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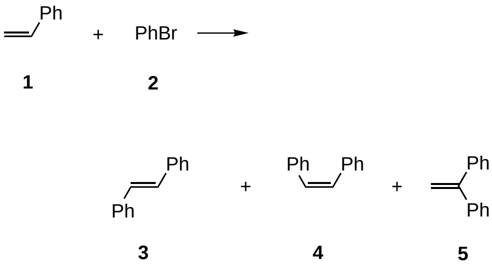
Phosphane-Free Palladium-Catalyzed Coupling Reactions: The Decisive Role of Pd Nanoparticles**

Manfred T. Reetz* and Elke Westermann

The number of examples of Pd-catalyzed C–C bond forming reactions continues to rise, for example, in the area of Heck, Suzuki, and Stille coupling reactions.[1] One of the most common catalysts is $[Pd(PPh_3)_4]$, but precatalysts such as PdX_2 in the presence of excess PPh_3, which reduces Pd^{II} to Pd^0, are also used. In addition to new types of catalysts or precatalysts such as Pd–carbene complexes[2] or phosphapalladacycles,[3] simple Pd salts such as $PdCl_2$ or $Pd(OAc)_2$ in the *absence* of stabilizing phosphane ligands are increasingly being used in Heck and Suzuki reactions.[1] Preparatively significant examples are the Jeffery system[4] in which $Pd(OAc)_2$ in the presence of an excess of a phase-transfer catalyst such as $n\mathrm{Bu_4N^+Cl^-}$ is used, or $Pd(OAc)_2$ in an aqueous medium.[5] In both cases aryl iodides are usually employed as the arylating agent. In the case of the industrially more interesting aryl bromides, $Pd(OAc)_2$ (or $PdCl_2$) with or without *N,N*-dimethylglycine (DMG) as an additive is currently one of the cheapest and most active catalysts.[6] How can such simple phosphane-free catalyst systems be understood, given that it is generally assumed that phosphanes exert a stabilizing and activating effect?[1] We report here a mechanistic study[7] supported by transmission electron microscopy (TEM) which points to the involvement of intermediary Pd nanoparticles as colloids in such systems.

First the Heck reaction of styrene (**1**; 12 mmol) with bromobenzene (**2**; 10 mmol) at 130 °C in *N*-methylpyrrolidinone (NMP; 10 mL) was studied. Our previously reported catalyst system with $[PdCl_2(C_6H_5CN)_2]$ (1.5 mol%)/DMG as the precatalyst and sodium acetate (20 mmol) as the base was used.[6] As expected, essentially complete conversion with formation of the Heck products **3**–**5** in a ratio of 96:1:3 was observed over 6 h [Eq. (1)].



(1)

The course of the reaction was monitored by periodically taking samples and analyzing them by gas chromatography. Parallel to these analyses, the samples were studied by TEM.

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The reaction begins after an induction period of about one hour (Figure 1).[8] We found that only samples that were taken after the induction period contained Pd colloids. They have an average particle size of 1.6 nm (Figure 2). The fact that not all samples contain Pd nanoparticles rules out the unlikely possibility of colloid formation following sample withdrawal. Since the samples were directly deposited on carbon film coated TEM grids by dip-coating without workup, the process can be viewed as "in situ" TEM analysis. We assume that $[PdCl_2(C_6H_5CN)_2]$ undergoes rapid ligand exchange with NaOAc to form $Pd(OAc)_2$, which undergoes thermolytic decomposition at 130 °C with formation of Pd^0 in the form of a colloid.[9] This is corroborated by our recent observation that thermolysis of $Pd(OAc)_2$ at 100 °C (3 h) in the likewise polar solvent propylene carbonate (PC) quantitatively affords PC-stabilized Pd colloidal particles 8–10 nm in size.[10] Such relatively large preformed thermostable colloids are capable of catalyzing Heck reactions.[10]

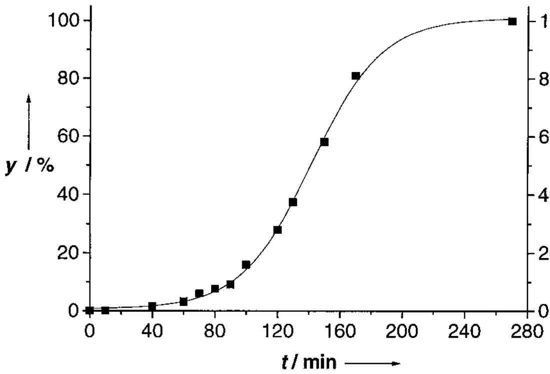


Figure 1. Plot of yield *y* versus time for the Heck reaction of styrene (**1**) with bromobenzene (**2**) at 130 °C in NMP; catalyst: $[PdCl_2(C_6H_5CN)_2]$ (1.5 mol %)/DMG.

