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Short Communication

PdO hydrate as an efficient and recyclable catalyst for the Suzuki–Miyaura reaction in water/ethanol at room temperature

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ABSTRACT

$PdO\cdot1.4H_2O$ **1** prepared in our laboratories, as well as commercially available palladium oxides **2–4** have been found to act as efficient catalysts for the Suzuki–Miyaura reaction in ethanol/water mixture at room temperature in air. Thus, in the presence of 1 mol% catalyst, the reaction between different aryl bromides and arylboronic acids afforded a wide range of functionalized biphenyls in quantitative yield. Catalyst **1** has shown to be the most active for all couples of substrates, and it can be recovered and recycled several times without marked loss of activity. It has been demonstrated by means of suitable tests that the true catalyst is a soluble form of palladium originated by metal leaching from the metal oxide precursor. It is worth of note that the amount of catalyst both in the solution and in the isolated organic product is about 1 ppm.

1. Introduction

The construction of asymmetric biaryls through the Suzuki–Miyaura (SM) C–C coupling is one of the most powerful synthetic methodologies in organic syntheses [1–15]. The explosive growth of studies in this area in the last decade is mainly due to low toxicity and high stability of organoboranes towards air and moisture. The SM reaction is applied to pharmaceutical and agrochemical drug productions and in the design of new materials, liquid crystals and polymers [16]. The metal-catalyzed synthesis of pharmaceuticals requires very low levels of residual metal (<5 ppm). To reach this goal, two alternative strategies can be adopted: a) use of soluble palladium(II) species in “homeopathic” amounts [17–21], and b) use of palladium-based recoverable heterogeneous catalysts [10–13]. Few catalysts, generally based on soluble Pd(II) complexes, are capable of activating the less reactive and cheap aryl chlorides [5,22–28], but they are of limited practical use because they are not reusable. Secondly, their decomposition products often cause contamination of the reaction products. For these reasons, the use of simple, ligandless, recoverable and recyclable heterogeneous (pre)catalysts applied to both electron-rich and electron-poor aryl bromides should be strongly taken into account, in particular when environmentally friendly and safe procedures are adopted.

We have recently reported on the excellent catalytic activity of the Pd/CeO_2 system for the SM reaction at room temperature in ethanol/water mixture [29]. The TPO characterisation of Pd/CeO_2 has revealed that about 75% of palladium is in the form of oxide, the remaining being fixed on the ceria surface as metal. By means of a suitable test it was demonstrated that the true catalyst is present in the solution phase and most probably it arises from nanosized colloidal Pd(0) [30–36] undergoing a release/re-deposition mechanism [37–41]. It should be noted that Köhler [42,43] and Djakovitch [44] have demonstrated that systems based on palladium supported on metal oxides (Al_2O_3 and TiO_2) or SiO_2 behave as very active precatalysts in the SM reaction, and even electron-poor aryl chlorides showed to react [42]. Interestingly, both authors have evidenced the fundamental role played by amorphous PdO present on the surface in forming the active soluble catalyst. In this communication we present the results of a study based on the screening and comparison of different PdO samples, all showing catalytic efficiency in the SM reaction even at room temperature. It should be noted that palladium oxide hydrate was found to promote the Heck reaction at high temperature (140 °C) [45].

2. Results and discussion

2.1. Synthesis of **1** and characterization of **1–4**

To carry out the present investigation we have synthesised from $PdCl_2$ a hydrated PdO sample ($PdO\cdot1.4H_2O$ **1**), and its catalytic activity in the SM reaction was compared with that of three commercially

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available products: $PdO\cdot 1.2H_2O$ 99.9+% (**2**) (Aldrich, cat. n. 520756), PdO 99.995% (**3**) (Aldrich, cat. n. 203971), and PdO 99.9% (**4**) (Strem, cat. n. 46-2110). Catalyst $PdO\cdot 1.4H_2O$ **1** can be easily synthesized by treating an acidified solution of $PdCl_2$ with a solution of NaOH until complete precipitation of a black insoluble material, which is filtered off and dried under vacuum without warming. The water content of compounds **1** and **2** was established by TGA, which also revealed that the correct formulation of **4** is $PdO\cdot 1.2H_2O$, analogously to **2**. Compounds **1**–**3** were also characterized by XRD and XPS analyses. (Supporting information: A1. XRD analysis and A2. XPS analysis) The X-ray Photoelectron Spectroscopy data have been collected in Table 1, while physical data are reported in Table 2. Compounds **1** and **2** showed very similar spectra that revealed the presence of both Pd^0 and Pd^{2+}. In fact, a couple of peaks around 335 and 341 eV can be attributed to Pd^0 while two other peaks at about 337 and 342 eV are assigned to Pd^{2+}. Interestingly, a roughly comparable percentage of the two oxidation states of the metal is displayed for both samples. On the contrary, only two bands were exhibited by **3** at ca. 337 and 342 eV, indicating that Pd in this compound is in the +2 oxidation state only.

