Propylene carbonate stabilized nanostructured palladium clusters as catalysts in Heck reactions

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Nanostructured Pd clusters, prepared either electrochemically using a sacrificial Pd anode or by thermolysis of $Pd(O_2CMe)_2$, are stable in propylene carbonate even at 140–155 °C; such colloidal solutions catalyse Heck reactions in the absence of phosphine ligands.

The chemical reduction of transition-metal salts such as PdX_2 is known to afford insoluble metal powders or mirrors, unless stabilizers such as special ligands, polymers or surfactants are present which prevent undesired agglomeration of the initially formed nanostructured metal clusters.[1] Similar effects have been reported in the case of metal cluster formation by metal vaporization.[2,3] In some cases polar solvents such as dimethylformamide (DMF),[2,3] propylene carbonate (PC)[4] or acetone[2] are also capable of stabilizing nanostructured metal clusters, their stability depending upon the nature of the metal, temperature and concentration. Irrespective of the mode of formation, solutions of such metal colloids have been shown to catalyse hydrogenation reactions.[1–4] However, no report of the use of metal colloids in solution as catalysts in C–C bond forming reactions has appeared. Here we describe two new methods for the preparation of PC-stabilized Pd clusters, and also report that they catalyse Heck reactions.[5]

Rather than employing metal vaporization of Pd metal or chemical reduction of Pd salts,[1–4] we devised an electrochemical process which transforms palladium bulk into Pd clusters. Accordingly, a Pd sacrificial anode was used as the metal source in a simple electrolysis cell,[6] NaCl in PC serving as the electrolyte containing 5% ethanol. Electrolysis at 60 °C afforded a black solution of Pd clusters. Undesired Pd powder formation was not observed. The electrochemical process involves anodic dissolution of the Pd sheet with intermediate formation of Pd^{II} ions which migrate to the cathode where they are reduced back to the zero-valent state. The adatoms at the cathode form clusters which are stabilized by PC (Scheme 1), thereby preventing metal powder formation.[7]

After cooling the solution to 0 °C, the NaCl precipitate was removed by filtration. Analysis by transmission electron microscopy (TEM) showed the presence of 8–10 nm sized Pd clusters, the particles being remarkably uniform in size (Fig. 1). At higher magnification the diffraction planes are visible, demonstrating the crystalline character of the particles (Fig. 1, inset).

An alternative preparation involves thermal decomposition of $Pd(O_2CMe)_2$ in PC at 100 °C (3 h). Sonication speeds up the quantitative cluster formation (< 1 h). In both cases the black colloidal solutions contain 8–10 nm sized Pd clusters, similar to those obtained electrochemically. The black Pd cluster solutions, irrespective of the mode of formation, are surprisingly stable. For example, 0.2 mol dm^{-3} solutions can be heated to 140–155 °C for several days without showing any sign of Pd powder formation! However, if the solvent is stripped off *in vacuo*, large amounts of palladium powder are formed which cannot be redispersed in PC. Thus, in any type of application, the originally formed PC solutions need to be used. For example, complete immobilization of these preformed clusters is possible simply by stirring the solutions in the presence of a solid support such as Al_2O_3.

Anode: $Pd_{bulk} \longrightarrow Pd^{2+} + 2\,e^-$

Cathode: $Pd^{2+} + 2\,e^- + \text{solvent} \longrightarrow \text{Pd cluster/solvent}$

Sum: $Pd_{bulk} + \text{solvent} \longrightarrow \text{Pd cluster/solvent}$

Scheme 1 Electrochemical fabrication of propylene carbonate stabilized Pd clusters

In order to test whether the colloidal solutions of these Pd clusters exhibit catalytic activity in C–C bond forming processes, the Heck reaction of halogenoaromatics **1** with styrene **2** was studied.† Table 1 shows that such reactions are, indeed, possible, especially in the case of activated bromobenzenes **1c**,**d**. Bromo- and chloro-benzene themselves show only poor to moderate conversion. In classical Heck reactions using Pd/PPh_3 catalysis, the rate and yield decrease in the series **1d** > **1c** > **1b** ≫ **1a**.[5] Indeed, chlorobenzene and other non-activated chloroaromatics still represent a synthetic challenge in a practical sense, in spite of several new approaches.[5,8] It is remarkable that the PC-stabilized Pd clusters catalyse the Heck reaction of chlorobenzene with styrene to an appreciable extent (30%). Nevertheless, further improvements are necessary for practical applications. This also applies to heterogeneous catalysis using Pd particles immobilized on solid supports. For

