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An Overview of Palladium Nanocatalysts: Surface and Molecular Reactivity

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The use of metallic nanoparticles in catalysis under homogeneous conditions leads to a discussion of their catalytic nature: whether the catalyst behaves as a molecular species or, on the contrary, the metallic surface is directly involved in the reactivity. This dilemma is intrinsically associated to the kinetic stability of the nanoclusters, favouring their agglomeration, and also to the formation of molecular species by reaction of the atoms placed at low-coordination positions at the metallic surface. In particular, for palladium-catalyzed processes, a large number of contributions have been reported in the last decade involving nanoparticles, but few of them analyze the mechanistic aspects. The present review aims to collect the more relevant research carried out in catalysis involving palladium nanoparticles in the liquid phase and addressing the nature of the catalytically active species. This kind of work is mainly focused on hydrogenation and C–C coupling processes.

Introduction

At present, several synthetic methods are used to obtain well-defined metallic nanomaterials in the liquid phase by following the "bottom-up" approach (formation of nanoclusters by metallic precursor decomposition).[1] As known, metallic nanoparticles (MNPs) are kinetically stable, because thermodynamics favours the formation of structures with a high surface/volume ratio and consequently the bulk metal represents the lowest energy.[2] Therefore, the presence of stabilizers is required to prevent the agglomeration of the nanoclusters by providing a steric and/or electrostatic barrier between particles.[3] In addition, the stabilizers play a crucial role in controlling both the size and shape of the nanoparticles.[4] Moreover, nanoparticles dispersed in solution can leach molecular species. This leaching is promoted by solvation effects, the presence of Lewis bases or other reaction factors like temperature.[5] This phenomenon can induce Ostwald ripening, because the system attempts to lower its overall energy, molecules on the surface of a small particle will tend to diffuse through the solution and add to the surface of larger particle.[6] Therefore, the smaller particles continue to shrink, while the larger particles continue to grow, a fact that can lead to a diminution of the catalytic activity.

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As a result, the nature of the active sites becomes crucial in understanding the reactivity observed when nanoparticles are used as catalytic precursors. For that, the control of nanoparticle size and morphology represents a crucial goal to achieve in order to tune the physical properties of nanomaterials.[7] In particular, silver and gold particles have received a special attention essentially due to their optical properties[8] and their structure–activity relationship observed in catalytic reactions.[9]

El-Sayed and co-workers have widely investigated the size and shape dependence of platinum nanoparticles in catalysis (electron-transfer reactions and Suzuki couplings).[10] Following this strategy, Trzeciak and co-workers have recently studied the influence of these parameters in methoxycarbonylation processes catalyzed by PVP-stabilized [PVP = poly(*N*-vinyl-2-pyrrolidone)] palladium nanoparticles.[11] As these studies have revealed, an increase in catalytic activity is observed when the fraction of surface atoms in the corners and edges increases, proving the influence of the morphology of the nanoparticles in catalysis. In fact, dissolution of metallic atoms placed on low-coordination positions at the metallic surface observed under Heck and carbonylation conditions is coherent with this reactivity trend.[12] Electronic effects can also modulate the catalytic behaviour of the metallic nanoparticles, but they are only relevant for very small nanoparticles (less than 1.5 nm),[13] as observed by Crooks and co-workers in PdNP-catalyzed (PdNP = Pd nanoparticle) hydrogenations.[14]

In the last decade, palladium nanoparticles have been largely applied in catalysis by taking advantage of their metallic surface as well as of their ability to generate molecular species. At present (this review covers the literature reports published until January 2008), more than 1600 references can be found in the Chemical Abstracts database in relation to the use of palladium nanocatalysts, but fewer than 40 examine the nature of the catalytically active species involved in the corresponding processes. The main part of these latter reactions involves hydrogenations and C–C couplings (Heck, Suzuki, Stille). A few reports are related to other processes like dehalogenation, hydrodechlorination, carbonylation or oxidation (see section 3. Miscellaneous).

Non-supported palladium nanoparticles have been efficiently used to study nanoparticle effects in catalysis.[5a,15] The present review focuses on the discussion of catalyst nature when palladium nanoparticles are involved, both preformed and generated in situ from molecular precursors. From a point of view of catalytic reactivity, we refer to Pd nanocatalysts (PdNCs) as heterogeneous or multi-site catalysts, and consequently homogeneous catalysis involves molecular catalytically active species (in general, single-site catalysts), following the definition established by Schwartz.[16] PdNPs on solid supports will not be considered in the present review except for relevant comparisons, in order to exclude the catalytic influence of the support and to focus on the nature of the catalyst under "wet" conditions.

This review is organized in the following three parts: (1) Hydrogenation processes: surface-like catalytic behaviour of PdNCs; (2) C–C bond formation: single-site or multi-site behaviour of PdNCs; and (3) Miscellaneous.

1. Hydrogenation Processes: Surface-Like Catalytic Behaviour of Pd Nanoparticles

For hydrogenation processes, the reactivity observed when non-supported PdNPs are used as catalysts points to a surface-like behaviour, excluding the active molecular catalysts, as shown below by the reported work in this area. In particular, PdNPs stabilized by branched amphiphilic polyglycerol (mean diameter 2.2 nm) have been applied to the hydrogenation of cyclohexene in a continuously operated membrane reactor. This study demonstrates that soluble PdNPs are responsible for the activity observed, ruling out the contribution of soluble molecular catalysts.[17]

In numerous reported studies, catalytic activity appears to be associated to the metallic particle size, but to evaluate this effect, it is absolutely necessary to know the reactivity of the different surface sites when anisotropic nanoclusters are formed. While spherical (isotropic) nanoparticles are obtained by slow growth under thermodynamic control, anisotropic shapes are expected for higher growth rates, because under kinetics conditions, high-energy faces tend to grow more rapidly than those exhibiting low energy.[4,18]

For Pd anisotropic clusters, several shapes can be formed and coexist in the same sample; their relative distribution depends basically on the synthesis methodology. For relatively big clusters (mean diameter in the range 8–20 nm), triangular, rhombohedral, pentagonal or tetrahedral morphologies are found among the most representative.[12,19] For small particles (mean diameter in the range 1–5 nm), cuboctahedron, icosahedron and truncated octahedron shapes are mainly observed,[20] analogous to the morphologies reported for gold nanoclusters.[21] Furthermore, these observations are in agreement with the similar calculated energies found for both icosahedron and cuboctahedron Pd nanoparticles constituted by more than one thousand atoms (mean diameter ca. 2.8–3.5 nm).[22]

Structure-sensitive catalytic processes, like hydrogenation, turn out to be strongly dependent on nanocluster shape. Taking into account the fcc cuboctahedron as a model for palladium nanoclusters,[23] the only surface atoms that increase in number with an increase in the particle size are those located on the facets of a (111) plane, decreasing both the percentage of total surface atoms and the percentage of edge plus vertex atoms. This fact can be correlated with the catalytic behaviour in different hydrogenation reactions, as described below.