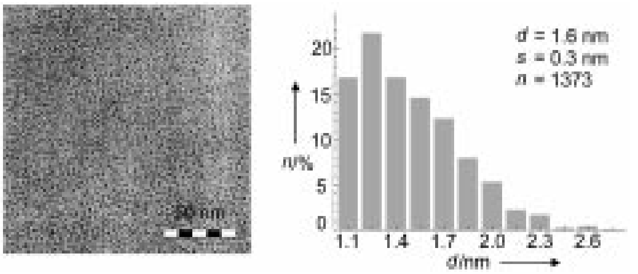
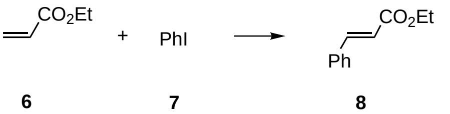


Figure 2. TEM image (left) of a typical sample of a Pd colloid formed in the reaction of **1** with **2** in the presence of $[PdCl_2(C_6H_5CN)_2]$/DMG as precatalyst. The size distribution of the nanoparticles (right) appears unsymmetrical because the TEM instrument does not detect particles smaller than 1 nm; *d* = average diameter; *s* = standard deviation; *n* = number of particles.

A similar TEM study was carried out with ethyl acrylate (**6**; 10 mmol) and iodobenzene (**7**; 5 mmol) under Jeffery conditions[4] (12.5 mmol NaOAc; 5 mmol $n\mathrm{Bu_4N^+Br^-}$; 0.25 mmol $Pd(OAc)_2$; 5 mL dimethylacetamide (DMA); 50 °C/1 h; >95 % conversion) [Eq. (2)]. The reaction starts immediately without an induction period and proceeds continuously (Figure 3).



6 **7** **8** (2)

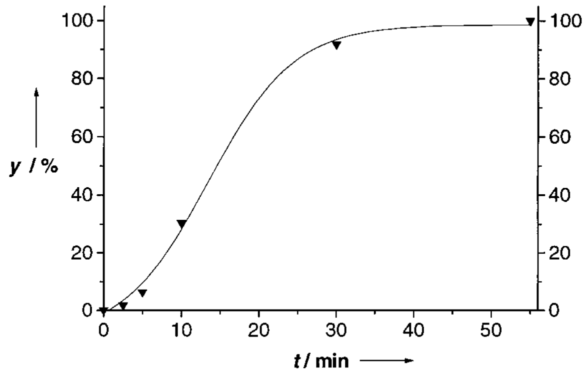
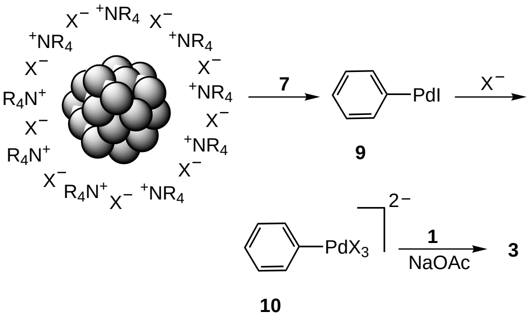


Figure 3. Plot of yield *y* versus time for the Heck reaction of ethyl acrylate (**6**) with iodobenzene (**7**) under Jeffery conditions at 50 °C in DMA; catalyst: $Pd(OAc)_2$ (5 mol %)/$n\mathrm{Bu_4N^+Br^-}$.

