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Exploring palladium nanoparticles protected with alkanethiolates functionalized with organometallic units as potential catalysts for sequential reactions

Mario Friederici, Inmaculada Angurell*, Oriol Rossell*, Miquel Seco, Guillermo Muller

Departament de Química Inorgànica, Universitat de Barcelona, Martí i Franquès, 1-11, 08028 Barcelona, Spain

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ABSTRACT

Palladium nanoparticles peripherally functionalized with “$RuCl_2$(*p*-cymene)” (NP2), “RhCl(cod)” (NP3) and “PdCl(η^3-2-MeC_3H_4)” (NP4) units show catalytic activity in C—C coupling reactions, hydrogenation and hydrovinylation processes. We report for the first time an example of a catalytic precursor for the hydrovinylation/C—C coupling sequential process by using the two catalytic centres displayed by NP4, the Pd core and the PdCl(η^3-2-MeC_3H_4) moieties.

1. Introduction

Over the last decade, a huge number of reports have appeared on the use of transition metal nanoparticles in catalysis because of their size, high ratio of surface area to volume [1] and ease of preparation [2]. It is well-known that the NPs are prone to formation of bulk metals and require the use of protecting ligands or linkers to prevent aggregation and precipitation. However, in many cases, the role of the linkers is not only restricted as protecting agents, but also they can play other relevant functions. For example, voluminous dendrons may act as selective gates to control access of small molecules to the metal core, that is, they can act as nanofilters [3]. On the other hand, the attachment of chiral ligands onto the surface of the core may induce enantiomeric activity [4–6]. The enantio control depends on how the ligands are able to transmit their influence to substrate molecules coordinated to the particle in their vicinity [7]. In this context, it is reasonable to assume that the synthesis of peripherally functionalized NPs with organometallic fragments would enhance their catalytic efficiency and applicability. For testing this hypothesis we have centred our studies on a set of palladium nanoparticles (Pd NPs) peripherally functionalized with diverse metal fragments recently reported by our group [8]. Our interest was to evaluate the possibility of using such kind of NPs as catalysts in multistep processes and, in turn, to detect potential synergetic effects between the Pd core and the organometallic units. To date, the number of examples of sequential reactions catalyzed by metal nanoparticles is scarce. Fan and co-workers [9] described a tandem reaction based on a Suzuki coupling, followed by a hydrogenation reaction and Gómez applied Pd NPs in sequential reactions involving C—C coupling and hydrogenation steps using ionic liquid phase [10]. Here we report for the first time an example of a two-step process in that two different metal catalytic centres of a same nanoparticle are involved at once. The sequential process consists of the hydrovinylation of 4-bromostyrene followed by a C—C coupling Suzuki reaction with phenylboronic acid. Although the yield obtained in the synthesis of the final compound is rather modest, the success of the process opens an area scarcely explored with metal nanoparticles, but with undeniable potential.

2. Experimental

2.1. Materials and methods

Phenylboronic acid and 1,3-cyclohexadiene were sourced from Fluka and 4-bromoanisole, $AgPF_6$, styrene and 4-bromostyrene (98%) from Aldrich. Palladium nanoparticles NP0, NP1, NP2, NP3 and NP4 were synthesized as reported in the literature [8]. Nanoparticles metal content (% in mass): NP0, 77.5% Pd; NP1, 55.5%

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* Corresponding author. Tel.: +34 934037057 (I.A.); +34 934039136 (O.R.).
E-mail addresses: inmaculada.angurell@qi.ub.es (I. Angurell), oriol.rossell@qi.ub.es (O. Rossell).

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Pd; NP2, 57.0% Pd and 3.4% Ru(II); NP3, 66.2% Pd and 2.9% Rh(I); NP4, 43.5% Pd(0) and 5.2% Pd(II).

All solvents were distilled from appropriate drying agents. Deionised water was obtained from Millipore Elix 3 purification system. All manipulations were performed under purified nitrogen using standard Schlenk techniques.

Hydrogenation reactions were carried out in a Fisher–Porter reactor.

Hydrovinylation reactions were performed in a stainless steel autoclave fitted with an external jacket connected to an isobutyl alcohol bath, and the temperature was controlled using a thermostat to ±0.5 °C. The internal temperature was monitored using a thermopar coupled to a digital recorder.

The routine GC analyses were performed on an Agilent Technologies 6890 N. Gas chromatography analysis coupled with mass spectrometry were performed on an Agilent Technologies 7820 coupled with a mass detector 5975, both instruments loading a 30 m HP5 capillary column.

2.2. *Typical procedure for Suzuki cross coupling reaction*

In a 100 mL Schlenk flask, 3.7 mg of NP0, or 5.2 mg of NP1, or 5.0 mg of NP2, or 6.6 mg of NP3, or 4.3 mg of NP4 (2.7×10^{-5} mol Pd) were dissolved in 24 mL of a solution of THF/H_2O (2:1) and 4-bromoanisole (1 mmol), phenylboronic acid (2 mmol) and NaOH (3 mmol) were added. The mixture was allowed to stir under N_2 at room temperature for the required time. To determine the composition of the mixture of catalysis, an aliquot was taken and CH_2Cl_2 and H_2O were added in equal volumes. The mixture was stirred and the organic phase was extracted and dried over anhydrous $MgSO_4$. The quantitative distribution of the fractions of the coupling products was determined by gas chromatography analysis.