Monodisperse PdNPs encapsulated in functionalized PAMAM [PAMAM = poly(amido-amine)] dendrimers have allowed the study of the effect of catalyst structure on hydrogenations.[24] Crooks and co-workers have observed that for this kind of PdNPs having diameters in the range 1.5–

1.9 nm, the hydrogenation rate of allylic alcohol increases with the size of nanoparticles, consequently the reaction occurs predominantly on the faces.[14] Doyle et al. have also investigated the size effect of PdNPs supported on alumina for 1,3-butadiene hydrogenation, demonstrating that the process is particle-size-independent and concluding that the hydrogenation takes place on (111) facets. STM (Scanning Tunnelling Microscopy) measurements provided information on the shape and surface structure of PdNPs. Doyle et al. also observed that for small nanoparticles (mean diameter ca. 2 nm) the isomerization products (*trans*- and *cis*-2-butene) are more abundant than the fully hydrogenated product (butane), in the opposite trend to that observed for bigger particles (mean diameter ca. 8 nm); in any case, 1-butene represents the minor compound. These results suggest that butadiene is more strongly bonded and that hydrogen adsorption is more hindered when small particles are involved.[25]

Recently, hydrogenation of alkynes catalyzed by monodisperse PdNPs has been investigated. Kiwi-Minsker and co-workers analyzed the effect of the size of the PdNPs (in the range 6–13 nm) in the hydrogenation of 2-methyl-3-butyn-2-ol.[26] As observed for other Pd-catalyzed structure-sensitive reactions, the initial turnover frequency (TOF) calculated per surface palladium atom increases with particle size, but this dependence disappears when only specific surface atoms are considered. In terms of the selectivity, the authors could establish a size dependence of the formation of byproducts: the more atoms located on Pd(111) facets, the lower the ratio of byproducts to saturated products. For the hydrogenation of 1-hexyne, however, the TOF is always dependent on the particle size.[27] Consequently, for particles bigger than 1 nm the electronic effect is negligible and the geometric effect could be the responsible for this behaviour: for particles smaller than 11 nm, the product distribution between hexenes and hexane varies with particle size in favour of alkenes. Therefore, bigger nanoparticles showing a large ensemble of Pd surface atoms are required for hydrogenation of 1-hexyne.

The hydrogenation selectivity of 1,3-butadiene towards the partially hydrogenated product, when palladium catalysts are used, can be used as a pattern reaction to discuss the nature of the catalytically active sites. Actually, heterogeneous palladium catalysts, such as Pd supported on silica or alumina, lead to butane and 2-butenes, as a result of the isomerization of 1-butene to internal olefins.[28] On the contrary, palladium complexes are known to catalyze selectively the hydrogenation of 1,3-butadiene to butenes, but favouring the formation of 2-butenes.[29] In connection with this aspect, selective hydrogenation of 1,3-butadiene to 1-butene has been reported by Dupont and co-workers with PdNPs immobilized in ionic liquids.[15c] Preformed PdNPs only stabilized by ionic liquids have been used as catalysts both in solution and also under solvent-free conditions. In solution, PdNPs become an effective catalyst to yield mainly 1-butene, providing higher yields than classical Pd/C catalysts and showing a multi-site catalytic behaviour. Related PdNPs have also been used as catalyst precursors in Heck C–C couplings. However, under these reaction conditions, the formation of active molecular species is postulated (see below).[5a]

2. C–C Bond Formation: Single-Site or Multi-Site Behaviour of Pd Nanoparticles

In this part, we will discuss the observed catalytic behaviour of PdNPs involved in different C–C couplings (Figure 1). Firstly, we will present the reported studies that suggest a multi-site reactivity (section 2.1.), followed by the research results pointing to a single-site behaviour (section 2.2). Fine-tuning between stabilizer, substrate and metallic surface can favour homogeneous or heterogeneous catalyst behaviour.

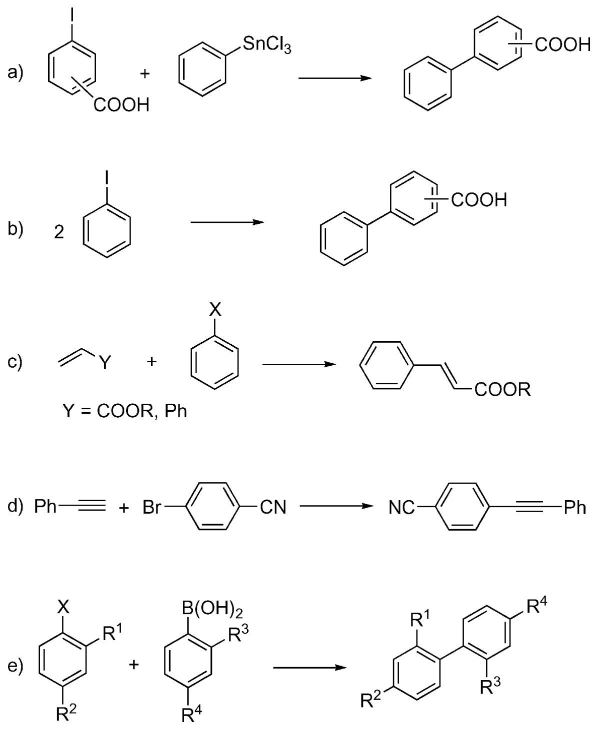


Figure 1. C–C bond formation reactions catalyzed by palladium systems discussed in the present review: (a) Stille coupling; (b) Ullmann coupling; (c) Heck coupling; (d) Sonogashira coupling; (e) Suzuki coupling.

2.1. Heterogeneous Behaviour

For reactions catalyzed by metallic nanoparticles in solution, no conclusive evidence for the cause of the change in the average size or in the size distribution after catalysis and for the role of each reagent present in the reaction mixture is reported in the literature.

El-Sayed et al. have reported that PdNPs stabilized by PVP [PVP = poly(*N*-vinyl-2-pyrrolidone), see Figure 2] in colloidal aqueous solution are efficient catalysts for Suzuki cross-couplings. The initial reaction rate, determined by the fluorescence intensity of the biphenyl obtained from iodobenzene and phenylboronic acid, is linearly dependent on the Pd concentration, suggesting that the catalysis takes place at the surface of the nanoparticles.[30]

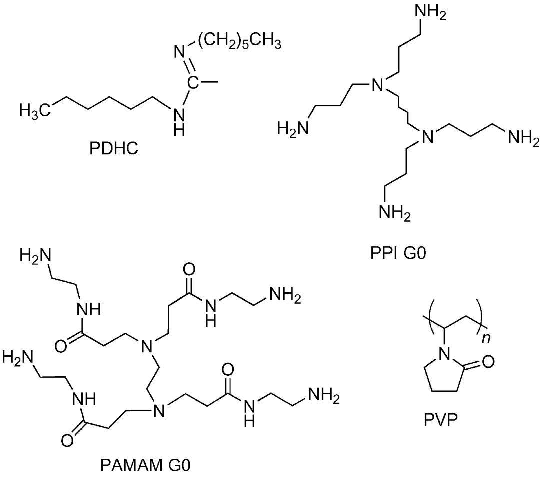


Figure 2. Structures of macromolecules involved in the stabilization of PdNPs.