The TEM images of the samples that were used for GC product analysis all showed the presence of Pd colloids with an average particle size of 1.6 nm. It has long been known that chemical or electrochemical reduction of transition metal salts in the presence of ammonium salts leads to $R_4N^+X^-$-stabilized colloids.[11] Recently, we achieved the size-selective preparation of $R_4N^+(RCO_2^-)$-stabilized Pd colloids simply by heating Pd salts such as $Pd(NO_3)_2$ or $PdCl_2$ in the presence of tetraalkylammonium carboxylates $R_4N^+(RCO_2^-)$ at 60 °C without any additional reducing agents. In this redox-controlled process, the carboxylate anions RCO_2^- induce electron transfer to Pd^{II} with formation of Pd^0 as a colloid, and methane, ethane, and CO_2 as inert side products.[12] Hence, it is likely that under Jeffery conditions, $R_4N^+X^-$-stabilized Pd colloids are formed and then function as in situ catalysts. Indeed, in previous studies it was demonstrated that preformed $R_4N^+X^-$-stabilized Pd colloids are catalytically active.[13] Differences in catalytic activity of in situ generated Pd colloids and preformed analogues may be due to different cluster sizes, impurities, or aging processes in the case of the preformed colloids, a hypothesis that needs to be examined in greater detail. For example, the Heck reaction of unactivated aryl bromides with catalysis by preformed $R_4N^+X^-$-stabilized Pd colloids gives low yields,[13b] whereas the coupling of **2** with **6** under Jeffery conditions proceeds smoothly (**2** (1 mmol); **6** (2 mmol); NEt_3 (2.5 mmol); $n\mathrm{Bu_4N^+Cl^-}$ (1 mmol); NMP/molecular sieve 4 Å; 130 °C/15 h: 100 % conversion (81 % yield of **8**) or 86 % conversion (70 % yield of **8**) with NaOAc as base).

Although the appearance of Pd colloids in the present cases occurs simultaneously with the initiation of the Heck reaction, this cannot be viewed as definitive proof for the actual participation of nanoparticles in the catalytic cycle. To shed light on this question, the reaction of a preformed Pd colloid with the stoichiometric amount of iodobenzene (**7**) was studied in the absence of an olefin.

If the hypothetical role of Pd colloids in the catalytic cycle were correct, then oxidative insertion of Pd into the C–I bond with formation of phenylpalladium species **9** (or **10**) and concomitant dissolution of the Pd colloid would be expected (Scheme 1). An $n\mathrm{Oct_4N^+(HCO_2^-)}$-stabilized Pd colloid[12]

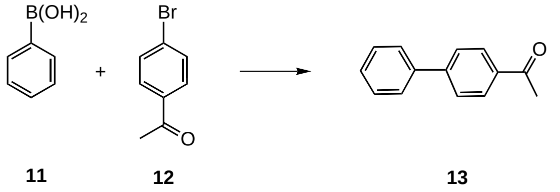


Scheme 1.

(average particle size 2.2 nm) was allowed to react with the calculated amount of iodobenzene (**7**) at room temperature (25 h) in NMP/THF (1/1) and at 70 °C for 2.5 h with stirring. The black color typical of Pd colloids changed to dark red. The reaction was monitored by UV/Vis spectroscopy, which revealed the continuous decrease of the broad plasmon band in the range 400–650 nm typical of transition metal colloids,[14] as well as the gradual appearance of a new band at 450 nm. The ^{13}C NMR spectrum at the end of the reaction shows a set of signals in the aromatic region at $\delta = 127.5, 127.8, 129.2$ and 141.1,[15] which is clearly different from the signals of iodobenzene ($\delta = 94.7, 128.1, 130.9, 139.1$). The signal at $\delta = 141.1$ appears in a range which is typical for Pd-bound C atoms of arylpalladium compounds.[16] Differentiating between **9** and the more likely anionic species of type **10** (which are known to occur as phosphane adducts)[1, 17] is not trivial. Dimeric structures are also possible.[18] Decisive is the proof of the participation of the species in the actual Heck reaction. Upon adding styrene **1** and NaOAc to the red solution at 70 °C, the Heck product **3** was indeed formed (Scheme 1). In the case of the analogous stoichiometric reaction of the preformed Pd colloid with chlorobenzene under the same conditions no reaction took place, that is, no dissolution of the Pd colloid occurred, as shown by UV/Vis and TEM studies.

