

Formation of Carbon–Carbon Bonds under Catalysis by Transition-Metal Nanoparticles

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ABSTRACT

This Account presents the fast-growing field of catalysis by transition metal nanoparticles, its present situation concerning scope and limitations, as well as future prospects. The Account is limited to reactions involving carbon–carbon bond formation.

Introduction

Transition-metal nanoparticles have attracted a great deal of attention in the last 10 years; their preparation, structure determination, and applications are topics of current interest.^{1–14} Nanoparticles are defined as having 1–50 nm diameter, a size range where metals can show size-dependent properties. The smaller the cluster of atoms, the higher the percentage of atoms are on the surface, rendering nanoparticles very interesting in catalysis.^{6,11,14} Thus, a nanoparticle of 10 nm diameter has about 10% of its atoms in the surface, but one of 1 nm has 100%.⁷

The metal atoms constituting nanoparticles can be generated by (i) chemical reduction of a metal salt, (ii) thermal, photochemical, or sonochemical decomposition of a metal(0) complex, (iii) hydrogenation of a coordinating olefinic moiety, and (iv) vapor phase deposition. To this list proposed by Bradley² should be added (v) electrochemical reduction of higher valent species of the metal.⁹ During generation of nanoparticles, the following steps have been identified: (i) generation of atoms as above; (ii) nucleation to form an initial cluster of atoms; (iii) growing of the cluster until a certain volume is reached; and (iv) surrounding the cluster by a protecting shell that prevents agglomeration. Therefore, nanoparticles should be formed in the presence of a protecting agent. These protectors can be broadly divided into two categories: those providing electrostatic and those pro-

viding steric stabilization. The electrostatic stabilization is based upon the double electric layer formed when ions of the same sign are adsorbed at the nanoparticle surface (the charges in Figure 1 could be inverted). The counterions form a second layer that repels the neighboring nanoparticle; for example, sodium citrate acts by this mechanism. In other cases, protecting molecules of considerable length interact attractively with the surface of the nanoparticle. The volume of these surrounding molecules prevents mutual approach of metal surfaces at bonding distance. Popular protecting agents are polymers (poly(vinylpyrrolidone)), cyclodextrins, dendrimers, and so forth. Particularly well-known is the mechanism of stabilization by large molecules featuring functional groups with high affinity for the metal, i.e., thiols,¹⁵ sulfides, amines, or phosphines. Other common stabilizers are ionic surfactants, i.e., sodium dodecyl sulfate and lauryl trimethylammonium chloride. These compounds protect nanoparticles by both electrostatic and steric mechanisms (Figure 1). Heavily fluorinated compounds have also been found to stabilize metal nanoparticles.¹⁶

Size and dispersity are important properties of nanoparticles that are mainly determined by transmission electron microscopy (TEM). The use of metal nanoparticles for catalysis in reactions generating carbon–carbon bonds is in its infancy; however, we anticipate an important growth of activity in this field soon. This is the reason of this account.

Palladium-Catalyzed Reactions¹⁷

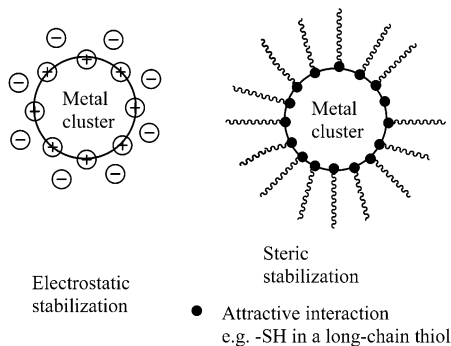
The Mizoroki–Heck Reaction. The Mizoroki–Heck (M–H) reaction is the arylation of olefins as indicated in Scheme 1.¹⁸ Aryl iodides are more active than bromides and chlorides in concordance with the energies of the C–X bonds. Main concerns are at present (i) finding catalytic systems that activate C–Cl bonds or alternatively, (ii) finding alternative cheaper leaving groups (e.g., diazonium cation, nitro, etc.), (iii) recovery and reuse of the catalysts without loss of activity, and (iv) development of phosphine-free palladium catalysts.