This group has carefully examined several catalytic parameters (like characterization of catalyst, recycling and the effect of reactants) involved in the Suzuki reaction (Figure 1e, coupling between iodobenzene and phenylboronic acid) in relation to the stability and catalytic activity of the PVP-stabilized Pd nanoparticles, hence studying the nature of the active species.[31] A first approach consists of TEM analysis (from PdNPs of mean diameter 2.1 nm), in particular looking at the size distribution of particles before and after the first catalytic cycle (Figure 3). In the Gaussian fits, widths are larger after the first cycle, and the mean diameter of PdNPs also shifts towards larger sizes, a fact that can be explained by the Ostwald ripening favoured under the harsh catalytic reaction conditions used.[6] As a result, the smaller clusters shrink or dissolve totally to be reattached on the more stable surface of larger clusters. After the second cycle widths and centres of the size distributions of the PdNPs become smaller due to the aggregation and precipitation of the large nanoparticles formed during the first cycle, leaving smaller nanoparticles in solution (Figure 3). This diminution of active particles leads to a lower catalytic activity in the second cycle.

During the first three hours PVP–Pd nanoparticles smoothly increase in size and then level off near the end of the first cycle. This fact suggests that Ostwald ripening oc-

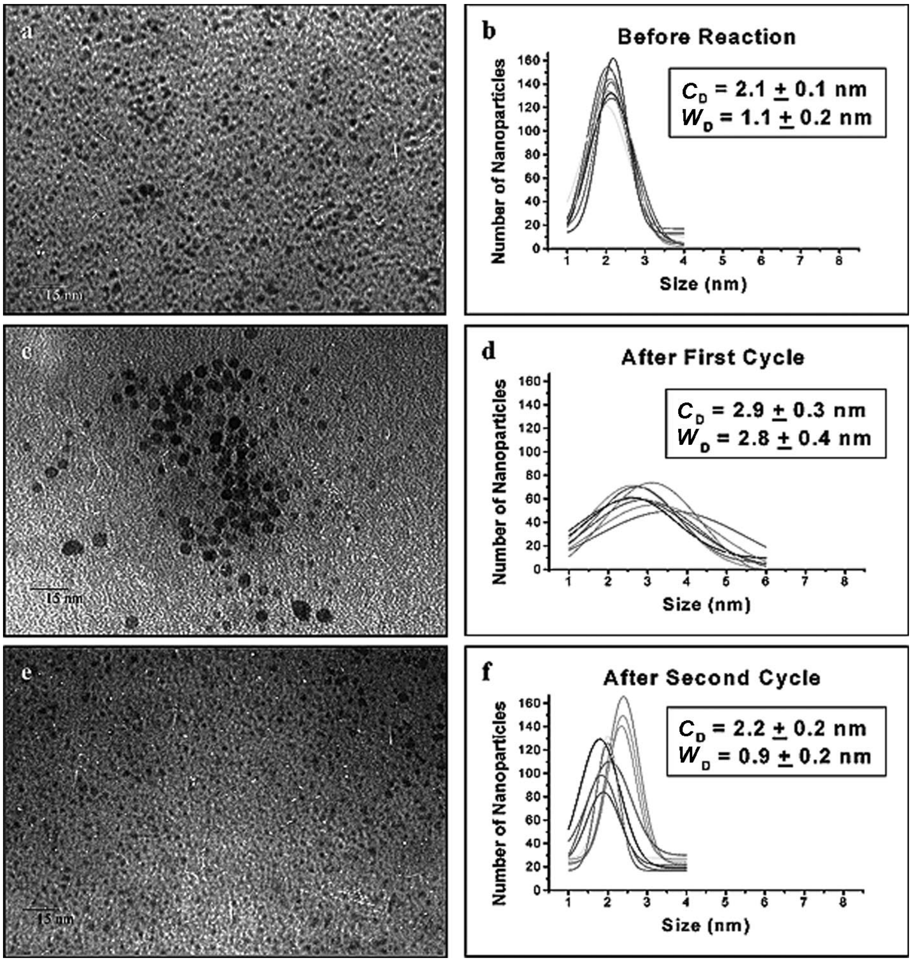


Figure 3. TEM images and Gaussian fits of the size distributions of PVP-stabilized PdNPs before Suzuki coupling (a, b), after the first cycle (c, d), and after the second cycle (e, f). Reprinted with permission from ref.[31] Copyright 2003 American Chemical Society.

curs in this period as a result of the depletion of small nanoparticles as well as free atoms in solution (Figure 4a). Also, the biphenyl produced can be a surface poison, because a rapid formation of biphenyl during the first hour is observed, but a significant diminution of its formation rate is clearly evidenced (Figure 4b). This fact is probably related to the coordination affinity of aromatic groups towards the metallic surface.[32]

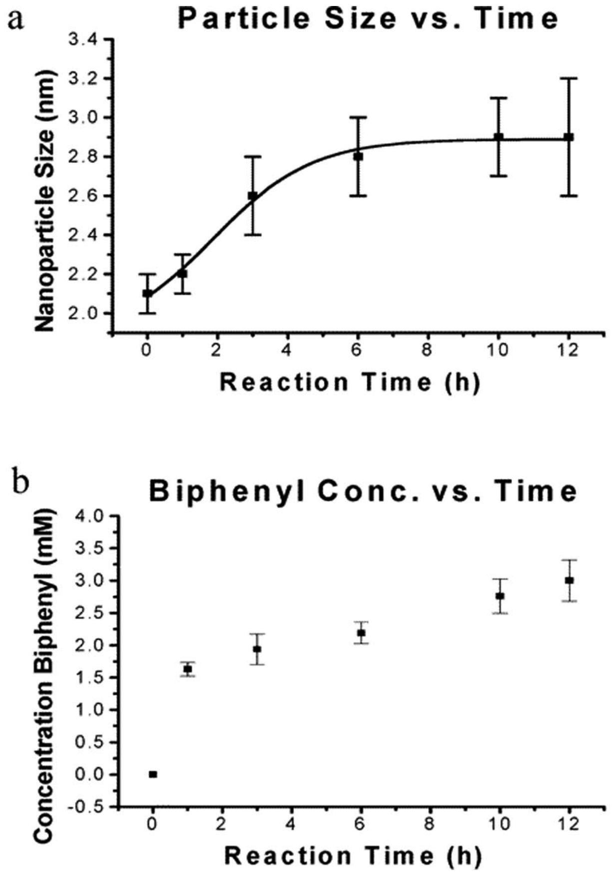


Figure 4. (a) PVP–Pd nanoparticle size as a function of reaction time; (b) biphenyl concentration as a function of reaction time. Reprinted with permission from ref.[31] Copyright 2003 American Chemical Society.

Another parameter that can give information about the nature of the catalytically active species is the effect of the amount of stabilizer (in this case, PVP). The addition of excess PVP to the catalytic mixture prevents an increase in the size of PdNPs, because the polymer diminishes the Ostwald ripening process by capping many of the free metallic surface sites. Actually, the diminution of the catalytic activity observed should be due to the diminished accessibility of the metallic atoms at the surface.

The size of the PdNPs increases in contrast to the sizes observed when phenylboronic acid and base without iodobenzene was used. In this last case the particles remain invariable in size. The reason for this observation is that phenylboronic acid in the presence of base (sodium acetate) is in the deprotonated form and as a result binds with the O$^-$ of the OH group to the free sites in the PdNPs and acts as a capping material. Phenylboronic acid acts as a stabilizer and then the Ostwald ripening process is greatly diminished. It is therefore proposed that phenylboronic acid binds to the surface and then reacts with iodobenzene by a collisional processes.