Finally, the reaction of styrene (**1**) with bromobenzene (**2**) was investigated with two other catalyst systems. According to TEM analyses, the conventional reaction with $Pd(OAc)_2$/$4PPh_3$ as catalyst[1] (2 mol %) in NMP as solvent at 130 °C did not lead at any time to Pd colloid formation. The same applies to the reaction with the phosphapalladacycle *trans*-di(μ-aceto)-bis[*o*-(di-*o*-tolylphosphanyl)benzyl]dipalladium as the precatalyst.[3]

The use of simple Pd salts as precatalysts in the Suzuki coupling is also increasing.[1, 5c, 19] We therefore studied the $Pd(OAc)_2$-catalyzed reaction of phenylboronic acid (**11**) with *p*-bromoacetophenone (**12**), which afforded the coupling product **13** in 93 % yield (1 mol % $Pd(OAc)_2$; 2.5 equiv $NaHCO_3$; DMF; 10 h/130 °C) [Eq. (3)]. The TEM images showed the presence of Pd nanoparticles, which in this case were a little smaller (1.3 nm) than those in the Heck reactions. Control experiments showed previously that preformed Pd colloids catalyze the Suzuki reaction.[13a]



(3)

Our studies point to the involvement of in situ generated nanosized Pd colloids in three preparatively significant phosphane-free catalyst systems based on simple Pd salts, namely, $Pd(OAc)_2$/DMG, $Pd(OAc)_2/(nBu)_4N^+Cl^-$ and $Pd(OAc)_2$. It is therefore likely that other phosphane-free Heck reactions and related C–C bond-forming processes in the presence of Pd salts without special ligands are also catalyzed by nanosized Pd colloids. Indeed, this suspicion was previously voiced in the case of $Pd(OAc)_2$-catalyzed Ullmann reactions.[20]

Although the systems described here involve colloidal solutions of Pd nanoparticles, processes of this kind do not belong to the traditional area of homogeneous catalysis.[21] Rather, catalysis is likely to occur at defect sites, steps, and kinks on the surface of the colloidal metal particles,[13a, 14] a process that is more closely related to heterogeneous catalysis.[22, 23]

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The Tetrakis(carbonyl)dioxoosmium(VI) Cation: *trans*-$[OsO_2(CO)_4]^{2+}$[**]

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Superacidic reaction media,[1, 2] in particular the Lewis superacid SbF_5 and the conjugate Brønsted Lewis superacid HF/SbF_5, have allowed in recent years the generation of a substantial number of previously unknown homoleptic metal carbonyl cations,[3] for example the octahedral cations $[M(CO)_6]^{2+}$ (M = Fe,[4] Ru, Os[5]). Thermally stable salts are generally obtained with the superacid anion $[Sb_2F_{11}]^-$.[6] Observations made during the synthesis of $[Os(CO)_6][Sb_2F_{11}]_2$ by reductive carbonylation of either $Os(SO_3F)_3$,[5] OsF_6,[7] or OsO_4[8] provide the motivation for this study: In the IR spectra of the products an additional band of varied intensity is observed at 2253 cm^{-1} in addition to the intense CO stretching band (F_{1u}) of $[Os(CO)_6]^{2+}$ at 2190 cm^{-1}. Since the highest intensities of the band at 2253 cm^{-1} are found in samples prepared from OsO_4,[8] we have modified the reaction conditions and intend to show that the high wavenumber band can be attributed to the new cation *trans*-$[OsO_2(CO)_4]^{2+}$.

When the reaction temperature is reduced from 60–90 °C[5] to room temperature and available CO is limited to a modest excess (about 1.4-fold), a yellow product is formed after 10 days. This product is free of $[Os(CO)_6][Sb_2F_{11}]_2$ according to the vibrational spectrum. The only volatile product, CO_2, is formed in a molar ratio of approximately 1:1 (based on OsO_4), as estimated from the intensity of $\nu_{as}(CO_2)$ in the gas-phase IR spectrum.

The new compound, tentatively identified as $[OsO_2(CO)_4]$-$[Sb_2F_{11}]_2$, is extremely sensitive to moisture and turns black in air within seconds. Upon heating in a sealed tube above 80 °C, decomposition to an inhomogeneous violet material and the release of CO are noted. All attempts to obtain single crystals of $[OsO_2(CO)_4][Sb_2F_{11}]_2$ and affect a separation from any

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