

Ion- and Atom-Leaching Mechanisms from Palladium Nanoparticles in Cross-Coupling Reactions

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Abstract: Leaching of palladium species from Pd nanoparticles under C–C coupling conditions was observed for both Heck and Suzuki reactions by using a special membrane reactor. The membrane allows the passage of palladium atoms and ions, but not of species larger than 5 nm. Three possible mechanistic scenarios for palladium leaching were investigated with the aim of identifying the true catalytic species. Firstly, we examined whether or not palladium(0) atoms could leach from clusters under non-oxidising conditions. By using our membrane reactor, we proved that this indeed happens. We

then investigated whether or not small palladium(0) clusters could in fact be the active catalytic species by analysing the reaction composition and the palladium species that diffused through the membrane. Neither TEM nor ICP analysis supported this scenario. Finally, we tested whether or not palladium(II) ions could be leached in the presence of PhI by oxidative addition and the formation of [Pd^{II}ArI] com-

plexes. Using mass spectrometry, UV-visible spectroscopy and ¹³C NMR spectroscopy, we observed and monitored the formation and diffusion of these complexes, which showed that the first and the third mechanistic scenarios were both possible, and were likely to occur simultaneously. Based on these findings, we maintain that palladium nanoparticles are not the true catalysts in C–C coupling reactions. Instead, catalysis is carried out by either palladium(0) atoms or palladium(II) ions that leach into solution.

Keywords: catalysis • cross-coupling • Heck reaction • membranes • nanoparticles

Introduction

Palladium-catalysed cross-coupling is a versatile synthetic protocol that is used to produce drugs, agrochemicals and fragrances.^[1–3] The main reactions in this family are Heck, Suzuki-Miyaura, Negishi and Stille coupling reactions.^[1] Traditionally, such reactions are catalysed by Pd^{II}/Pd⁰ complexes in the presence of phosphines or other ligands.^[4–6] However, these ligands are costly and require careful separation from the final product. Moreover, many ligands are air and moisture sensitive, which makes “ligand-free” Pd catalysis by using heterogeneous Pd/C^[7] or suspensions of Pd colloids an attractive alternative.^[8–10] Nanocolloids are attracting considerable attention as C–C coupling catalysts.^[10,11] They are not classical heterogeneous catalysts, but their dimensions (2–20 nm) are close to those of the crystallites that are used in traditional gas/solid heterogeneous catalysis reactions.^[9,12–14] Ligand-free Heck and Suzuki catalysis was reported by using Pd salt precursors,^[15] nanocluster suspensions^[16,17] and supported nanoclusters.^[14] In the last example different types of supports were used, which included carbon,^[13] (thiol-functionalised) silica,^[18] zeolites,^[19] resins,^[20]

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Supporting information for this article is available on the WWW under <http://www.chemeurj.org/> or from the author. It includes experimental procedures for Pd-species transport experiments, procedures for performing the cross-coupling reactions and UV-visible, ¹³C NMR and FABMS spectra of the oxidative Pd/I complexes.

and nanoparticles incorporated into polymers.^[21] The primary aims of these studies were to address the problem of catalyst separation and to enable reactions in diverse media, such as water, mixed solvents^[7] or ionic liquids.^[22]

Interestingly, many of the so-called Pd-complex-catalysed coupling reactions, and especially those performed at temperatures above 120 °C, were later shown to be catalysed by either Pd atoms or Pd clusters.^[23] De Vries recently proposed a unifying mechanism for all high-temperature Heck reactions, which showed that regardless of the catalyst precursor type, Pd is reduced at 120 °C to Pd⁰ and forms colloids.^[24] Similarly, our studies on more than 400 Heck reactions, by using partial least-squares (PLS) methods and artificial neural network (ANN) data-mining methods,^[25] showed that the reaction rate is indeed negatively correlated with the Pd precursor concentration, regardless of which precursor was used, with a clear cutoff point at 120 °C.^[26]

