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Efficient Palladium-Catalyzed Aminocarbonylation of Aryl Iodides using Palladium Nanoparticles Dispersed on Siliceous Mesocellular Foam

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The amide functionality constitutes a key element in organic synthesis, which is reflected by its frequent use in a wide range of chemical products, such as adhesives, pesticides, pharmaceuticals and polymers.^[1] Consequently, there is a substantial demand for the development of new and efficient catalytic protocols for amide bond formation.^[2] Most available methods for the formation of the amide bond rely on the reaction of an acyl chloride with an amine or the condensation of a carboxylic acid and an amines by the use of an amide coupling reagent.^[3] These methods are associated with several disadvantages, such as poor atom economy, concomitant production of large quantities of waste, tedious purifications as well as the cost and toxicity of the many amide coupling reagents. Catalytic methods for the direct formation of amides from non-activated carboxylic acids and amines have recently emerged as an area of increased interest. Although, several catalytic systems based on enzymes,^[4] boronic acids/esters^[5] and Lewis acids^[6] have been developed so far, there is still a lack of a general method.^[7] Specifically, benzoic acid derivatives constitute a problematic issue in direct amidation as they require higher temperatures/catalytic loadings and/or longer reaction times in order to react.^[5b,6b-c,8] An attractive alternative approach for accessing benzamides is to employ an aminocarbonylation protocol, in which inexpensive and readily available aryl halides are coupled with carbon monoxide and amines in a one-step procedure (Scheme 1).

Scheme 1. General scheme for aminocarbonylation of aryl halide compounds.

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The concept of palladium-catalyzed aminocarbonylation has been known since 1974 when Heck and co-workers presented their pioneering work on this subject, and today there is a vast number of homogeneous palladium-catalyzed protocols available.^[9] Heterogeneous catalysis possesses several advantages over homogeneous catalysis, such as simple separation of the catalyst and the possibility of recycling, making it more favorable from an environmental perspective. Although aminocarbonylation has been studied immensely for almost four decades, there are still only a few examples of heterogeneous catalyzed protocols available.^[10] The group of Bhanage has dedicated substantial efforts in finding a suitable catalyst for this purpose and have reported on methods utilizing palladium on carbon^[11] and supported palladium-*N*-heterocyclic carbene complexes^[12] as heterogeneous and recyclable catalysts. Furthermore, Seayad and co-workers have recently made contributions to heterogeneous aminocarbonylation by investigating the use of palladium nanoparticles.^[13] Their initial study was based on a catalyst stabilized by the ionic liquid tri-*n*-butyltetradecylphosphonium dodecylbenzenesulfonate ([TBTdP][DBS]), which required harsh conditions (130–150 °C/ P_{CO} 180 psi) in order to be active. In general, high pressure and high reaction temperature is required for heterogeneous catalysts in this transformation; however, in the following work by Seayad the first example of a heterogeneously catalyzed aminocarbonylation at low pressure (1 atm) was demonstrated by employing Pd/MOF-5 (Pd/metal-organic framework). The MOF-5 support was reported as moisture-sensitive and a ZIF-8-support (zeolitic imidazole framework) was therefore explored in a subsequent study, with the intention of obtaining a bench-stable catalyst. The Pd/ZIF-8 catalyst proved to be efficient even for the transformation of aryl bromides, although bidentate phosphine ligands were required. We have recently developed a highly dispersed nanopalladium catalyst suspended on mesocellular foam (MCF), which has shown excellent activity in a wide range of transformations such as aerobic alcohol oxidation, Suzuki cross-couplings, racemization, DKR of primary amines and various transfer hydrogenation reactions.^[14] Considering the fact that there are only a few heterogeneous procedures available for aminocarbonylation, we were motivated in conducting an evaluation of the Pd⁰-AmP-MCF for this transformation. During the preliminary evaluation of this catalyst it was discovered that the supported palladium nanoparticles exhibited a “release and catch” effect, meaning that a minor amount of the heterogeneous palladium became soluble and catalyzed the reaction, after which it re-deposited onto the

support. There are several reports on heterogeneous palladium catalyzed reactions where a “release and catch” or “boomerang” effect have been described for carbon-carbon coupling reactions;^[15] however, to the best of our knowledge this has not been described previously for the aminocarbonylation.