To determine the effect of the size of PVP-stabilized Pd nanoparticles in the Suzuki reaction, PdNPs of different size (6.6, 5.2, 3.9 and 3.0 nm) were investigated.[15a] The general trend observed is that the catalytic activity of PdNPs increases as the particle size decreases, suggesting that the Suzuki reaction is "structure-sensitive"; that is, the low-coordination-number vertex and edge atoms on the particle surface are the active centres for catalysis. Here, the low catalytic activity for the smallest particles might be due to the stronger adsorption of the intermediates on the particle surface, in which the strongly adsorbed species act as a poison, leading to low reaction rates.

Polymers containing donor groups have also been employed as stabilizers of PdNPs, introducing, besides the steric stabilization, the ability of the Lewis base groups to coordinate to the metallic surface.[33] Poly(*N*,*N*-dihexylcarbodiimide) (PDHC, Figure 2) was found to be an efficient polymeric ligand system for preparing and stabilizing palladium nanoparticles (mean diameter from 1 to 5 nm). The catalytic activity of PDHC–PdNPs was examined in the Suzuki coupling reaction, and nearly quantitative yields of biphenyl derivatives were observed in almost all cases.[34] No significant aggregation of nanoparticles in PDHC–Pd was observed, although colloidal metal catalysts tend to aggregate.[30,31] A small amount of black precipitate occurs in the cross-coupling between 5,5′-dibromo-2,2′-bithiophene and phenylboronic acid, due to the poisoning of the colloidal catalyst by the thiophene moiety.

Dendrimers represent another type of steric stabilizers of PdNPs applied in catalysis, showing specific properties.[35,36] When metallic nanoparticles are not encapsulated in the dendrimer structure, the terminology used is dendrimer-stabilized metal nanoparticles (DSNs). The group of Esumi studied the effect of the concentration of reactants on the size of particles stabilized by PAMAM [PAMAM = poly(amido-amine)] and PPI [PPI = poly(propylene-imine)] dendrimers as DSNs (Figure 2), and other examples can also be found in the literature.[37,38]

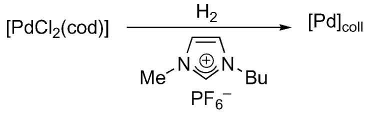
The solubility of dendrimer-encapsulated nanoparticles (DENs) is controlled principally by the chemical composition of the dendrimer periphery,[39] providing a means for carrying out reactions in green solvents such as water and supercritical CO_2.[40] As in the case of polymers, no additional ligands are required to stabilize NPs, because the particles are confined in the dendrimer, which results in small sizes and therefore high surface-area-to-volume ratios.

A comparative study of the stability and catalytic activity of PAMAM–OH generation 4 dendrimer–Pd nanoparticles (1.3 ± 0.1 nm) with those of the previously studied PVP–Pd nanoparticles (2.1 ± 0.1 nm) in the same Suzuki reaction described above has been conducted.[41] PAMAM–OH generation 4 dendrimer–Pd nanoparticles are known to be very strong encapsulators of metal clusters.[42–44] In the case of dendrimer-stabilized Pd nanoparticles and in contrast to PVP stabilized PdNPs, the growth process continues during the second cycle of the Suzuki reaction. This fact can be associated to the preparation of nanoparticles at room temperature. Under catalytic conditions, the particles become larger in size (2.7 ± 0.1 nm) because of the increase in the temperature. The biphenyl ratio (second cycle/first cycle) is higher for the dendrimer–Pd nanoparticles than it is for PVP–Pd nanoparticles because the dendrimer–Pd nanoparticles are larger during the second cycle and thus have more active sites, and also because nanoparticles do not precipitate out of solution.

The Stille reaction (Figure 1a) can be catalyzed by DENs consisting of size-monodisperse palladium nanoparticles within PAMAM dendrimers in water at room temperature,[45] expanding the catalytic scope of DENs for carbon–carbon coupling reactions, and most particularly for Heck and Suzuki cross-couplings.[46–49] Because the particles are encapsulated within the dendrimer, no additional ligands are required for stabilization, in contrast to the molecular systems in which a phosphane ligand and a co-catalyst are generally required with the use of high reaction temperature.[50] Three iodobenzoic acid isomers were tested in this coupling of aryl halide with organostannanes. The yield for 3- and 4-iodobenzoic acid was 100%, but the yield dropped to less than 15% for 2-iodobenzoic acid. This poor turnover is explained by the close proximity of the iodine and acid groups allowing both of them to interact with the Pd-nanoparticles in the step of oxidative addition (the first step in this kind of catalytic carbon–carbon coupling reaction[51]). This bidentate interaction results in irreversible attachment of the substrate to the catalyst, thereby poisoning it.

Palladium nanoparticles generated in situ efficiently catalyze Ullmann-type reactions (Figure 1b) and have been described as an alternative to the stoichiometric protocol with copper.[52] Monitoring the kinetics of the model reaction with PhI as substrate, an induction period of almost 3 h is observed. This induction period supports the involvement of palladium clusters in the cycle, because the long induction period observed cannot be justified by a model assuming that molecular species (Pd^0 atoms or adatoms) are responsible for the catalytic behaviour. After 3 h, the reaction rate increases, probably as a result of the formation of active PdNPs of optimal size, analogous to those described by Finke and co-workers for the hydrogenation of olefins catalyzed by iridium.[53] In addition, Schmidt and Smirnov have interpreted this kinetic profile on the basis of "cluster magic number".[54] For the Ullmann reaction, TEM micrographs at the end of the induction period show spherical, well-dispersed particles with a mean size of 2.5 ± 0.5 nm corresponding to a "magic number" nanocluster of 300 atoms. The kinetic data could support a cycle involving the formation of a phenyl radical anion that coordinates on the surface of the palladium nanoparticles.

PdNPs only stabilized by ionic liquid without "passivating" agents on the metallic surface have been synthesized and studied in Suzuki C–C coupling by our research group.[55] PdNPs were prepared in [BMI][PF_6] by decomposition of [$PdCl_2$(cod)] for the first time (Scheme 1).



Scheme 1. Synthesis of palladium nanoparticles in [BMI][PF_6] from [$PdCl_2$(cod)] precursor.

TEM analyses of these particles show star-like-shaped interparticle organizations (Figure 5). In contrast, no superstructures were observed for nanoparticles formed from $PdCl_2$ salt or from [$Pd_2(dba)_3$·$CHCl_3$], giving, in both cases, quite well-dispersed material formed by nanoparticles. As a result, the electrostatic stabilization of PdNPs by the ionic liquid (IL) depends on the palladium precursor. For material formed from [$PdCl_2$(cod)] by using 0.25 mol-% palladium, after one hour at 100 °C, total conversion of bromobenzene was reached, yielding 92% biphenyl. The palladium content in biphenyl (as determined by ICP-MS) is in the range 3–5 ppm. The IL phase containing the catalyst was reused up to ten times, and the palladium content in the biphenyl isolated after each recycling was still low. Moreover, the inactivity detected for both molecular precursor [$PdCl_2$(cod)] and palladium powder agrees with a catalyst of colloidal nature for the preformed PdNPs from [$PdCl_2$(cod)]. Also, addition of mercury after 30 min of catalytic reaction stopped the evolution of the reaction, pointing to the heterogeneous nature of the catalyst.[56]

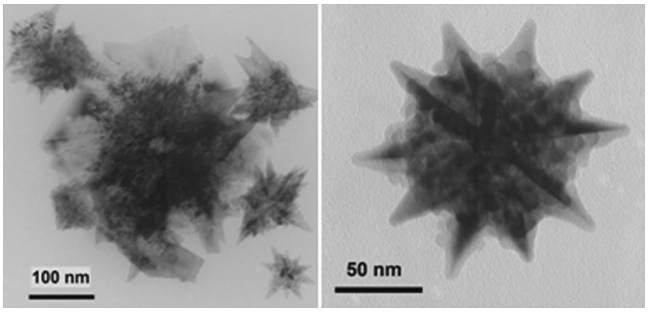


Figure 5. TEM micrographs of palladium nanoparticles stabilized by [BMI][PF_6].