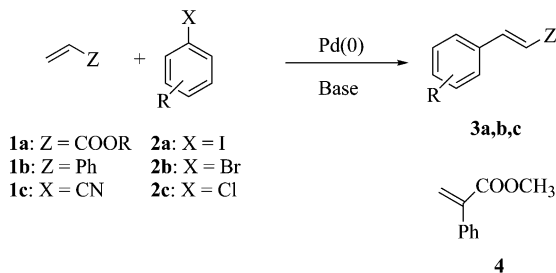
Reetz and co-workers showed in 1996 that tetraalkylammonium-stabilized palladium nanoparticles of 3 nm catalyzed the reaction of butyl acrylate, **1a**, with iodobenzene to afford butyl cinnamate **3a**.¹⁹ Reetz also reported M–H reactions of aryl bromides **2b** (R = H, *p*-COCH₃, *p*-NO₂) with styrene **1b**.²⁰ The catalysts were palladium nanoparticles (8–10 nm) generated either electrochemically or by thermolysis of palladium acetate (Scheme 2). The stabilizing shell was made of propylene carbonate. Chlorobenzene, **2c**, was only moderately active. Later on, Reetz and co-workers reported more details on the in situ generation of nanoparticles (1.3–1.6 nm) by thermolysis of palladium acetate (or palladium chloride plus sodium acetate) mainly in the presence of tetraalkylammonium

Marcial Moreno-Mañas was born in Barcelona, Spain, in 1941. After postdoctoral studies with Prof. Alan R. Katritzky at the University of East Anglia (U.K.), he joined the National Research Council in Spain (CSIC) and finally the “Universitat Autònoma de Barcelona”, where he became full Professor in 1977. His interests embrace transition metals in organic chemistry, recovery and reuse of metal catalysts, fluorine chemistry, and nanoparticles.

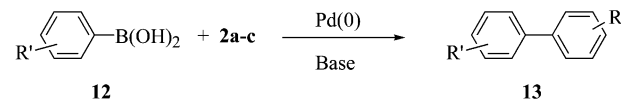
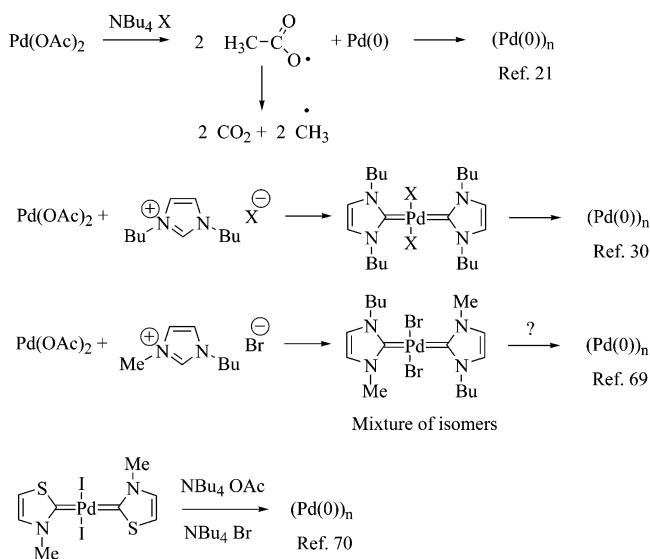
Roser Pleixats studied chemistry at the “Universitat Autònoma de Barcelona”, where she obtained her PhD in 1984. After postdoctoral research with Prof. R. J.P. Corriu and E. Colomer at the University of Montpellier II, she became Associate Professor at the “Universitat Autònoma de Barcelona” in 1991. Her research interests include palladium and other transition metal catalysts, metathesis reactions, nanoparticles, and catalyst recovery (fluorous biphasic systems, anchoring to organic and inorganic polymers).

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FIGURE 1. Mechanisms of nanoparticle stabilization.