The Pd⁰-AmP-MCF used for this study was prepared according to a previously reported protocol.^[14d] This catalyst possesses several desirable properties that makes it attractive for use in organic chemistry, such as high loading of Pd per weight of support, high bench stability, good tolerance to water, high activity, and good recyclability.^[14b-e]

The initial screening using the Pd⁰-AmP-MCF was carried out employing 4-iodotoluene (**1a**) and benzyl amine (**2a**) as model substrates and the reaction was performed in toluene at 100 °C for 24 h with 1 atmosphere of carbon monoxide (Table 1). DABCO was found to be the best choice of base, and full conversion was obtained using 2 equivalents of DABCO, after only 8 h at a reaction temperature of 95 °C (Table 1, entries 6-8).

Table 1. Screening of conditions for Pd⁰-AmP-MCF catalyzed aminocarbonylation^[a]

entry	Temp. (C°)	Time (h)	Base	Conv. (%)
1	100	24	Et ₃ N 2 eq.	42
2	100	24	DBU 2 eq.	90
3	100	24	K ₂ CO ₃ 2 eq.	50
4	100	24	Barton's base 2 eq.	n.r
5	100	24	DABCO 1 eq.	90
6	100	24	DABCO 2 eq.	Full
7	100	8	DABCO 2 eq.	Full
8	95	8	DABCO 2 eq.	Full
9	90	8	DABCO 2 eq.	87
10	80	8	DABCO 2 eq.	70
11	95	8	DABCO 2 eq.	

[a] Reaction conditions: 4-iodotoluene (0.5 mmol), benzyl amine (1.5 eq.), dry toluene 2 mL, Pd-AmP-MCF (2 mol%).

Two byproducts, identified as α -keto amide and urea, were observed to a minor extent after the reactions. Furthermore, the formation of the byproducts was favored by a lower reaction temperature. Hence it was not possible to carry out the aminocarbonylation reaction at a lower temperature over a longer reaction time and still maintain a good yield of the desired amide product.

The main objective of employing heterogeneous catalysts is the possibility to recover and reuse the catalyst, and a particularly important aspect in industry is to avoid toxic metal contamination in the final product. Therefore it is imperative to establish the extent of metal leaching when working with heterogeneous catalysis and to investigate whether the non-supported metal is involved in the catalytic reaction. Appropriate measures should always be taken and a simple filtration test could provide sufficient evidence of leaching, however, suggestions have been raised that this alone cannot prove true heterogeneous palladium catalysis, due to the rate in which leached palladium species can be re-deposited.^[15a]

To determine the metal leaching under the studied reaction

conditions, a liquid aliquot was withdrawn from the aminocarbonylation reaction between 4-iodotoluene and benzyl amine, and analyzed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analysis. The analysis revealed that a minimal amount of palladium was in solution after 24 h (0.8 ppm/0.13%); however, since the reaction could be accomplished much faster than 24 h, a leaching test was also performed for the reaction completed after 8 h. Interestingly, the analysis showed a significantly elevated content of dissolved palladium (67 ppm/11%), which demonstrates that palladium becomes soluble during the course of the reaction and furthermore that the dissolved palladium re-adsorbs on to the support after a prolonged reaction time of 24 h together with the depletion of aryl iodide and amine. To determine whether the non-supported palladium could catalyze the reaction, a hot filtration test was carried out where the heterogeneous Pd⁰-AmP-MCF was separated from the reaction by filtration after 1.5 h at 30% conversion. The solid-free filtrate was subsequently allowed to stir under similar reaction conditions for 16 h and this experiment showed that the reaction continued after the heterogeneous catalyst had been separated, proving that the homogeneous palladium species were catalytically active. The observation prompted us to investigate the cause of leaching and the results from this study are summarized in Table 2.^[16]