2.2. Catalytic activity of compounds 1–4

The reaction between 1-bromo-4-nitrobenzene and 4-methylphenylboronic acid in ethanol/water was used to preliminary evaluate the catalytic activity of **1**–**4**. The results of the screening, which are collected in Table 3, indicated the following sequence of activity: **1**>**2**≈**4**>>**3**, independently from the ethanol/water ratio. Owing to these findings, **3** was not further investigated, while all subsequent trials were carried out using **1** and **2** only, as **2** and **4** showed very similar catalytic behaviour also in other (unreported) preliminary SM couplings. Then, **1** and **2** were applied to a broad spectrum of reagents to compare their activity and to evaluate scope and limits of the PdO hydrate-catalyzed SM reaction. Selected significant couplings, leading to biaryls **5**–**17**, are listed in Table 4. Conveniently, the coupling of less reactive substrates (entries 8–14) was performed at 60 °C. Noticeably, all substrates reached quantitative conversion into the corresponding biaryls generally in short reaction times, even in the case of less reactive heterocycles (entries 12 and 14), and in all cases the "home-made" catalyst **1** showed higher activity. It should be noted that also electron-poor aryl chlorides were activated by **1**, but these substrates afforded low yields of the cross-coupling product. For example, 1-chloro-4-nitrobenzene reacted with 4-methylphenylboronic acid with a maximum observed yield of 35% 4-methyl-4′-nitro-1,1′-biphenyl. This limit value was obtained also using a strong excess of the boronic acid, which was mainly converted into the homocoupling product.

2.3. Studies on catalyst reuse

The reaction between 1-bromo-4-nitrobenzene and 4-methylphenylboronic acid was chosen for testing the reusability of the catalyst (Supporting information: A3. Catalyst recycling). Measurements were carried out employing 1 mol% palladium, and the results are shown in Fig. 1, where yields of 4-methyl-4′-nitro-1,1′-biphenyl for the first use and eight subsequent reuses of **1** are reported. For each trial, the reaction was stopped after 45 min, the time necessary for the complete conversion of the substrates using the virgin catalyst. As shown by the histogram, the catalytic activity was nearly maintained after several reuses of the catalyst. In the first four uses of **1** the GC yield was around 99%, then it slightly decreased, however the values were never below 94%. In a second set of experiments, twenty consecutive reuses of **1** in the reaction between 1-chloro-4-bromobenzene and phenylboronic acid allowed to isolate 1.843 g of 4-chloro-1,1′-biphenyl (97.7% overall yield, purity>97%) employing 0.7 mg of catalyst. Thus, in principle, more than 2.5 kg of product can be isolated using 1 g of **1**. The palladium content of the product, determined by ICP-MS, was only 1.1 ppm.

Table 1
XPS data for compounds **1**–**3**.

Compound	Binding energy (eV)				%	
	$3d_{5/2}$ Pd^0	$3d_{5/2}$ Pd^{2+}	$3d_{3/2}$ Pd^0	$3d_{3/2}$ Pd^{2+}	Pd^0	Pd^{2+}
1	335.3	336.8	340.6	342.3	57	43
2	335.4	336.9	340.6	342.2	52	48
3	–	336.9	–	342.2	–	100

Table 2
Physical data for compounds **1**–**4**.