Scheme 1. Mizoroki–Heck and Suzuki Reactions


Suzuki cross-couplings


Scheme 2. Generation of Palladium Nanoparticles in the Presence of Tetraalkylammonium or Imidazolium Salts and of *N*-Heterocyclic Carbenes


salts (Scheme 2).²¹ These materials permitted the M–H reaction of **1a** (R = Et) and **1b** with **2a,b**. In no case was the catalytic material recovered. It is worth commenting that these findings could explain the role of the tetraalkylammonium salts under the popular Jeffery conditions (Pd(OAc)₂, XNBU₄, base, in an aprotic polar solvent) to perform M–H reactions.²²

In 1996 Beller also reported other examples of M–H reactions of a broad selection of bromides **2b** (aryl

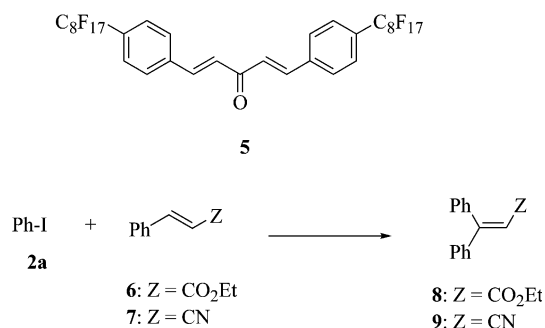
chlorides failed) with all alkenes **1** (R = Bu for **1a**) under catalysis by palladium nanoparticles generated by reduction of PdCl₂ with [(*n*-octyl)₄N] (BEt₃H).²³ The protecting quaternary ammonium was already present in the reducing agent.

Since then the interest continues unabated and other groups have reported the use in the M–H reactions of Scheme 1 of palladium nanoparticles generated by (i) reduction of palladium(II),^{24–36} (ii) sonochemical decomposition of Pd₂(dba)₃,³⁷ and (iii) hydrogenation of the coordinating olefins of Pd₂(dba)₄.³⁸ In some cases remarkably high turnover numbers (TON) and/or turnover frequencies (TOF) have been reported,^{23,24,38} as well as repeated recycling of the catalytic material.^{26,28–30,33–36} Sometimes even inert aryl chlorides can perform in the M–H reaction.^{32,35}

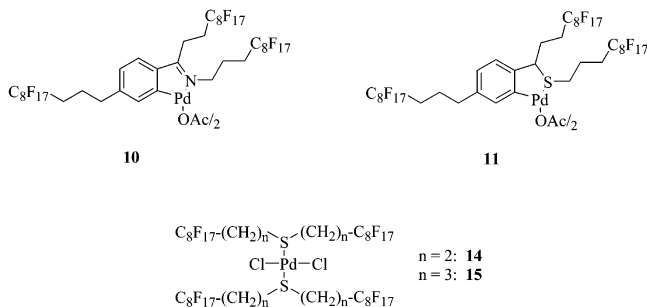
Srinivasan and co-workers proved the formation of nanoparticles when using palladium acetate in liquid 1,3-dibutylimidazolium salts.³⁰ Those authors suggested that in situ reaction of palladium acetate with the ionic solvent produces a *N*-heterocyclic palladium–carbene complex that is at the origin of the nanoparticles (Scheme 2). Xiao and co-workers identified the in situ formation of the *N*-heterocyclic palladium–carbene complex in the M–H reaction using palladium acetate as palladium source in the ionic solvent 1-butyl-3-methylimidazolium bromide (Scheme 2).⁶⁹ They did not prove the formation of nanoparticles but insinuate that nanoparticulate material could be the catalytically active species. Moreover, when this Account was in the refereeing process, Caló and co-workers reported the formation of nanoparticles in a stereospecific M–H reaction that affords trisubstituted alkenes using a *N*-heterocyclic carbene complex as palladium source in ionic liquids (Scheme 2).⁷⁰ These reports by Srinivasan and Caló open the question of whether nanoparticles are the real catalytic material when working in ionic solvents,⁷¹ and when using *N*-heterocyclic carbenes as palladium sources.

Attempts to combine the advantages of palladium nanoparticles with their recovery in biphasic organic-fluorous solvent systems have been reported. Thus, Crooks and co-workers have entrapped palladium nanoparticles, formed by reduction of Pd(II) with sodium borohydride, within the branches of modified poly(propyleneimine) (PPI) dendrimers of fourth and fifth generations. The PPI dendrimers possess 32 and 64 amino groups in the periphery that were modified by amide formation with a perfluoroacid CF₃-(OCF₂CF(CF₃))_{*m*}-(OCF₂)_{*n*}-COOH. The catalytic material, modified dendrimer plus entrapped nanoparticles, can be recovered after M–H reaction by extraction with the fluorous part of a heptane-fluorous solvent.^{39,40} Another variant consists of the use of palladium nanoparticles encapsulated in a fluorous dendrimer in supercritical CO₂.⁴¹ Curiously the M–H reaction of methyl acrylate, **1a** (R = CH₃), and iodobenzene **2a** (R = H) in supercritical CO₂ affords the branched ester **4**.⁴¹ HO-terminated poly(amidoamine) (PAMAM) dendrimers are also efficient as entrapping agents for palladium nanoparticles very active in the M–H reaction.⁴²