Table 2. Investigation of the cause of leaching

Entry	CO	DABCO	2a	1a	Leaching
1	✓				no
2		✓			no
3			✓		no
4				✓	no
5	✓	✓			no
6		✓		✓	no
7	✓	✓		✓	no
8		✓	✓	✓	yes
9			✓	✓	yes

As shown in Table 2, none of the components in the aminocarbonylation reaction could individually affect the Pd⁰-AmP-MCF (Table 2, Entries 1-4). It is a commonly accepted view that the oxidative addition is responsible for releasing Pd^{II} into solution and therefore we expected to observe leaching by aryl iodide alone; however, we could not observe any leaching even with combination of DABCO and aryl iodide (Table 2, entry 6). We then looked upon different combinations of the reagents, and we found that the leaching occurred when we subjected the palladium catalyst to a combination of aryl iodide, base and primary amine (Table 2, entry 8). Leaching was also detected if the base was left out, and we could therefore conclude that the aryl iodide in combination with amine is responsible for the dissolution of the palladium.

Two sets of recycling studies were carried out with reaction times of 8 and 24 h respectively and the results are summarized in Figure 3. This study shows that the activity was rapidly decreasing in the reactions of 8 h, which is not surprising since upon separation of the product, homogeneous palladium in solution is lost and less catalyst is therefore available in each cycle. In the 24 h reactions basically all of the palladium remains in the heterogeneous phase and we expected an improvement of the catalysts recyclability; however, a drop in yield was still observed after the third cycle.

Figure 3. Comparative recycling study at 8/24 h respectively.

TEM images of the collected catalyst after the third cycle in the 24 h reaction showed some areas of agglomerated palladium, which may be due to the harsh reaction conditions required for the aminocarbonylation to take place, and/or an inefficient re-deposition of the homogeneously dissolved palladium.^[17] This observation can explain the loss of activity that was seen already after the third run of the recycling study.

A condensed library of substrates was evaluated under the optimized conditions (Scheme 2).

Scheme 2. Scope evaluation of the palladium catalyzed aminocarbonylation.

Although the majority of the reactions were complete within 8 h, it should be stressed that the re-deposition of palladium required the reaction to be left for 24 h.

As can be seen in Scheme 2, differently substituted aryl iodides were converted to secondary and tertiary amides in good to high yields. Aryl iodides substituted with electron-donating or electron-withdrawing groups did not seem to significantly affect the outcome of the reaction (**3b**, **3c**); however, a decrease in reactivity was observed when sterically demanding substrates were used (**3d**, **3g**). Aliphatic amines (**3h**, **3j**), aryl (**3i**) and heteroaryl containing amines (**3k**) were all successfully transformed into the corresponding amides, with the exception of *N*-methylaniline (**3n**) where only traces of product could be detected after 24 h. An ester functionality was tolerated (**3f**), and interestingly, the formation of the Weinreb amide proceeded smoothly employing *N*-methoxymethylamine hydrochloride salt as the amine source (**3m**). Unfortunately, aryl bromides and chlorides, as well as phenyliodonium triflate were unreactive under the reaction conditions employed; however, this enabled us to react 1-bromo-4-iodobenzene (**4**) with benzyl amine (**2a**) to obtain 83% of the mono-substituted amide *N*-benzyl-4-bromobenzamide (**4b**). The antidepressant drug Moclobemide (4-Chloro-*N*-(2-morpholinoethyl)benzamide) (**4c**), was also efficiently prepared from 1-chloro-4-iodobenzene (**5**) and 2-morpholinoethanamine (**2b**) using the present catalytic system.^[18]

Scheme 3. Chemoselective formation of mono-substituted amides.