2.2. Exclusive Homogeneous Reactivity?

2.2.1. C–C Coupling

Since the 1990s, Pd-catalyzed C–C couplings have developed into an important tool in organic synthesis. In particular, Heck and Suzuki couplings have been especially investigated because of the small loading of metal required to afford very high turnover numbers, which is named homeopathic catalysts.[57]

Pd^{II} molecular catalytic precursors have been reported as sources of soluble Pd^0 nanoparticles responsible for the high activity. For instance, Dupont and co-workers reported the use of a palladacycles as catalyst precursors for the Heck reaction using aryl halides under mild reaction conditions.[58] Hg tests and comparison with more stable palladacycle complexes (showing a lower tendency to generate ligand-free metallic species) are in favour of a mechanism involving the formation of colloidal species. At the same time, de Vries and co-workers reported the use of $Pd(OAc)_2$ leading, under the catalytic conditions used for the Heck reaction, to the formation of soluble metallic nanoparticles that are catalytically very active at very low concentrations.[59] However, an increase in the palladium loading results in the quick formation of inactive palladium black. In both studies, the colloids formed in situ are stabilized by quaternary ammonium salts to retard or prevent their aggregation.

Palladium nanoparticles, either preformed or generated in situ, can act as a reservoir of molecular complexes, being the true catalytically active species.[60,61]

The accepted mechanism involves the following elementary steps: oxidative addition of the aryl halide substrate to the colloid surface, leaching of Pd^{II} molecular species that enter the catalytic cycle and then reforming of the nanoparticles at the end of the reaction (Figure 6). This mechanism is supported by kinetic studies, poison tests, TEM monitoring (analyses performed before, during and after the reaction) and the Pd content in the organic phase at different conversions.

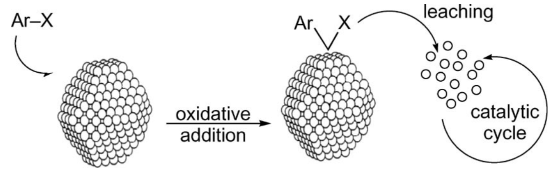


Figure 6. Schematic representation of the accepted mechanism for Heck coupling with PdNPs as catalytic precursors.

Although it is often assumed that all the observations made in the course of these detailed studies could be extended to other palladium-catalyzed C–C coupling reactions, experimental evidence remains scarce.

In 2000, Reetz and co-workers reported the involvement of Pd colloids, generated in situ and stabilized by ammonium salts, in the Heck reaction (mean diameter = 2.2 nm).[62] It was observed that reaction starts after an induction period, which is in agreement with the formation of metallic colloids. The study of the reaction of the palladium colloids with one equivalent of the aryl halide provided evidence, from ^{13}C NMR and UV/Vis spectroscopy, for the formation of molecular species that were then active in the Heck reaction. It is assumed that leaching is likely to occur from more reactive sites of the metallic surface; a similar behaviour was also observed for the Suzuki coupling between phenylboronic acid and *para*-bromoacetophenone.

The use of a membrane reactor, which allows the passage of ions and atoms but not of clusters larger than 5 nm, led Rothenberg et al. to conclude that molecular species leached from palladium nanoparticles during both Heck and Suzuki coupling reactions (Figure 1c and 1e) are the true catalytic species and not the preformed palladium colloids of ca. 15 nm.[63] It was proved that Pd^0 atoms can leach from the surface under non-oxidizing conditions, but $[Pd^{II}ArI]$ species can also be formed in presence of ArI, suggesting these two types of mechanism for the formation of the catalytically active molecular species that enters the catalytic cycle.

Dupont and co-workers have recently reported a study on the Heck coupling, including kinetic studies and poisoning tests. This study evidences the role of preformed Pd nanoparticles (prepared by decomposition of palladacycles) as a reservoir of active species in ionic liquids,[64] according to the mechanism proposed by de Vries in organic solvent.[5b,65]

The use of nitrile-functionalized ionic liquids as solvent in cross-coupling reactions, which significantly reduce the amount of palladium leaching from nanoparticles formed in situ starting from $PdCl_2$, leads to efficient catalysts for the Suzuki and Stille processes as reported by Dyson and co-workers.[66] However, the true nature of the catalytic species is not unambiguously stated, because the functionalized ionic liquids could favour the stabilization of Pd molecular species through coordination of the nitrile moiety.[67]

Rothenberg and co-workers reported the Sonogashira reaction (Figure 1d) catalyzed by preformed palladium nanoparticles and demonstrated a homogeneous mechanism, thanks to kinetic and recycling studies. Indeed, it was assumed by the authors that the molecular species leached from the original colloids are the active species that reform, after completion of the catalytic reaction, less reactive nanoparticles, explaining thus the very low activity observed in the course of recycling experiments.

Moreover, and unlike what is usually observed in the case of the Heck reaction, TEM analysis evidenced that the nanoparticles are smaller after reaction than before, in contradiction with the Oswald ripening process. In addition to the mechanism previously described, it was suggested that leaching could also occur by release of Pd^0 atoms from defect sites of the surface (edges and vertex), leading to Pd^0 molecular species that subsequently react with aryl halides.[68]

On the other side, we have recently demonstrated the influence of the solvent and the decisive role of nanoparticles generated in situ for palladium-catalyzed Suzuki reactions. PdNPs generated in situ from a molecular precursor in the presence of various ligands derived from norbornene (Figure 7) in the ionic liquid $[BMI][PF_6]$ was evidenced, and a detailed investigation of the true catalytic species has been recently carried out by our group.[69]

While in organic solvents, good donor ligands like bidentate amines lead to the formation of stable complexes, in ionic liquids, palladium systems are only active when nanoparticles are generated. Poison tests, the inhibiting effect of oxygen, the formation of byproducts resulting from homocoupling and TEM analysis evidenced that Pd^0 colloids are involved in the catalytic process, probably acting as a reservoir. Indeed, the palladium content in the isolated organic product was determined and appeared to decrease as the

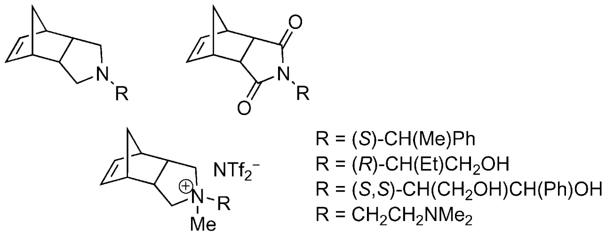


Figure 7. Ligands derived from norbornene containing amine, amide and ammonium functional groups.

conversion increased. Preformed palladium nanoparticles tested under the same conditions led to low conversion relative to the colloids generated in the course of the catalytic reaction. All these results suggest that the palladium nanoparticles are necessary in order to get an active system working in ionic liquids and with poor donor ligands (Figure 8).