2.3. *Typical procedure for hydrogenation of 1,3-cyclohexadiene*

In a 50 mL Schlenk flask, 5.0 mg of NP0 (3.6×10^{-5} mol Pd), or 5.0 mg of NP1 (2.6×10^{-5} mol Pd), or 5.0 mg of NP3 (3.1×10^{-5} mol Pd, 1.4×10^{-6} mol Rh(I)) were dissolved in 10 mL of CH_2Cl_2 and 0.027 mL (0.283 mmol) of 1,3-cyclohexadiene were added. The mixture was placed in a reactor and charged with H_2 to a pressure of 3 bar at room temperature under stirring. After the desired time the reactor was depressurized and the solution was filtered through a small SiO_2 column. The conversion was determined by gas chromatography using ethylbenzene as internal standard.

2.4. *Typical procedure for styrene hydrovinylation*

In a Schlenk, a mixture of 0.055 g of NP4 (2.7×10^{-5} mol Pd(II)) or 0.011 g of NP4 (5.4×10^{-6} mol Pd(II)), $AgPF_6$ (2.7×10^{-5} or 5.4×10^{-6} mol) and styrene or 4-bromostyrene (5.4×10^{-3} mol) in 10 mL of freshly distilled CH_2Cl_2 was kept stirring for 15 min in the dark under N_2. After filtering the AgCl formed, the solution was placed in an autoclave thermostatically controlled (25 °C). The autoclave was then pressurized with ethylene to a pressure of 15 bar. After the desired time, the autoclave was depressurized slowly and 10 mL of 10% HCl was added. The mixture was kept stirring for 10 min to quench the catalyst. The CH_2Cl_2 layer was decanted and dried with anhydrous $MgSO_4$. The quantitative distribution of the fractions of the products was determined by gas chromatography analysis using ethylbenzene as internal standard. TOF was calculated respect to the amount of Pd(II) in the nanoparticle surface.

2.5. *Typical procedure for the sequential reaction (4-bromostyrene hydrovinylation and Suzuki–Miyaura cross coupling)*

In a 100 mL Schlenk flask, a mixture of 0.028 g (1.37×10^{-5} mol Pd(II), 1.14×10^{-4} mol Pd(0)) or 0.056 g (2.74×10^{-5} mol Pd(II), 2.28×10^{-4} mol Pd(0)) of catalyst precursor NP4, $AgPF_6$ or NaBARF (BARF = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) (1.38×10^{-5} or 2.76×10^{-5} mol) and 4-bromostyrene (1.38×10^{-3} mol) in 20 mL of freshly distilled CH_2Cl_2 was maintained stirring for 15 min in the dark under N_2. After filtering off the NaCl or AgCl formed, the solution was placed in an autoclave thermostatically controlled (25 °C). The autoclave was then pressurized with ethylene to a pressure of 15 bar. After 6 h the autoclave was depressurized slowly. Then, the reaction mixture was placed in a 50 mL Schlenk flask, and CH_2Cl_2 was evaporated almost to dryness under vacuum. 20 mL of a 4:1, toluene/water mixture were added (or alternatively more CH_2Cl_2 and water to reach a ratio of 4 to 1 (CH_2Cl_2/H_2O)) and successively 2.06×10^{-3} or 2.76×10^{-3} mol of phenylboronic acid and 2.76×10^{-3} or 3.45×10^{-3} mol of K_2CO_3 were added. The mixture was kept to stir under reflux or placed in a reactor at 110 °C for 24 h. After the reaction mixture was processed, the quantitative distribution of the fractions of the products was determined by gas chromatography analysis coupled with mass spectrometry using ethylbenzene as internal standard.

3. Results and discussion

The Pd NPs used in this work are shown in Scheme 1. NP1 is formed by a Pd core protected with two different thiol ligands. The shorter one, hexanethiolate is introduced to provide solubility to the system in organic solvents and the larger is the alkanethiolate $HS(CH_2)_{11}OOCC_6H_4PPh_2$. The free phosphine ligand permits facile coordination to different metal units: "$RuCl_2$(*p*-cymene)" (NP2), "RhCl(cod)" (NP3) and "PdCl(η^3-2-MeC_3H_4)" (NP4). For comparative purposes we have carried out some catalytic tests using the Pd NPs containing uniquely 1-hexanethiol as protected ligands (NP0).

Our initial studies began by screening the catalytic behaviour of the metal core and that of the peripheral metal fragments of the NPs. In some cases, the simultaneous participation of both catalytic centres could be evidenced. The results given in Tables 1–4 were obtained as a mean of at least three runs.

3.1. *Suzuki–Miyaura C—C coupling reaction*

Palladium-catalyzed Suzuki–Miyaura cross couplings of aryl halides and arylboronic acids to give biaryl structures have found applications in fine chemical and pharmaceuticals synthesis [11]. Here, we analyzed the C—C coupling reaction between 4-bromoanisole and phenylboronic acid in a biphasic mixture of THF–water with NaOH as a base under ambient conditions, in presence of NP0–NP4 (Scheme 2). Table 1 shows the reaction conditions and conversion. The results obtained in entries 1 and 2 are in line with those previously published in similar reaction conditions [12]. That is, the Pd core is an efficient catalyst thanks to the fact that the hexanethiol linkers do not prevent the approach of the reagents to its surface. The cross-coupling/homocoupling ratio is about 5:1. The use of NP1 modifies clearly the efficiency of the system since after 24 h only traces of the products are obtained (entries 4 and 5) because of the robust blocking phosphine units. However, after 96 h the conversion is complete (entry 6) with complete selectivity. This behaviour suggests that the reaction only takes place after NP degradation, due to the strong basic medium, giving Pd–phosphine species which are very active and selective species. Using NP2 as catalyst the results are similar to those observed with NP1. That is,