Despite these important works, we still know very little about the mechanism of cluster catalysis in the liquid phase.^[27] The main problem with determining the mechanism for catalysis is the leaching of Pd atoms and/or ions from the clusters.^[28] There has been much scientific argument about this point, especially with regards to the actual catalytic species involved.^[13,29,30] Bradley and co-workers^[31,32] and El-Sayed and Narayanan^[33,34] reported that low coordination sites on the clusters catalyse the reaction. Conversely, Shmidt and Mametova,^[35] Arai and co-workers,^[36] de Vries and co-workers^[15,23,24] and Reetz and co-workers^[37] suggested a homogeneous mechanism in which the Pd clusters act as reservoir of active Pd atoms or ions.^[38] Combining these two views, the mechanistic studies of Biffis and co-workers suggested that Pd^{II} species leach into solution, catalyse the coupling reactions and then re-form the cluster.^[39] Dupont and co-workers reported that aryl iodide attacks the cluster surface and forms the oxidative complex that then leaches into the solution and catalyses the reaction.^[40] Recently, Richardson and Jones suggested a simple way to entrap those soluble species.^[41] In summary, these studies show that finding the true catalytic species is an important and relevant challenge.

In a recent preliminary communication, we presented the first direct and unambiguous test that proved that leached Pd species are the true catalysts in Pd-cluster-catalysed C–C coupling reactions.^[42] We obtained these results by using a special reactor in which the clusters and the reactants are physically separated by an alumina membrane.^[43] This membrane allows Pd atoms and ions to pass, but not clusters. Herein, we present a detailed study of the possible leaching pathways and the species involved. We explored three hypotheses: Firstly, that the leached species are Pd⁰ atoms that re-form into clusters on the other side of the membrane. Secondly, that the leached species are Pd^{II} ions. And thirdly, that Pd forms an oxidative complex with the ArX substrate that is then transferred through the membrane. We tested these hypotheses by monitoring Heck and Suzuki reaction profiles in our membrane reactor. Further experimental support was provided by using ¹H, ¹³C NMR and UV-visible

spectroscopy, fast atom bombardment mass spectrometry (FABMS) and transmission electron microscopy (TEM).

Results and Discussion

Pd nanocolloids were synthesised by reducing Pd(OAc)₂ with tetraoctylammonium glycolate (TOAG), which was used as both a reducing and a stabilising agent.^[31] This method forms clusters with an average size of 15 nm and a narrow particle size distribution ((14 ± 3) nm, see Figure 1). No particles smaller than 11 nm were observed.

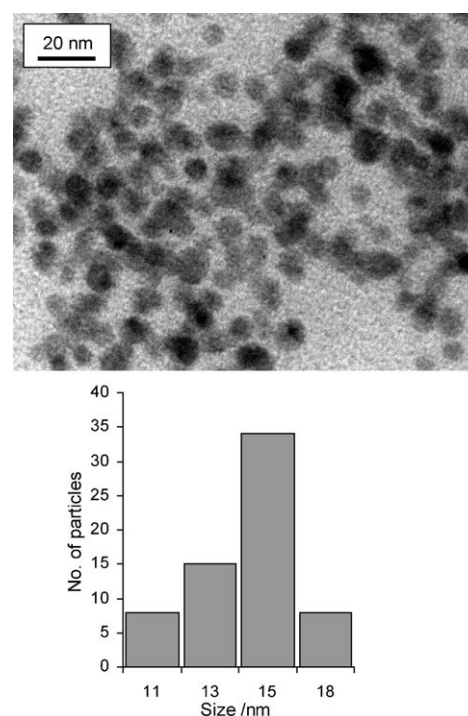


Figure 1. Transmission electron micrograph of Pd nanocolloids prior to reaction (top) and the corresponding size distribution (bottom, based on 62 particles counted).