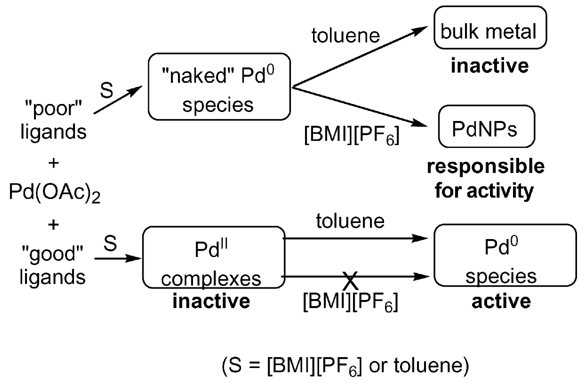


Figure 8. Palladium species involved in Suzuki cross-coupling reactions in toluene and in [BMI][PF_6], generated from palladium acetate with use of poor and good donor ligands.

2.2.2. *A Particular Study: Allylic Alkylation*

In the last years, we have been interested in looking for specific catalytic reactivity in order to distinguish homogeneous (single-site) and heterogeneous (multi-site) catalysis.[70] In particular, Pd-catalyzed asymmetric allylic alkylation permits to discriminate the catalytic behaviour between molecular precursors and preformed PdNPs by using optically pure diphosphites as the source of chirality (Figure 9).[71]

As shown in Table 1, only the colloidal system Pd**1** induced kinetic resolution, reacting in preference with the (*R*) isomer of the substrate (entry 4). When these results are compared with those obtained by using molecular precursors as catalysts (entries 1–3), even at very low palladium/substrate ratio (up to 1:10.000), we observed that the reaction rate of both enantiomers of the starting allylic acetate remain similar. However Pd**2** nanoparticles are not stable under the catalytic conditions, leaching molecular species (entries 2 and 5). In addition, Pd**1** and Pd**3** nanoparticles are inactive when non-aromatic substrates are used (Figure 9), in contrast to the high activity obtained by using the corresponding molecular catalytic systems. These results suggest that Pd**1** and Pd**3** show a surface-like catalytic behaviour. It is important to note the need for aromatic groups on the substrate in order to obtain active systems, which is probably due to the π interaction with the metallic surface, in agreement with the coordination study carried out for ruthenium nanoparticles by using a pyridine derivative as stabilizer.[32]

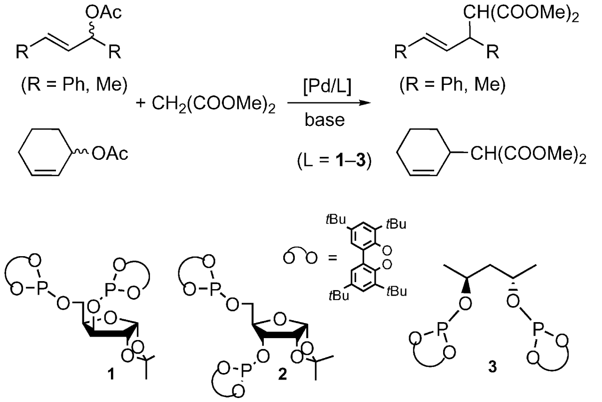


Figure 9. Asymmetric allylic alkylation catalyzed by molecular species and preformed PdNPs containing chiral diphosphites **1**–**3**, Pd**1**–Pd**3**.

Table 1. Pd-catalyzed allylic alkylation of *rac*-3-acetoxy-1,3-diphenyl-1-propene by using dimethylmalonate as nucleophile.[a]

Entry	Catalyst	Conversion (%)[b]	*ee* S (%)[c]	*ee* P (%)[d]
1	Pd/**1**[e]	83	0	90 (*S*)
2	Pd/**2**[e]	80	0	0
3	Pd/**3**[e]	100	–	94 (*S*)
4	Pd**1**[f]	56	89 (*S*)	97 (*S*)
5	Pd**2**[f]	100	–	11 (*S*)
6	Pd**3**[f]	88	–	90 (*S*)

[a] For the experimental conditions, see ref.[71b]. [b] Based on the substrate and determined by ^1H NMR spectroscopy. [c] Enantiomeric excess of the substrate determined by HPLC on a Chiracel-OD column. [d] Enantiomeric excess of the alkylation product determined by HPLC on a Chiracel-OD column. [e] Catalytic precursor generated in situ from [PdCl(allyl)]$_2$ and the corresponding ligand. [f] Preformed palladium nanoparticles used as catalytic precursor.

3. Miscellaneous

At present, a small number of PdNP-catalyzed processes other than hydrogenation and C–C coupling reactions focusing on the nature of the true catalyst have been reported. The majority of them suggest surface-like catalyst behaviour.[72]

Dechlorination and hydrodechlorination of aromatic compounds have been successfully achieved by using PdNPs in water (stabilized by ammonium salts),[72b] in $scCO_2$ (stabilized by high-density polyethylene)[72c] and in ionic liquid medium;[72d] in all cases, PdNPs are reusable.

The various sizes and shapes obtained for PVP-stabilized PdNPs under different synthetic reaction conditions have been applied in the methoxycarbonylation of iodobenzene, showing high activities when relatively small nanoparticles of well-shaped polyhedral morphology are used.[72e]

Conclusions

From a mechanistic point of view, the use of palladium nanocatalysts requires the analysis of the catalytically active species, because of their kinetic stability. In solution, these materials can agglomerate, but they can also leach molecular species because of the high reactivity of the low-coordination atoms at the metallic surface.

Structure-sensitive catalytic processes, like hydrogenation, turn out to be strongly dependent on nanoclusters shape and size, showing multi-site catalyst behaviour. On the other hand, for C–C bond formation reactions, fine-tuning between stabilizer, substrate and metallic surface can favour homogeneous or heterogeneous reactivity. Therefore, macromolecular stabilizers (dendrimers, polymers) can avoid the leaching of molecular complexes.

Although there are a large number of contributions on the application of PdNPs in catalysis, few reports deal with the nature of the catalytically active species.[73] Future work in this area could allow the design of even more efficient nanocatalysts, together with new approaches to discriminate the nature of the catalyst.

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[1] a) B. L. Cushing, V. L. Kolesnichenko, C. J. O'Connor, *Chem. Rev.* **2004**, *104*, 3893–3946; b) A. Roucoux, J. Schulz, H. Patin, *Chem. Rev.* **2002**, *102*, 3757–3778; c) H. Bönnemann, R. M. Richards, *Eur. J. Inorg. Chem.* **2001**, 2455–2480.

[2] R. G. Finke in *Metal Nanoparticles: Synthesis, Characterization and Applications* (Eds: D. L. Feldheim, C. A. Foss Jr.,), Marcel Deker, New York, **2002**, pp. 17–54.

[3] L. S. Ott, R. G. Finke, *Coord. Chem. Rev.* **2007**, *251*, 1075–1100.

[4] Y. Yin, A. P. Alivisatos, *Nature* **2005**, *437*, 664–670.

[5] For Heck reactions, see: a) C. C. Cassol, A. P. Umpierre, G. Machado, S. I. Wolke, J. Dupont, *J. Am. Chem. Soc.* **2005**, *127*, 3298–3299; b) J. G. de Vries, *Dalton Trans.* **2006**, 421–429.

