. This Pd/PEG-system is suitable for copper-free and phosphorus ligand-free Suzuki and Sonogashira couplings on air with moderate/good conversions (Scheme 8). The authors explained the low catalytic activity of the reactions performed in the ILs due to the poor solubility of caesium acetate and unconsidered ILs as practical media for this Pd-catalyst. In contrast, the authors identified the PEG as more promising medium for these catalysed reactions, due the observed stability of the complex and of the Pd-NPs and the solubility of caesium acetate.

Scheme 8. Pd-catalysed C-C coupling PEG (conv.: 5–99%, X = Br, Cl and ILs BMI.PF₆ (conv.: <5–57%; Br, I) and BM₂I.PF₆ (conv.: 38–52%; Br) [79].



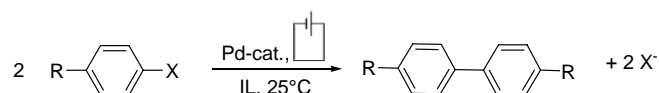
Ullmann Reaction

Dimerisation of aromatic halides is a convenient method for the synthesis of biaryls. Here, the Ullmann reaction is a suitable tool, but the original protocol uses excess of copper as promoting agent and very high temperatures, above 200 °C [81]. A suitable alternative is the palladium-catalysed coupling of aryl halides, which gives access to symmetrical biaryls, but it requires reductive conditions using amines, zinc dust, molecular hydrogen, hydroquinone, alcohols, carbon monoxide, ascorbic acid or formic acid salts [81].

For further improvement towards recyclable catalyst systems, two IL-based protocols for the Ullmann reaction were published by the groups of Rothenberg and Nacci [81,82]. In 2006, Rothenberg reported a room temperature Pd-NPs catalysed Ullmann reaction based on electroreductive coupling of haloarenes [82]. The Pd-NPs (particle size: 2.5 ± 0.5 nm) are generated in an electrochemical cell (Pd-anode and Pt-cathode), and electron-transfer plays a crucial role to close the catalytic cycle. This system gives good yields using aryl bromides and iodides and applying electric current and water as reaction medium. For enhancing the electric conductivity and Pd-NPs stabilisation they introduced 1-methyl-3-*n*-octylimidazolium tetrafluoroborate (OMI.BF₄) IL as recyclable solvent. Kinetics at various electrode potentials led to the conclusion that a two-electron oxidation of water closes the catalytic cycle by regenerating the Pd(0). The system is limited to functionalised aryl bromides and

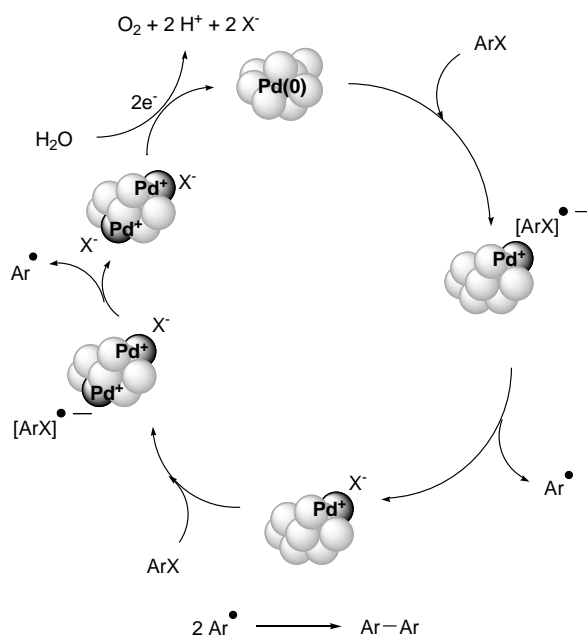
iodides with conversion varying from 20 to 99% with reaction times varying from 8 to 24 h at 25 °C, applying currents of 10 mA with 1.0–1.6 V (Scheme 9). Aryl chlorides do not undergo homocoupling under the described conditions.

Scheme 9. Ullmann-typed aryl halide coupling with Pd nanoscale catalysts in IL under electroreductive conditions at room-temperature. (R = H, NO₂, CH₃, NH₂, OCH₃, CN, CF₃, OH; X = Br, I). Adapted from reference [82].



This set up is a rare example of electroreductive Pd-NPs catalysis in IL. The kinetic studies support a catalytic cycle with a phenyl radical anion (Scheme 10). The advantage of this set up is that simply electrons and water are crucial for closing the catalytic cycle [82].