The coupling reactions were studied by using a special membrane reactor that was designed and built in-house.^[44] This reactor consists of two stainless steel compartments separated by an alumina membrane (henceforth referred to as sides **A** and **B**, see Figure 2). Each compartment has a gas inlet and a sampling port. The alumina membrane was made by coating mesoporous α -alumina with a layer of microporous γ -alumina.^[43] This gave pores of approximately 5 nm in diameter (the pore size distribution of the membrane was determined by permoporometry^[45,46]). A few pores were larger than 5 nm, with a maximum size of 11 nm. However, owing to the amorphous structure of the membrane, all the paths through it are “tortuous wormholes”, and no path consists of only maximum-size pores. Thus, this membrane also retains particles smaller than 11 nm (a detailed

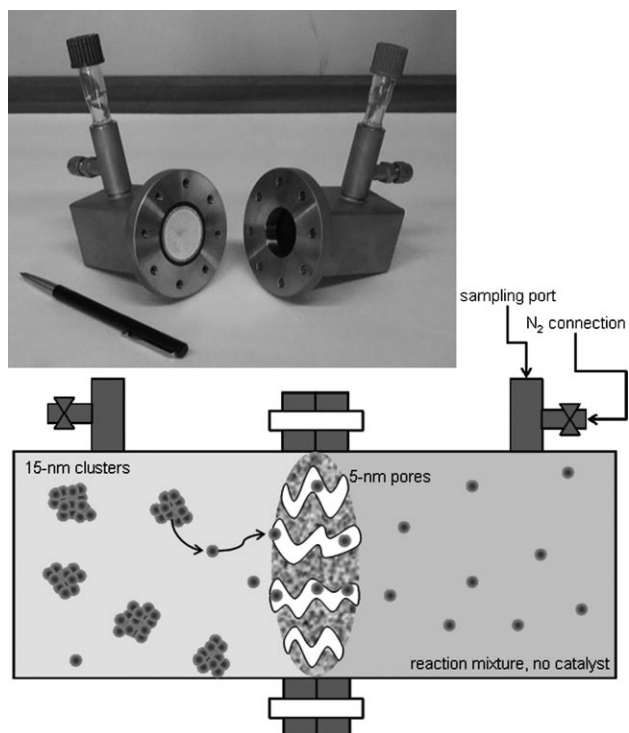
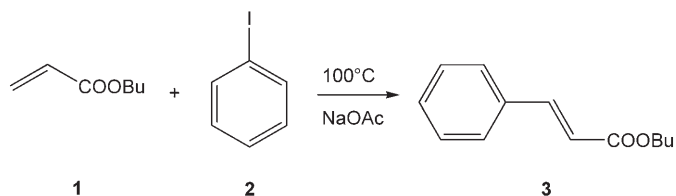


Figure 2. Photograph (top) and schematic representation (bottom) of the two-compartment membrane reactor and the cluster-exclusion concept.

description of the reactor and the membrane is given elsewhere^[42].

Firstly, we studied the Heck coupling of *n*-butyl acrylate **1** with iodobenzene **2** to form *n*-butyl cinnamate **3** in DMF (Scheme 1). Identical starting mixtures that contained an ac-

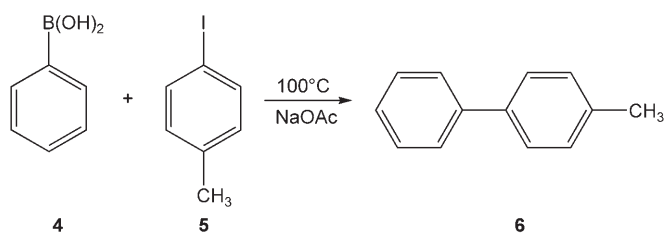


Scheme 1.

rylate/iodobenzene molar ratio of 1.5:1.0 were placed on both sides of the membrane to avoid the formation of concentration gradients. Subsequently, a suspension of Pd clusters (0.01 equiv) was added to side **A** and NaOAc (1.5 equiv) was added to side **B**. The base is necessary to complete the catalytic cycle. As there was no base on side **A**, no product could form there. We then monitored the yield of *n*-butyl cinnamate (**3**) on both sides of the membrane by using gas chromatography. No reaction was observed for the first five hours because the leached Pd species from side **A** must diffuse through the membrane to side **B** for reaction to occur. After 120 h, the yield on side **B** was 88%, which shows that Pd catalyst has diffused across the membrane. Formation of a further 4.9% of product was observed on side **A**. Control

experiments confirmed that this product could not form on side **A** in the absence of base (a detailed description of these experiments is given in our preliminary communication^[42]). Importantly, the solubility of the base, NaOAc, is negligible and control experiments confirmed that the amount of solid NaOAc that dissolves in DMF (100 mL) under the reaction conditions gives <1.5% conversion. Thus, the product observed on side **A** must have diffused from side **B**. No Pd precipitation was observed on either side.