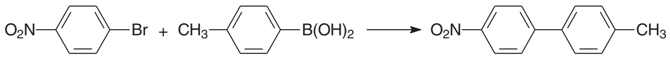
Sample	1	2	3	4
Surface area	147 $m^2 g^{-1}$	137 $m^2 g^{-1}$	7 $m^2 g^{-1}$	185 $m^2 g^{-1}$
Average pore width	21 Å	22 Å	167 Å	30 Å
Cumulative volume of pores	0.044 $cm^3 g^{-1}$	0.039 $cm^3 g^{-1}$	0.035 $cm^3 g^{-1}$	0.120 $cm^3 g^{-1}$

2.4. On the nature of the catalytic process

Starting from a Pd-containing solid precursor, the experimental determination of both the chemical nature and phase of the *true* active species should be accomplished by performing different tests that have to be carefully analyzed and compared to avoid any misinterpretation [9]. Thus, an exhaustive set of experiments was carried out on the model reaction (Supporting information: A4. Poisoning tests). The heterogeneous chelation test [29,46–48] was performed by introducing in the reaction mixture a diamine ligand grafted on silica, (Scheme 1). In the presence of an equimolar amount of $–NHCH_2CH_2NH_2$ functionality with respect to palladium, no coupling product was detected within 6 h. Thus, the catalytic activity resulted completely suppressed, and such a finding clearly shows that the true catalyst is leached, soluble palladium [29,48], easily captured by the diamine moiety (Scheme 1). It is well known that diamine ligands form very stable complexes with the Pd^{2+} ion, but there are however a few examples of Pd(0)-diamine complexes [49,50]. Noticeably, it has been reported that such species are catalytically active in C–C bond forming reactions. Different filtration tests and the CS_2 test were then carried out to confirm the homogeneous nature of the catalytic process. The results of the CS_2 test were as expected as no coupling product was detected within 6 h using 1:10 or 1:50 CS_2/Pd molar ratios. The hot filtration test was conveniently done on the reaction between 5-bromopirimidine and phenylboronic acid at 333 K. After heating for 90 min, the black solid was discarded by filtration and the resulting clean solution was heated again at 333 K and monitored by GC. Yields of the coupling product were very close to that observed when the test was done without elimination of **1** by filtration. Three further filtration tests were run at 298 K on the model reaction trying to understand how the true catalyst is formed (Supporting information: A4. Poisoning tests). Taken together, these experiments confirmed that the catalytically active species cannot be generated by the solvent alone, while determinant to start the cross-coupling process is the presence of the base (K_2CO_3). Nevertheless, the catalytic efficiency of the species formed in the initial absence of both organic substrates is very low, thus indicating a crucial role played by these compounds. Palladium leaching from Pd/Al_2O_3 precursor even at low temperature to afford an active soluble catalyst for the SM reaction has been elegantly demonstrated by Köhler [42,43]. To confirm the occurrence of a homogeneous catalytic process, the kinetic plot (Fig. 2) shows the typical sigmoidal shape due to the presence of the induction period commonly observed when catalytically active soluble species are generated by Pd-containing solid precursors [40,47,48,51–54].

To tentatively explain the order of catalytic activity (**1**>**2**≈**4**>>**3**), different parameters can be taken into account. First, the surface area of **1**, **2** and **4** is comparable, while that of **3** is about twenty times lower (Table 2). The average pore width varies accordingly. Thus, it spans in

Table 3
Comparison of the catalytic activity of palladium oxides **1–4** in the SM coupling reaction.[a]



Catalyst	Time[b]		
	3:1[c]	1:1[c]	1:3[c]
1	0.75 h	1 h	1.75 h
2	3 h	2.5 h	2 h
3	6 h	8 h	19 h
4	2.5 h	2 h	2 h

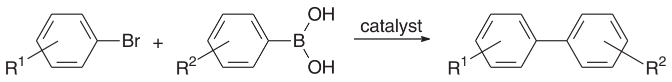
[a] Reagents and conditions: 1-bromo-4-nitrobenzene (0.5 mmol), 4-tolylboronic acid (0.6 mmol), K_2CO_3 (0.6 mmol), catalyst (mol aryl bromide/mol Pd = 100), and 2 mL solvent, T = 298 K.

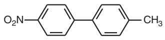
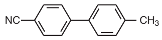
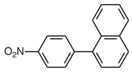
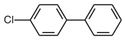
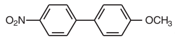
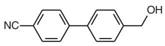
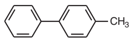
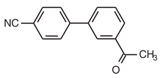
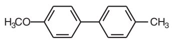
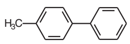
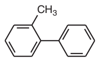
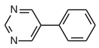
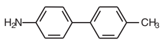
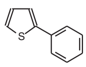
[b] Time necessary to achieve >99% yield of product, determined by GC using diethylene glycol di^{n}butyl ether as internal standard.