Scheme 3. Stabilizer Used and Reactions Performed in Ref 43



Scheme 4. Precursors of Nanoparticles in Refs 44, 45, and 53



Our group reported the stabilization of palladium nanoparticles by the heavily fluorinated ketone **5** (Scheme 3). These unusually stabilized nanoparticles catalyzed the formation of ethyl cinnamate, **3a** (R = H), from iodobenzene, as well as ester **8** and nitrile **9** (Scheme 3). Efficient recovery and reuse without loss of activity was achieved by extraction of the catalytic material with fluoruous solvents.⁴³

Finally, Gladysz and co-workers have used palladium(II) complexes of fluoruous palladacycles **10**⁴⁴ and **11**⁴⁵ as catalyst precursor in M–H reactions (Scheme 4). They gave evidence favoring nonfluorous nanoparticles as the actual catalytic species. Palladacycle **10** acts as steady-state source of very reactive, DMF-soluble nanoparticles, probably stabilized by ammonium ions during the M–H reaction. TON's are as high as 1.51 million, making this catalytic system exceptional.

The Suzuki Cross-Coupling. The Suzuki cross-coupling between arylboronic acids **12** and aryl halides produces biphenyls **13** (Scheme 1).⁴⁶ Possibly the first report on the use of palladium nanoparticles in Suzuki coupling is due to Reetz and co-workers.^{19,21} This pioneering work¹⁹ described simple biphenyl formation from aryl bromides and even from activated aryl chlorides possessing electron-attracting groups.

Some groups already mentioned in connection with the M–H reaction tested their catalytic materials also in Suzuki couplings.^{27,32,35} More examples of palladium nanoparticles as catalysts in the Suzuki cross-coupling have been described.^{47–52} El-Sayed et al. concluded that vertex and edge atoms on the palladium particle surfaces are the active sites.⁴⁹ The most salient features of these contributions are some examples of recycling of the catalytic material^{35,51} and the activation of aryl chlorides.^{19,32,35} We have reported that palladium particles stabilized by fluo-

rous ketone **5** are also active in the Suzuki-type coupling of arylboronic acids with cinnamyl bromide (sp²–sp³ coupling).⁴³

Gladysz et al. reported Suzuki couplings in the presence of fluoruous sulfide complexes **14** and **15** (Scheme 4).^{45,53} As for the case of M–H reactions (vide supra), they concluded that the complexes were precursors of nanoparticles stabilized by nonfluorous shells.

Miscellaneous Reactions Catalyzed by Palladium Nanoparticles. Some examples of Stille-type^{27,32,35} and Sonogashira couplings^{30,35} have been reported (Scheme 5). Curiously, these Sonogashira couplings do not require copper(I) species in the catalytic system, as it happens with more conventional palladium catalysts.

Hydrocarbonylation of olefins,⁵⁴ aromatic couplings,⁵⁵ and hydrodechlorination of tetrachloromethane⁵⁶ are reactions involving C–C bond formation that have been catalyzed by palladium nanoparticles (Scheme 5).

For two cases of Tsuji–Trost allylation of carbon nucleophiles with palladium nanoparticle catalysis, see the discussion in the following cobalt paragraph.^{61,62}

Cobalt-Catalyzed Reactions

The Pauson–Khand (P–K) reaction permits preparation of cyclopentenones by condensation of alkenes, alkynes, and carbon monoxide (see Scheme 6 for the intramolecular version). The classical P–K reaction uses stoichiometric amount of Co₂(CO)₈ as source of carbon monoxide, but attempts to use catalytic metal in an atmosphere of carbon monoxide have been reported.⁵⁷ Colloidal cobalt (reduction of Co(II) or thermal decomposition of Co₂(CO)₈) has been applied successfully as catalyst in the reactions of Scheme 6,^{58–62} and in some cases recovery has been possible.^{58–61} Catalytic material containing both cobalt and palladium nanoparticles catalyze sequentially Pauson–Khand and Tsuji–Trost allylation of nucleophile (Scheme 6).^{61,62}