To determine whether or not these results also apply to other coupling reactions, we examined the Suzuki coupling between phenylboronic acid **4** and *p*-iodotoluene **5** (Scheme 2). Figure 3 shows the yield of *p*-methylbiphenyl **6**



Scheme 2.

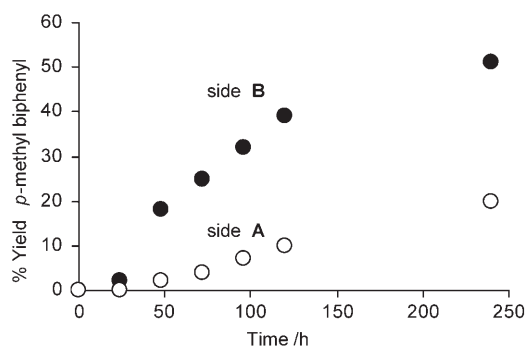


Figure 3. Reaction profile for the Suzuki coupling product, *p*-methylbiphenyl **6**. The product observed on side **A** had diffused from side **B**. Reaction conditions: phenylboronic acid (1.5 equiv), *p*-iodotoluene (1 equiv), NaOAc (3 equiv), Pd clusters suspension (0.02 equiv), DMF, 100°C, N₂.

on sides **A** and **B**. Note that the Heck reaction requires a stoichiometric amount of base, whereas the Suzuki reaction does not. The role of the base in the latter is more subtle: the base quaternises the boronic acid and thereby facilitates the transmetalation step. For this reason, the rates of product formation on sides **A** and **B** are more similar for the Suzuki reaction. Nevertheless, in both cases the results show that leaching occurs (cf. with the studies of Hu and co-workers^[47,48]). However, these experiments do not give us precise information about the type and the amount of catalytic Pd species on side **B**.

We then investigated if Pd⁰ atoms or small Pd⁰ clusters could leach through the membrane. Firstly, we examined if the original Pd clusters fragment to form smaller clusters

(<5 nm) that could then diffuse through the membrane.^[49] In this experiment, a suspension of Pd clusters in DMF was placed on side **A**, whereas pure DMF was placed on side **B**. The contents of both sides were stirred at 100 °C under nitrogen for 144 h. The amount of Pd on side **B** was periodically quantified by inductively coupled plasma (ICP) analysis. After 144 h, the metal species on side **B** were analysed by using TEM. Figure 4 shows the amount of Pd (ppm)

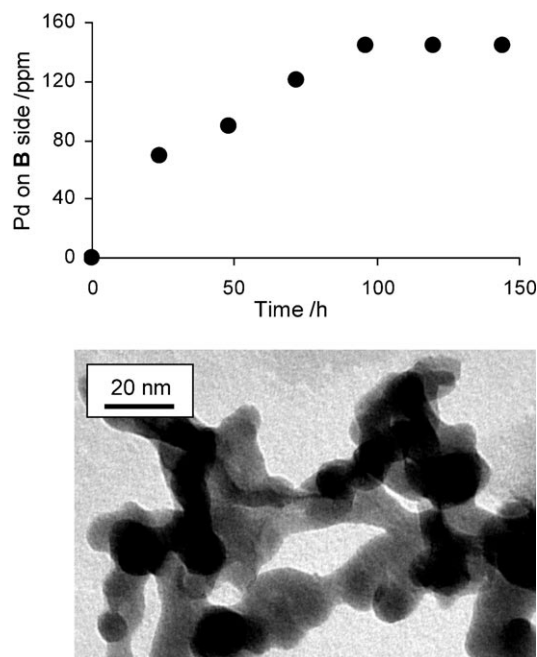


Figure 4. Top: Amount of Pd (ppm) transferred to side **B** versus time. Reaction conditions: Pd clusters (30 mL, 10 mm) in DMF on side **A**, pure DMF on side **B**, 100 °C, N₂ atmosphere. Bottom: micrograph of the Pd species on side **B** after 144 h.