[c] Ethanol/water ratio.

the range of 21–30 Å for **1**, **2** and **4**, while it assumes a very large value (167 Å) in **3**. On these bases only, it can be argued that the higher the surface area, the better the catalytic performance of the precatalyst. The XPS analysis showed that, while **1** and **2** exhibit comparable amounts of Pd(0) and Pd^{2+}, PdO only is present in **3** (Table 1). Djakovitch and Köhler have demonstrated that the amount of surface amorphous PdO (in Pd/Al_2O_3 and Pd/SiO_2 precatalysts) plays a fundamental role in determining the extent of the leaching process

Table 4
Scope of the SM reaction catalyzed by **1** and **2.**[a]



Entry	R^1	R^2	Product	Time (h)[b]		Temperature
				1	**2**	
1	4-NO_2	4-CH_3	 **5**	0.75	3	298 K
2	4-CN	4-CH_3	 **6**	1.25	2	298 K
3	4-NO_2	[c]	 **7**	1.25	3	298 K
4	4-Cl	-	 **8**	1.5	2.5	298 K
5	4-NO_2	4-OCH_3	 **9**	1.75	2	298 K
6	4-CN	4-CH_2OH	 **10**	3	4.5	298 K
7	–	4-CH_3	 **11**	5	9	298 K
8	4-CN	3-$COCH_3$	 **12**	0.25	0.5	333 K
9	4-OCH_3	4-CH_3	 **13**	0.25	0.75	333 K
10	4-CH_3	–	 **11**	0.25	0.5	333 K
11	2-CH_3	–	 **14**	0.75	1	333 K
12	[d]	–	 **15**	4	5	333 K
13	4-NH_2	4-CH_3	 **16**	4.5	5	333 K
14	[e]	–	 **17**	24	28	333 K

[a] Reaction conditions: aryl bromide (0.5 mmol), arylboronic acid (0.6 mmol), K_2CO_3 (0.6 mmol), catalyst 1 mol%, ethanol 1.5 mL, and water 0.5 mL.

[b] Time necessary for reaching >99% GC yield. Measurements for the faster reactions were performed every 15 min; diethylene glycol di^{n}butyl ether was used as internal standard.

[c] 1-Naphthylboronic acid.

[d] 5-Bromopyrimidine.

[e] 2-Bromothiophene.

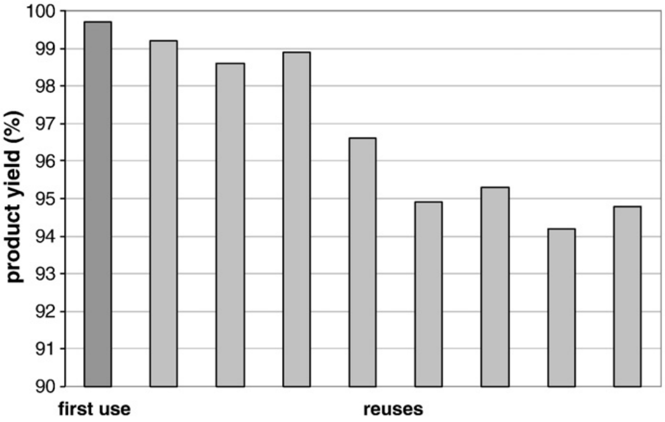


Fig. 1. Recycling tests for the standard reaction. Reagents and conditions: 1-bromo-4-nitrobenzene (0.5 mmol), 4-methylphenylbenzene (0.6 mmol), K_2CO_3 (0.6 mmol), catalyst **1** (0.7 mg), ethanol 1.5 ml, H_2O 0.5 ml, 25 °C. Yields were determined by GC after 45 min.

[42–44,55]. Their studies demonstrated that the Pd^{2+} ion in the solution is then reduced to catalytically active Pd(0). Considering this feature only, the very low catalytic activity shown by **3**, which, on the contrary, is expected to be higher than that of **1** and **2** giving its Pd^{2+} content, can be explained on the bases of the very high crystallinity of this material. This is clearly shown by the XRD spectra of 1–3 (Supporting information: A1. XRD analysis). In conclusion, both very low surface area and high crystallinity may explain the low activity observed using **3** as compared to **1** and **2**.