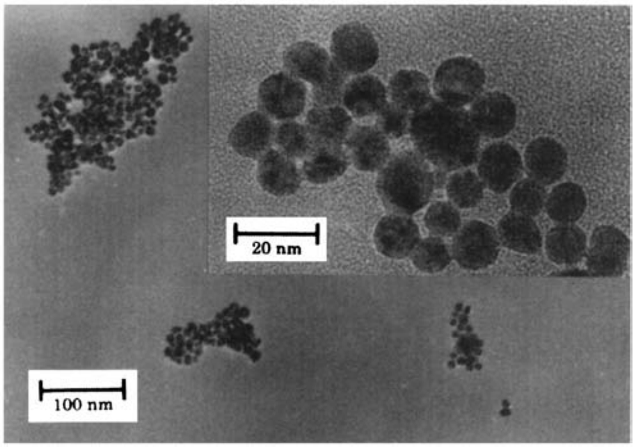

Fig. 1

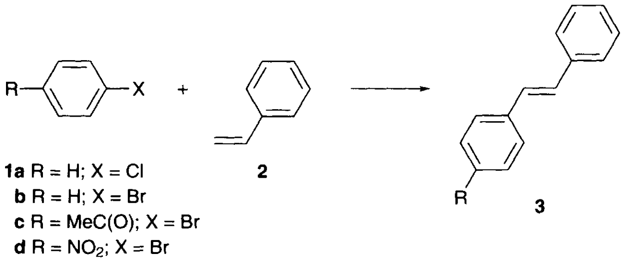

Table 1 Heck reactions of **1** with **2** catalysed by PC-stabilized Pd clusters[a]

Aryl halide	Base[b]	T/°C	t/h	Conv. (yield)[c]/%	E:Z
1a	NaO_2CMe	160	17	10 (40)	99:1
1a	Na_2CO_3	160	17	27 (54)	94:6
1a	Na_2CO_3	155	65	55 (58)	97:3
1b	Na_2CO_3	147	15	8 (89)	96:4
1c	NEt_3	130	21	70 (79)	97:3
1c	NaO_2CMe	130	21	19 (97)	96:4
1d	NEt_3	130	5	100 (96)	93:7
1d	NaO_2CMe	130	21	22 (97)	90:10

[a] 3.5 mol% Pd. [b] 2 equiv. with respect to **1**. [c] Determined by gas chromatography.

example, Pd on Al_2O_3 (Condea Pural 200), prepared by immobilizing the PC-stabilized clusters on this support, is a poor catalyst for the reaction of **1a** with **2** (3.5 mol % Pd at 155 °C for 17 h in PC: 1% stilbene obtained).

In summary, nanostructured palladium clusters stabilized by propylene carbonate (PC) are readily accessible from bulk Pd by an electrochemical method or simply by heating $Pd(O_2CMe)_2$ in this solvent. Colloidal solutions of such Pd clusters are principally capable of catalysing Heck reactions. Since catalysis is likely to occur on the surface of the clusters, these processes are probably more related to heterogeneous than to homogeneous catalysis.[9]

Footnote

† *Typical procedure*: The mixture of an aryl halide **1** (1.08 mmol), styrene **2** (1.35 mmol), a base (2.16 equiv.) in 1 ml of dry propylene carbonate containing the Pd clusters (3.5 mol% Pd) was added with stirring under argon (temperature and reaction time as in Table 1). The mixture was diluted with diethyl ether (2 ml) and filtered over Celite® and the filtrate was analysed by GC. The yields of coupling products **3** are given in Table 1. Side products are benzene (or the corresponding arene produced by reduction) and diphenyl (or the corresponding diaryl compounds). Use of 1 mol% affords similar results.

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