transferred versus time, as well as the TEM results after 144 h. Initially, the Pd transfer rate was high and reached a plateau after 120 h. A total of 140 ppm Pd was found on side **B**, which is 20% of the Pd originally placed on side **A**. The TEM micrograph shows irregularly shaped particles and no spherical clusters. We do not know why these irregular shapes form. It may be as a result of a different stabiliser/reducing agent composition on side **B**. This observation shows that smaller clusters do not form on side **A** and then diffuse to side **B**. Moreover, it shows that Pd⁰ species (i.e., Pd atoms) do transfer across the membrane because the experiments were performed under inert conditions and there was no oxidising agent present that could oxidise Pd⁰ to Pd^{II}. The mixture on side **B** was also analysed by using ¹³C and ¹H NMR spectroscopy, showing the presence of tetraoctyl ammonium ions. These are stabilising ions that were released from the cluster surface on side **A** and diffused to side **B** owing to the concentration gradient. Note that no precipitation of inactive Pd black was observed on either side. The Pd aggregates formed on side **B** retained some catalytic activity. Adding 2 mL (2.7 μmol Pd, 0.27 mol % rela-

tive to substrate) of the suspension from side **B** to a mixture of **1** and **2** (1.5:1) gave 90% conversion to the Heck coupling product after 120 h. Although the reaction conditions differ from the original membrane experiment, the similar outcome observed supports the hypothesis that Pd atoms leach from these aggregates.

To rule out any possibility of Pd^{II} transfer in this system, we also analysed samples from both sides after 144 h by using UV-visible spectroscopy. Pd^{II} ions show an absorption signal at 340 to 360 nm, whereas Pd clusters show a shoulder at 390 nm and Pd aggregates do not show any signals in the UV-visible region.^[50] Figure 5 shows the UV-visible spec-

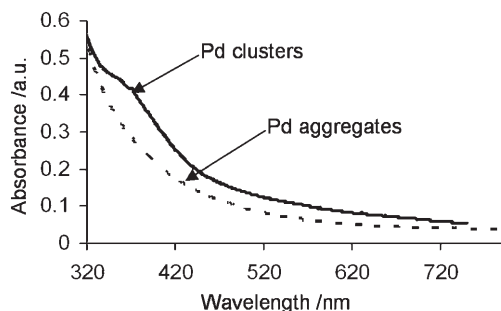


Figure 5. UV-visible absorption spectra of the original cluster suspension from side **A** (continuous curve) and the mixture on side **B** after 144 h (broken curve). Reaction conditions are the same as in Figure 4.

trum of the original cluster suspension that was added to side **A** as well that of the sample taken from side **B**. The sample on side **B** does not show a shoulder, which supports our hypothesis that Pd⁰ atoms transfer through the membrane and not Pd^{II} ions.

We then examined if Pd^{II} ions could leach from the clusters as a result of oxidative addition through the mechanisms originally proposed by Schmidt and Mametova^[35] and Arai and co-workers.^[36] They suggested that the aryl halide attacks the Pd cluster to form a complex with a Pd^{II} ion and thereby extract Pd^{II} into the solution. To investigate this hypothesis, we added Pd clusters to side **A** together with iodobenzene (100 equiv) in DMF, whereas on side **B** we only added iodobenzene (100 equiv) in DMF, and thus, avoided concentration gradient effects. Because of the sensitivity of the oxidative complexes to oxygen and water, extra care was taken in these experiments to use a dry N₂ atmosphere and freshly degassed and dried solvents. Samples were taken every 24 h from both sides. After 24 h, the characteristic black colour of the suspension of Pd clusters changed to dark reddish on side **A**. One day later, this red colour also appeared on side **B**. Figure 6 shows the UV-visible spectra of the mixtures from both sides of the membrane after 144 h. We see absorption maxima at λ = 320, 420 and 540 nm. These results correlate with the observations of Dupont and co-workers.^[40] The spectra also correspond to those of PdX_n⁻ salts. Moreover, ¹³C NMR spectroscopy showed signals at δ = 127.9, 128.5, 130.0 and 141.8 ppm. The signal at δ = 141.8 ppm is typical for Pd-bound carbon atoms