[6] a) L. Ratke, P. W. Voorhees in *Growth and Coarsening: Ostwald Ripening in Material Processing*, Springer, Dordrecht, **2002**, pp. 117–125; b) A. Howard, C. E. J. Mitchell, R. G. Egdell, *Surf. Sci.* **2002**, *515*, L504–L508; c) A. Imre, D. L. Beke, E. Gontier-Moya, I. A. Szabo, E. Gillet, *Appl. Phys. A* **2000**, *71*, 19–22.

[7] a) G. Schmid (Ed.), *Nanoparticles*, Wiley-VCH, Weinheim, **2004**; b) C. Burda, X. Chen, R. Narayanan, M. A. El-Sayed, *Chem. Rev.* **2005**, *105*, 1025–1102.

[8] J. Pérez-Juste, I. Pastoriza-Santos, L. M. Liz-Marzán, P. Mulvaney, *Coord. Chem. Rev.* **2005**, *249*, 1870–1901.

[9] M. S. Chen, D. W. Goodman, *Catal. Today* **2006**, *111*, 22–33.

[10] a) T. S. Ahmadi, Z. L. Wang, T. C. Green, A. Henglein, M. A. El-Sayed, *Science* **1996**, *272*, 1924–1925; b) R. Narayanan, M. A. El-Sayed, *J. Phys. Chem. B* **2004**, *108*, 5726–5733; c) R. Narayanan, M. A. El-Sayed, *Nano Lett.* **2004**, *4*, 1343–1348; d) R. Narayanan, M. A. El-Sayed, *Langmuir* **2005**, *21*, 2027–2033.

[11] A. Gniewek, J. J. Ziólkowski, A. M. Trzeciak, L. Kepinski, *J. Catal.* **2006**, *239*, 272–281.

[12] A. Gniewek, A. M. Trzeciak, J. J. Ziólkowski, L. Kepinski, J. Wrzyszcz, W. Tylus, *J. Catal.* **2005**, *229*, 332–343.

[13] G. C. Bond, *Surf. Sci.* **1985**, *156*, 966–981.

[14] O. M. Wilson, M. R. Knecht, J. C. García-Martínez, R. M. Crooks, *J. Am. Chem. Soc.* **2006**, *128*, 4510–4511.

[15] a) Y. Li, E. Boone, M. A. El-Sayed, *Langmuir* **2002**, *18*, 4921–4925; b) O. M. Wilson, M. R. Knecht, J. C. García-Martínez, R. M. Crooks, *J. Am. Chem. Soc.* **2006**, *128*, 4510–4511; c) A. P. Umpierre, G. Machado, G. H. Fecher, J. Morais, J. Dupont, *Adv. Synth. Catal.* **2005**, *347*, 1404–1412.

[16] J. Schwartz, *Acc. Chem. Res.* **1985**, *18*, 302–308.

[17] R. Sablong, U. Schlotterbeck, D. Vogt, S. Mecking, *Adv. Synth. Catal.* **2003**, *345*, 333–336.

[18] G. Berhault, M. Bausach, L. Bisson, L. Becerra, C. Thomazeau, D. Uzio, *J. Phys. Chem. C* **2007**, *111*, 5915–5925.

[19] H. Choo, B. He, K. Y. Liew, H. Liu, J. Li, *J. Mol. Catal. A* **2006**, *244*, 217–228.

[20] a) M. J. Yacamán, M. Martín-Almazo, J. A. Ascencio, *J. Mol. Catal. A* **2001**, *173*, 61–74; b) R. Segura del Río, G. Cárdenas, *J. Cryst. Growth* **2008**, *310*, 495–500; c) Y. Sun, A. I. Frenkel, R. Isseroff, C. Shonbrun, M. Forman, K. Shin, T. Koga, H. White, L. Zhang, Y. Zhu, M. H. Rafailovich, J. C. Sokolov, *Langmuir* **2006**, *22*, 807–816; d) B. Veisz, Z. Király, *Langmuir* **2003**, *19*, 4817–4824.

[21] Z. Y. Li, N. P. Young, M. Di Vece, S. Palomba, R. E. Palmer, A. L. Bleloch, B. C. Curley, R. L. Johnston, J. Jiang, J. Yuan, *Nature* **2008**, *451*, 46–49.

[22] C. Barreteau, M. C. Desjonquères, D. Spanjaard, *Eur. Phys. J. D* **2000**, *11*, 395–402.

[23] R. van Hardeveld, F. Hartog, *Surf. Sci.* **1969**, *15*, 189–230.

[24] a) S.-K. Oh, Y. Niu, R. M. Crooks, *Langmuir* **2005**, *21*, 10209–10213; b) C. Ornelas, L. Salmon, J. Ruiz Aranzaes, D. Astruc, *Chem. Commun.* **2007**, 4946–4948; c) T. Mizugaki, M. Murata, S. Fukubayashi, T. Mitsudome, K. Jitsukawa, K. Kaneda, *Chem. Commun.* **2008**, 241–243.

[25] J. Silvestre-Albero, G. Rupprechter, H.-J. Freund, *Chem. Commun.* **2006**, 80–82.

[26] N. Semagina, A. Renken, D. Laub, L. Kiwi-Minsker, *J. Catal.* **2007**, *246*, 308–314.

[27] N. Semagina, A. Renken, L. Kiwi-Minsker, *J. Phys. Chem. C* **2007**, *111*, 13933–13937.

[28] A. Molnar, A. Sarkany, M. Varga, *J. Mol. Catal. A* **2001**, *173*, 185–221.

[29] G. W. Parshall, *J. Am. Chem. Soc.* **1972**, *94*, 8716–8719.

[30] Y. Li, X. M. Hong, D. M. Collard, M. A. El-Sayed, *Org. Lett.* **2000**, *2*, 2385–2388.

[31] R. Narayanan, M. A. El-Sayed, *J. Am. Chem. Soc.* **2003**, *125*, 8340–8347.

[32] I. Favier, S. Massou, E. Teuma, K. Philippot, B. Chaudret and M. Gómez, *Chem. Commun.* **2008**, DOI: 10.1039/b804402c.

[33] I. Favier, M. Gómez, G. Muller, D. Picurelli, A. Nowicki, A. Roucoux, J. Bou, *J. Appl. Polym. Sci.* **2007**, *105*, 2772–2782.

[34] Y. Liu, C. Khemtong, J. Hu, *Chem. Commun.* **2004**, 398–399.

[35] R. M. Crooks, M. Zhao, L. Sun, V. Chechik, L. K. Yeung, *Acc. Chem. Res.* **2001**, *34*, 181–190.

[36] R. W. J. Scott, O. M. Wilson, R. M. Crooks, *J. Phys. Chem. B* **2005**, *109*, 692–704.

[37] E. Badetti, A.-M. Caminade, J.-P. Majoral, M. Moreno-Mañas, R. M. Sebastian, *Langmuir* **2008**, *24*, 2090–2101.

[38] K. Esumi, R. Isono, T. Yoshimura, *Langmuir* **2004**, *20*, 237–243.

[39] Y. Niu, R. M. Crooks, *C R. Chim.* **2003**, *6*, 1049–1059.