3. Experimental

3.1. Preparation of compound **1**

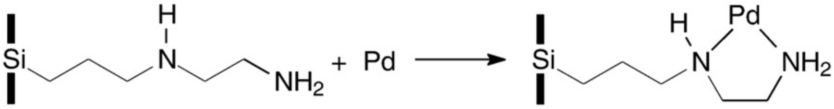
395 mg of $PdCl_2$ were suspended in 175 mL of water, the mixture was warmed to 60 °C, treated with 25 mL of a 0.5 M solution of HCl and stirred until complete dissolution was achieved. To the clean solution, was added dropwise 25 mL of a 0.8 M solution of NaOH with formation of a black precipitate. The solid was filtered off and washed with water and a 0.1 M solution of acetic acid until Cl^- ions were not further detectable and the pH reached neutrality. Drying under vacuum at room temperature overnight gave 304 mg (92% yield) of pure $PdO \cdot 1.4H_2O$ **1** (the water content was established by TGA analysis).

3.2. Catalytic runs

The following general procedure was adopted for all reactions catalyzed by **1–4** (1 mol% Pd). In a thermostated bath at 25 °C, a 10 mL Schlenk flask was charged in air with a magnetic stir bar, catalyst (0.7 mg for **1**, **2** and **4** or 0.6 mg for **3**), arylboronic acid (0.6 mmol), diethylene glycol di^{n}butyl ether (GC internal standard, 0.5 mmol), K_2CO_3 (0.6 mmol), ethanol (1.5 mL) and H_2O (0.5 mL). Then the reaction was started by the addition of aryl bromide (0.5 mmol). About 0.1 mL of mixture was extracted from the flask by means of a syringe and to the sample was added 0.5 mL of water, followed by extraction with dichloromethane (2 × 1 mL). The solution was dried over Na_2SO_4 and analysed by GC after purification on a microcolumn filled with silica gel. All coupling products **5**–**17** reported in Table 4 are known (Supporting information: A5. Coupling products) and their identity has been confirmed by GC–MS analysis.

4. Conclusion

In conclusion, the cheap and easy to prepare catalyst $PdO \cdot 1.4H_2O$ **1** shows excellent catalytic properties in the SM cross-coupling of arylboronic acids with a wide range of aryl bromide precursors. The reaction can be run under mild catalytic conditions (room temperature, water/ethanol mixture as the solvent, 1% catalyst) affording always a quantitative formation of the asymmetric biaryl. In the case of less reactive aryl chlorides, only in the presence of an electron withdrawing group on the ring the coupling product is formed,



Scheme 1. Palladium “trapping” by a diphosphane ligand anchored to silica.

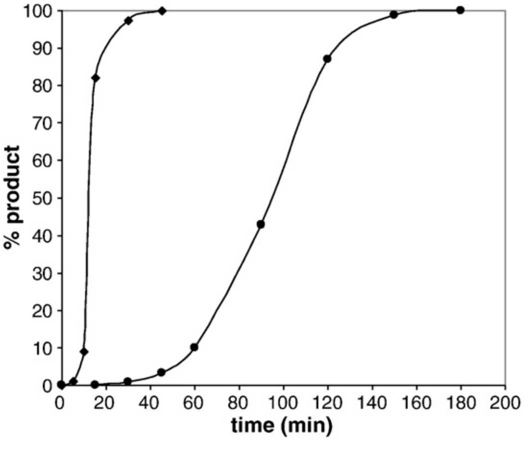
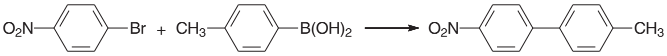


Fig. 2. Kinetic plot of the reaction:



Reagents and conditions: 1-bromo-4-nitrobenzene (0.5 mmol), 4-tolylboronic acid (0.6 mmol), K_2CO_3 (0.6 mmol), catalyst 0.7 mg (mol aryl bromide/mol Pd = 100), 1.5 mL ethanol, and 0.5 mL water, T = 298 K. (◆) catalyst **1**; (●) catalyst **2**.

although in low yield. Precatalyst **1**, which acts as source of the *true* catalytic species through a metal leaching process, can be recycled at least twenty times without loss of activity. Given the simplicity and low cost of **1**, the employment of a safe and environmentally friendly solvent and the possibility of reuse of the catalyst, this protocol seems to be a good candidate for its application to the production of asymmetric biaryls on a large-scale.

Supplementary materials related to this article can be found online at doi:10.1016/j.catcom.2010.11.026.

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