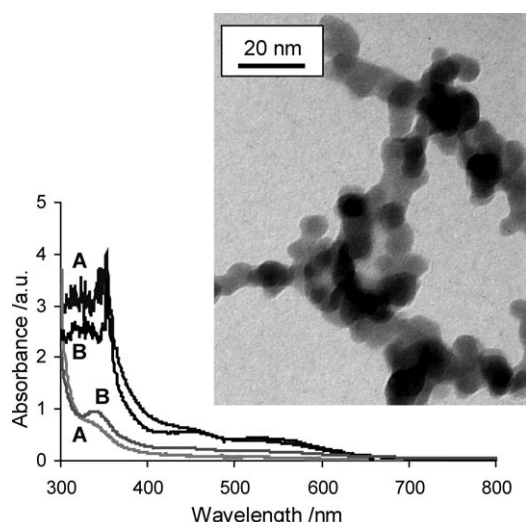


Figure 6. UV-visible spectra of oxidative complex formation on sides **A** and **B**. The black and grey lines correspond to concentrated and diluted samples, respectively. The inset shows a TEM image of the aggregates that form on side **B** after 144 h. Reaction conditions: suspension of Pd clusters (10 mM, 30 mL) on side **A**, iodobenzene (100 equiv) on both sides, 100 °C, N₂ atmosphere.

of arylpalladium compounds. These results are in agreement with the values reported by Reetz and Westermann.^[37] Furthermore, FABMS measurements showed polymeric species of oxidative complexes, which is in agreement with observations by de Vries et al.^[15] (full NMR and FABMS data are included in the Supporting Information). Importantly, no spherical clusters are observed on side **B** in this case. Examining the sample from side **B** by using TEM, one sees some aggregation of Pd species (inset in Figure 6). If we compare Figure 4 with the inset in Figure 6, we see that the aggregate sizes are similar. Note that no complex formation was observed in control experiments performed by using a PhI/Pd ratio of 1:1.

To rule out the possibility of formate reduction by the DMF solvent, we ran analogous experiments in THF. UV-visible spectroscopy confirmed that the same processes occur regardless of the solvent present. Interestingly, complex formation and Pd^{II} leaching depends strongly on the solvent; in THF, we observed the formation of Pd^{II} complexes even when a PhI/Pd ratio of 1:1 was used. A full description of these additional experiments is given in the Supporting Information.

Based on these observations, we can distinguish between three different mechanisms by which a palladium species can transfer from sides **A** to **B**. Firstly, Pd⁰ clusters may fragment or decrease in size owing to Pd-atom leaching. The resulting small clusters could then transfer across the membrane (Figure 7, top). However, our results clearly show that this does not happen. No clusters are observed on side **B** in this case. Leaching of palladium atoms or ions does result in smaller clusters (as we have shown previously for the Sonogashira cross-coupling reaction^[51]), but these clusters cannot transfer through the membrane. In the second scenario, Pd⁰