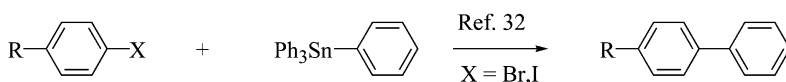
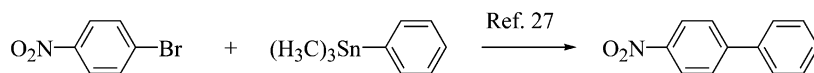
Reactions Catalyzed by Other Metal Nanoparticles

Nanoparticles made from several transition metals catalyze biphenyl formation by Suzuki cross-coupling of **2a**, **b** with **12**. The particles were prepared by reduction of pure or mixed metal chlorides with tetraoctylammonium formate. The following combinations gave interesting results: Cu, Pd, Ru, Cu/Pd, Pd/Pt, Pd/Ru, Cu/Pd/Pt, Cu/Pd/Ru, Pd/Pt/Ru, and Cu/Pd/Pt/Ru.⁶³ This paper particularly is noteworthy since it is a step forward in finding alternatives to palladium catalysts.

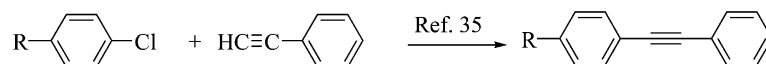
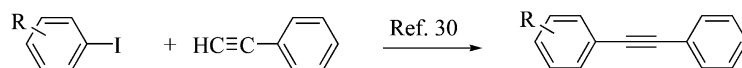
Some other cases pertinent to this Account have been described: acetylene polymerization under copper nanoparticle catalysis,⁶⁴ ring-opening metathesis polymerization under catalysis by a ruthenium complex supported on gold colloids,⁶⁵ McMurry-type couplings induced by nanostructured titanium clusters,⁶⁶ [3+2] cycloaddition reactions under nickel clusters catalysis,⁶⁷ and carbonylation of methanol catalyzed by rhodium colloids.⁶⁸

Scheme 5. Other Reactions Catalyzed by Palladium Nanoparticles

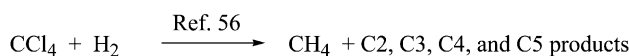
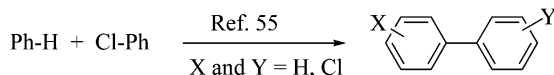
Stille-type cross-couplings



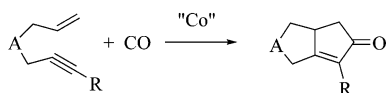
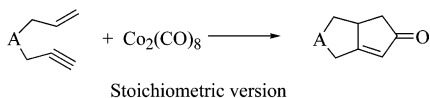
Sonogashira couplings



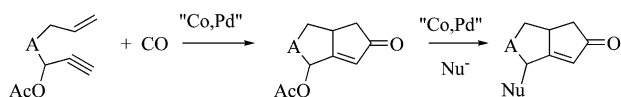
Other reactions



Scheme 6. The Pauson–Khand Reaction

A = (ROCO)₂C, CH₂, O

Catalytic version



Ref. 61 and 62

expected soon. Some difficulties have to be solved before the use of nanoparticles in C–C and C-heteroatom bonds will be generalized. In our opinion, reproducibility in the properties of nanoparticles (size, dispersity, and performance), and recovery and reuse without loss of activity are of paramount importance. Therefore, efforts to deal with more reactions and to use more metals will be significant, but efforts to solve those important issues of reproducibility and recovery will be particularly welcome.

It might be that the use of ionic solvents could help to solve the problem of reutilization of the catalytic material. Studies related to the Mizoroki–Heck reaction have opened the question of whether nanoparticles are the actual catalytic material in ionic solvents, as well as when using *N*-heterocyclic carbenes as palladium sources.^{30,69,70}

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Conclusions

The papers collected below dealing directly with original research on the topic of this account were published in 1996 (4), 1997 (3), 1998 (3), 1999 (4), 2000 (9), 2001 (8), 2002 (15), and 2003 (3 until January). An increase is

Note Added after ASAP Posting

This paper first appeared on the Web with an error in Scheme 1. The correct version was published 7/9/2003.

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