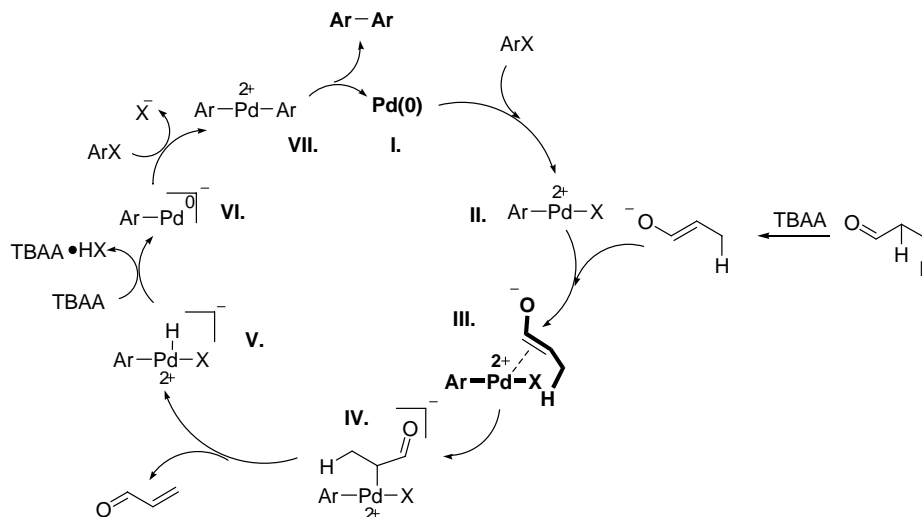
Scheme 10. Proposed catalytic cycle for the electroreductive Pd-NPs catalysed coupling of aryl halides, where Pd⁺ ions are depicted in dark grey. This model includes two single electron transfers from the same cluster, but in general interaction between different clusters is most likely to occur. Adapted from reference [82].



In 2009, Nacci and coworkers presented a Pd-NPs catalysed Ullmann-type reductive homocoupling of aryl, vinyl and heteroaryl with aldehyde as reductant in TBAB and TBAA ILs under very mild reaction conditions, resulting in symmetrical biaryls [81]. The IL plays here a crucial role as base, the reaction medium and the IL acts as ligand for stabilisation of the Pd-NPs which behave as a reservoir for catalyst species. Substituted aryl bromides and iodides are coupled to biaryls in absence of other additives, under relatively mild conditions (T = 40–90 °C) with good conversions (70–90%). The advantage of the method is the simple preparation by mixing the substrates and palladium acetate in the IL, followed by the *in Situ* formation of the catalytically active species. With propanal as reductant,

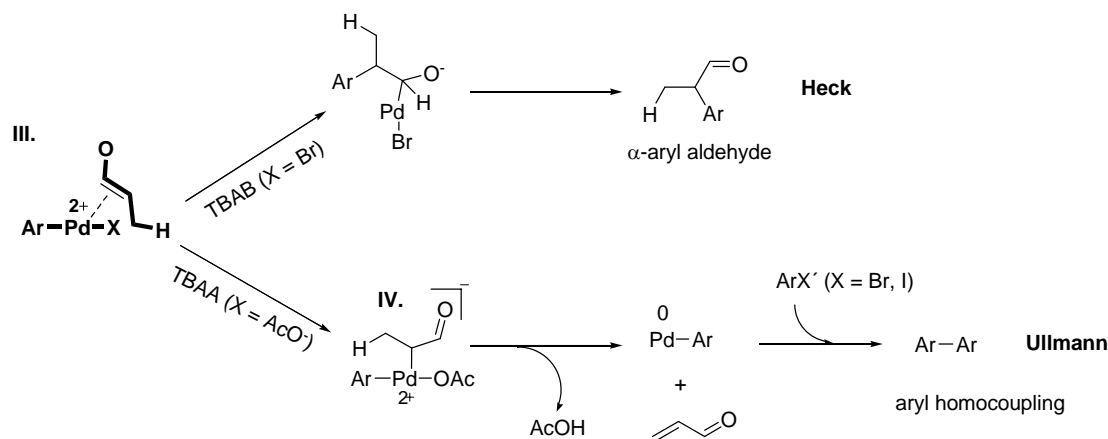
the work-up is facilitated by evaporation of the by-product (acrolein). The base TBAA generates the enolate ion, which is pronounced to be a key intermediate for the palladium reduction (Scheme 11).

Scheme 11. Proposed mechanism with propanal. Adapted from reference [81].



It should be pointed out that the palladium species changes the selectivity by choice of the IL-anion, where the Heck reaction is followed with TBAB ($X = \text{Br}$) and Ullmann reaction with TBAA ($X = \text{AcO}^-$) (Scheme 12). This novel anion-dependent selectivity is highly interesting and innovative for applied synthesis.

Scheme 12. Anion-dependence of the reaction pathway: Pd-NPs catalysed Heck reaction with TBAB (top) and Ullmann reaction with TBAA (bottom). Adapted from reference [81].



Summary and Outlook

The presented contributions in the area of C-C cross-coupling reactions with palladium NPs in IL show promising reactivity and are suitable as recyclable catalyst systems. In general, the ILs prevent agglomeration of the Pd-NPs, which act as reservoir for catalytically active molecular Pd species. The reactivity, stability and reaction pathways can be influenced by the choice of cations, anions and

additive bases. 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 such as Negishi, Kumada, Hiyama or Buchwald-Hartwig coupling will be performed with Pd-NPs in ILs, and of course, further mechanistic studies might reveal that homogeneous catalytic systems involve NPs as reservoir for molecular species. Furthermore, the initially addressed critical drawback of stoichiometric formed salts which remain in the IL-layer, must be resolved to enhance the recyclability. One attempt is to use novel *tunable* ILs, so called “switchable solvent systems” under CO₂ (“ionic liquid mode”), respectively under argon/N₂ (“molecular solvent mode”). Regarding product *and* salt separation, and catalyst recycling, these *switchable solvents* seems to have a suitable potential to substitute “classical” ILs.

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