To further evaluate the scope of the developed catalytic protocol it was of interest to study the coupling between aryl halide and ammonia or an ammonia equivalent for the synthesis of primary amides.^[9i, 9m] Aqueous ammonia is not compatible with the Pd⁰-AmP-MCF catalyst and we therefore investigated the reaction between 4-iodotoluene and ammonium carbamate, for the formation of a primary amide. Interestingly, a 33% conversion to amide was observed after 24 h, which indicates that the present catalytic protocol may indeed be used for this type of transformation. In addition, the Pd⁰-AmP-MCF was briefly assessed in the related alkoxycarbonylation reaction, using benzyl alcohol and 4-iodotoluene as model substrates. In this reaction, the Pd nanocatalyst displayed modest activity, and the desired benzyl ester was obtained in 39% yield after 24 h.^[19] However, no optimization attempts were conducted and these two transformations will be further investigated in a separate study.

In conclusion, we have disclosed the use of the Pd⁰-AmP-MCF nanocatalyst for the aminocarbonylation reaction of aryl iodides employing aliphatic or aromatic amines in the presence of 1 atm. carbon monoxide. The Pd⁰-AmP-MCF catalyst was found to operate through a release and catch mechanism, which has not been observed previously for other heterogeneous aminocarbonylation protocols. Interestingly, the leached Pd species proved to

efficiently redeposit onto the solid support upon completion of the reaction, as only 0.13% (0.8 ppm) of the Pd remained in solution after 24 h. Moreover, the current protocol enabled efficient coupling of a variety of aryl iodides and amines to be carried out under relatively mild conditions, i.e. low carbon monoxide pressure and moderate reaction temperature. Overall, this protocol combines the advantages of homogeneous and heterogeneous catalysis, such as high catalytic efficiency, mild reaction conditions, low levels of metal-contamination in the final product, as well as easy separation and recycling of the catalyst.

Experimental Section

General method: Toluene (1 mL) was added to aryl iodide (0.5 mmol) and Pd-AmP-MCF (2 mol%) and the atmosphere was exchanged to carbon monoxide (1 atm). The mixture was added to a pre-heated oil bath at 95 °C and a stock solution of DABCO (1 mmol/mL) and the amine (0.75 mmol) were added. The reaction was stirred for 8 or 24 h and then purified by column chromatography using silica gel, eluted with a gradient of toluene/ethyl acetate.

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Keywords: Aminocarbonylation • Release and Catch • Palladium • Catalysis • Amides

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- [16] Pd nanocatalyst (13.0 mg, 0.01 mmol) and dry toluene was added to a microwave vial that was capped and subjected to the specific components of the reaction as stated in table 2 for 1.5 h at 95 °C. Hot filtration was performed directly into a new microwave vial and the reagents as in Table 1 (except Pd nanocatalyst) were added. The reaction was then stirred for 24 h under 1 atm. of CO and then analyzed to see if the corresponding amide **3a** had been formed. In entries 1-7 no amide product was detected, in entries 8-9 full conversion into amide **3a** was observed.
- [17] See the *Supporting Information*
- [18] U. Bonnet, *CNS Drug Reviews*, **2003**, *9*, 97-140.
- [19] The use of phenol (in place of benzyl alcohol) and 4-iodotoluene afforded the corresponding ester in 36 % yield according to ¹H NMR.

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It's Catchy!

F. Tinnis, O. Verho, K. P. J. Gustafsson, Dr. C.-W. Tai, Prof. Dr. Jan.-E. Bäckvall, Prof. Dr. H. Adolfsson** Page – Page

Efficient Palladium-Catalyzed Aminocarbonylation Using Palladium Nanoparticles Dispersed on Siliceous Mesocellular Foam

Herein, we report upon an efficient palladium catalysed protocol for aminocarbonylation of aryl iodides, in which the palladium immobilized on the amino-functionalized mesocellular foam (MCF) was found to operate through a “release and catch” mechanism.

A very low content of palladium was found in solution upon completion of the reaction and a variety of different aryl iodides were converted to the corresponding amides under mild conditions.