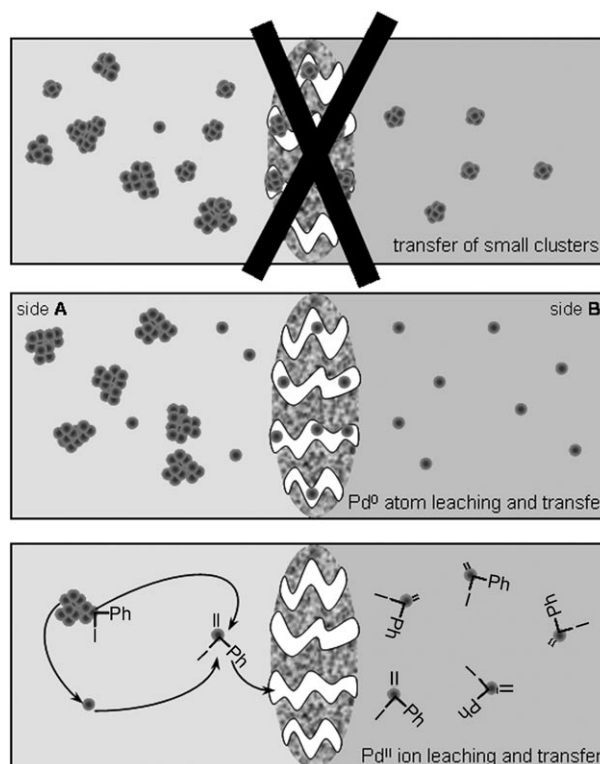


Figure 7. Suggested mechanisms for palladium transfer from side **A** to side **B**. Top: cluster fragmentation followed by small cluster transfer; middle: Pd⁰-atom leaching and transfer under non-oxidising conditions; and bottom: formation and subsequent transfer of Pd^{II} complexes.

atoms leach from the clusters under non-oxidising conditions and transfer as Pd⁰ across the membrane (Figure 7, middle). Indeed, we observed this scenario under carefully controlled reaction conditions in which the formation of oxidative Pd^{II} complexes was not possible. Transfer of “naked” Pd⁰ atoms incurs a high energy penalty and it may be that they are complexed to a stabilising agent.

The third mechanism pertains to the situation in which an oxidative reagent, such as PhI, is present. PhI can attack the cluster surface to form Pd^{II} complexes that can then leach into solution and transfer across the membrane to side **B** (Figure 7, bottom). In this case, the aggregates observed on side **B** can come from two sources, either as Pd⁰ atoms (as in the previous scenario) or as [Pd^{II}ArX] complexes. The formation of the oxidative complex is solvent dependent and proceeds more easily in THF than in DMF.^[52] We cannot say if oxidative addition occurs on the cluster surface or on Pd⁰ atoms that are already present in solution.

Conclusion

By using a simple approach based on physical separation, we have shown here that Pd atoms and ions do leach from Pd clusters under Heck and Suzuki coupling conditions. There are two leaching mechanisms that can occur, which depend on the reaction conditions used. In the absence of

any oxidising agent, Pd⁰ atoms leach from the clusters. Conversely, in the presence of iodobenzene, Pd^{II} complexes can form by oxidative addition, either on the cluster surface or through reaction with Pd⁰ atoms that have already leached into solution. Both Pd⁰ atoms and Pd^{II} complexes can then enter the cross-coupling catalysis cycle. The remaining (smaller) Pd clusters are not catalytically active species.

Acknowledgements

We thank T. Franssen-Verheijen (Wageningen University) for performing the TEM analysis, L. Hoitinga (UvA) for the ICP analysis, H. Peeters for the FABMS analysis, J.-M. Ernstig for the NMR analysis, and Dr. M.C. Mittelmeijer-Hazeleger (UvA) for technical assistance. This research was funded by the Netherlands Organization for Scientific Research (NWO) Vernieuwingsimpuls program.

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- [45] Permporometry is a characterization technique that is used to determine pore size distributions in membranes. It is based on the controlled blocking of the pores by capillary condensation and the simultaneous measurement of the inert gas diffusion flux through the remaining open pores. When a condensable vapour (e.g., cyclohexane) is introduced into the system at low vapour pressures, a molecular adsorption layer (the so-called "t-layer") is formed on the inner surface of the pores. The pore size (d , in nm) is defined by $d = 2(r_K + t)$, in which r_K is the Kelvin radius, and t is the thickness of the t-layer (≈ 0.3 nm). For more details, see: a) A. Mey-Marom, M. G. Katz, *J. Membr. Sci.* **1986**, *27*, 119; b) M. G. Katz, G. Baruch, *Desalination* **1986**, *58*, 199.
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Received: January 22, 2007

Published online: May 31, 2007