[40] L. K. Yeung, C. T. Lee Jr., K. P. Johnston, R. M. Crooks, *Chem. Commun.* **2001**, 2290–2291.

[41] R. Narayanan, M. A. El-Sayed, *J. Phys. Chem. B* **2004**, *108*, 8572–8580.

[42] E. Kunio, M. Keiko, Y. Tomokazu, *Colloid Interface Sci.* **2002**, *254*, 402–405.

[43] M. Zhao, R. M. Crooks, *Angew. Chem. Int. Ed.* **1999**, *38*, 364–366.

[44] V. Chechik, R. M. Crooks, *J. Am. Chem. Soc.* **2000**, *122*, 1243–1244.

[45] J. C. Garcia-Martinez, R. Lezutekong, R. M. Crooks, *J. Am. Chem. Soc.* **2005**, *127*, 5097–5103.
[46] E. H. Rahim, F. S. Kamounah, J. Frederiksen, J. B. Christensen, *Nano Lett.* **2001**, *1*, 499–501.
[47] M. Ooe, M. Murata, T. Mizugaki, K. Ebitani, K. Kaneda, *J. Am. Chem. Soc.* **2004**, *126*, 1604–1605.
[48] M. Pittelkow, K. Moth-Poulsen, U. Boas, J. Christensen, *Langmuir* **2003**, *19*, 7682–7684.
[49] Y. Li, M. A. El-Sayed, *J. Phys. Chem. B* **2001**, *105*, 8938–8943.
[50] V. Farina, V. Krishnamurthy, W. J. Scott in *The Stille Reaction*, John Wiley & Sons, New York, **1998**.
[51] J. K. Stille, *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 508–519.
[52] L. Durán Pachón, C. J. Elsevier, G. Rothenberg, *Adv. Synth. Catal.* **2006**, *348*, 1705–1710.
[53] C. Besson, E. E. Finney, R. G. Finke, *Chem. Mater.* **2005**, *17*, 4925–4938.
[54] A. F. Schmidt, V. V. Smirnov, *Top. Catal.* **2005**, *32*, 71–75.
[55] J. Durand, E. Teuma, F. Malbosc, Y. Kihn, M. Gómez, *Catal. Commun.* **2008**, *9*, 273–275.
[56] J. A. Widegren, R. G. Finke, *J. Mol. Catal. A* **2003**, *198*, 317–341.
[57] a) A. Alimardanov, L. Schmieder-van de Vondervoort, A. H. M. de Vries, J. G. de Vries, *Adv. Synth. Catal.* **2004**, *346*, 1812–1817; b) I. P. Beleskaya, A. V. Cheprakov, *Chem. Rev.* **2000**, *100*, 3009–3066.
[58] C. S. Consorti, M. L. Zanini, S. Leal, G. Ebeling, J. Dupont, *Org. Lett.* **2003**, *5*, 983–986.
[59] A. H. M. de Vries, J. M. C. A. Mulder, J. H. M. Mommers, H. J. W. Henderickx, J. G. de Vries, *Org. Lett.* **2003**, *5*, 3285–3288.
[60] For recent reviews on C–C coupling reactions catalyzed by palladium nanoparticles, see: a) M. Moreno-Mañas, R. Pleixats, *Acc. Chem. Res.* **2003**, *36*, 638–643; b) D. Astruc, *Inorg. Chem.* **2007**, *46*, 1884–1894.
[61] For recent reviews on the role of palladium nanoparticles in the Heck reaction, see: a) A. M. Trzeciak, J. J. Ziólkowski, *Coord. Chem. Rev.* **2005**, *249*, 2308–2322; b) N. T. S. Phan, M. Van Der Sluys, C. W. Jones, *Adv. Synth. Catal.* **2006**, *348*, 609–679; c) A. M. Trzeciak, J. J. Ziólkowski, *Coord. Chem. Rev.* **2007**, *251*, 1281–1293.
[62] M. T. Reetz, E. Westermann, *Angew. Chem. Int. Ed.* **2000**, *39*, 165–168.
[63] A. V. Gaikwad, A. Holuigue, M. B. Thathagar, J. E. ten Elshof, G. Rothenberg, *Chem. Eur. J.* **2007**, *13*, 6908–6913.
[64] C. S. Consorti, F. R. Flores, J. Dupont, *J. Am. Chem. Soc.* **2005**, *127*, 12054–12065.
[65] M. T. Reetz, J. G. de Vries, *Chem. Commun.* **2004**, 1559–1563.
[66] D. Zhao, Z. Fei, T. J. Geldbach, R. Scopelliti, P. J. Dyson, *J. Am. Chem. Soc.* **2004**, *126*, 15876–15882.
[67] Z. Fei, D. Ahoa, D. Pieraccini, W. H. Ang, T. J. Geldbach, R. Scopelliti, C. Chiappe, P. J. Dyson, *Organometallics* **2007**, *26*, 1588–1598.
[68] M. B. Thathagar, P. J. Kooyman, R. Boerleider, E. Jansen, C. J. Elsevier, G. Rothenberg, *Adv. Synth. Catal.* **2005**, *347*, 1965–1968.
[69] F. Fernández, B. Cordero, J. Durand, G. Muller, F. Malbosc, Y. Kihn, E. Teuma, M. Gómez, *Dalton Trans.* **2007**, 5572–5581.
[70] a) S. Jansat, D. Picurelli, K. Pelzer, K. Philippot, M. Gómez, G. Muller, P. Lecante, B. Chaudret, *New J. Chem.* **2006**, *30*, 115–122; b) O. Illa, C. Rodríguez-García, C. Acosta-Silva, I. Favier, D. Picurelli, A. Oliva, M. Gómez, V. Branchadell, R. M. Ortuño, *Organometallics* **2007**, *26*, 3306–3314; c) M. Gómez, I. Favier in *Metal Nanoclusters in Catalysis and Materials Science: The Issue of Size Control*, (Eds: B. Corain, G. Schmid, N. Toshima), Elsevier, **2008**, ch. 31, pp. 427–436.
[71] a) S. Jansat, M. Gómez, K. Philippot, G. Muller, E. Guiu, C. Claver, S. Castillón, B. Chaudret, *J. Am. Chem. Soc.* **2004**, *126*, 1592–1593; 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*, 2459–2469.
[72] a) M. A. Omole, I. O. K'Owino, O. A. Sadik, *Appl. Catal. B* **2007**, *76*, 158–167; b) B. Léger, A. Nowicki, A. Roucoux, J.-P. Rolland, *J. Mol. Catal. A* **2007**, *266*, 221–225; c) W. Liao, Y.-C. Chen, J. S. Wang, H. Kwang Yak, C. M. Wai, *Ind. Eng. Chem. Res.* **2007**, *46*, 5089–5093; d) V. Calò, A. Nacci, A. Monopoli, A. Damascelli, E. Ieva, N. Cioffi, *J. Organomet. Chem.* **2007**, *692*, 4397–4401; e) A. Gniewek, J. J. Ziólkowski, A. M. Trzeciak, L. Kepinski, *J. Catal.* **2006**, *239*, 272–281.
[73] In the course of the preparation of the present Microreview, a perspective related to this subject, entitled "*Transition-Metal Nanoparticles: Synthesis, Stability and the Leaching Use*", has appeared: L. Durán Pachón, G. Rothenberg, *Appl. Organomet. Chem.* **2008**, *22*, 288–299.

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