

# ***In situ* generated Pd(0) nanoparticles stabilized by bis(aryl)acenaphthenequinone diimines as catalysts for aminocarbonylation reactions in water**

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## **Abstract**

Aminocarbonylation of aryl iodides with aromatic and aliphatic amines, leading to formation of the corresponding **amides**, was efficiently carried out in water under 1 atm of CO using palladium nanoparticles (Pd NPs) formed *in situ* from [PdCl<sub>2</sub>(Ar<sub>2</sub>-BIAN)] complexes. The role of Ar<sub>2</sub>-BIAN ligands in the stabilization of Pd NPs was evidenced. The nature of the catalytically active species was confirmed by poisoning experiments, which highlighted that the catalyst is actually in the form of **Pd NPs** rather than soluble palladium complexes. In the aminocarbonylation of iodobenzene with substituted anilines good yields of amides were obtained, although the activity was depleted by the presence of substituents in the *ortho* positions of the aniline. On the other hand, in the reaction with aliphatic **amines** **α-ketoamides** were formed in addition to the amides. The selectivity towards α-ketoamides was increased by increasing the CO pressure to 10 atm, **at equimolar** amounts of PhI and amine. Pd NPs were successfully recovered after the catalytic reaction and recycled in five subsequent runs with only a marginal loss of activity after the fourth cycle.

**key words:** *palladium; α-diimines; aminocarbonylation; aqueous medium; α-ketoamides;*

## **1. Introduction**

Amides constitute an interesting structural motif that is often present in pharmaceuticals (Atorvastatin, Mosapride, Imatinib, Nitroxazepine)<sup>1-3</sup> as well as in biologically active compounds (Acetaminophen, Aniracetam, Methacetin).<sup>4, 5</sup> Amides are also important building blocks for the

synthesis of numerous pesticides, color pigments and natural products <sup>6</sup>. Traditionally, amides can be prepared in reactions of amines with acyl chlorides or carboxylic acids according to the relatively environmentally harmful processes. <sup>7,8</sup> For these reasons, development of new, cheap and efficient methods of their synthesis is greatly expected.

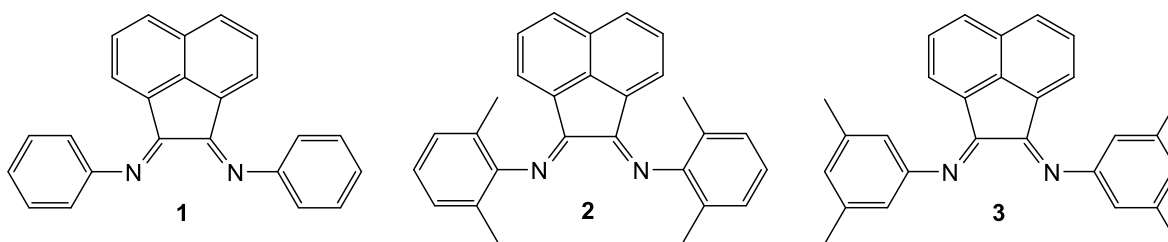
An alternative technique for the amide synthesis is based on the palladium-catalyzed direct aminocarbonylation. In this three-component reaction, an aryl halide, an amine and carbon monoxide react to form the corresponding amide in a single-step process. <sup>9,10</sup> **The first aminocarbonylation reactions of aryl heterocyclic and vinylic halides with primary or secondary amines have been reported by Heck in 1974.** <sup>11</sup> Advantageously, all these substrates are inexpensive and easily available, and high **yields of the** amide are obtained under relatively mild conditions (up to 120°C and 1-15 bar). <sup>12</sup> Aminocarbonylation was efficiently catalyzed by a Bedford palladacycle and dppf (dppf = bis-1,1-(diphenylphosphino)ferrocene) <sup>13</sup> and palladium complexes with NHC (NHC = N-heterocyclic carbene) ligands. <sup>14</sup> Palladium NHC complex supported on polymer was employed for the aminocarbonylation of aryl iodides with primary and secondary amines in aqueous **medium.** <sup>15</sup> The one-pot diazotization/aminocarbonylation conversion of anilines to benzamides has been reported. <sup>16</sup> The palladium-catalyzed aminocarbonylation using aqueous ammonia in toluene has been developed. <sup>17</sup> Commercially available Pd/C has been successfully employed as catalyst for the synthesis of amides. <sup>18, 19</sup> **Recently, the palladium-catalyzed aminocarbonylation of 5-iodoindole and 7-iodoindole derivatives with various primary and secondary amines has been reported.** <sup>20</sup> Kollár described efficient aminocarbonylation of iodoalkenes and iodoaromatic with primary and secondary amines, catalyzed by Pd(OAc)<sub>2</sub> with addition of PPh<sub>3</sub> <sup>21-26</sup>. The same catalytic system has been used in aminocarbonylation of iodoalkenes and iodobenzene with diethyl  $\alpha$ -aminobenzyl-phosphonate <sup>27</sup> and aminoacid methyl esters in ionic liquids. <sup>28</sup>

In the last decade palladium nanoparticles have found application as the catalysts of the aminocarbonylation reaction. <sup>29-32</sup> They have been stabilized with ionic liquid <sup>29</sup>, immobilized on magnetic nanoparticles, <sup>30</sup> **supported** on carbon nanotubes <sup>31</sup> or on **polymers.** <sup>32, 33</sup> Pd nanoparticles supported on **MOF-5,** <sup>34</sup> or **ZIF-8,** <sup>35</sup> on mesocellular foam <sup>36</sup> or on binaphthyl <sup>37</sup> catalyzed aminocarbonylation according to the heterogeneous mechanism.

Other heterogeneous catalysts, active in a double carbonylation of aryl iodides and amines to  $\alpha$ -ketoamides, such as Pd/C with PPh<sub>3</sub> <sup>38</sup> or palladium supported on silica <sup>39, 40</sup> have also been presented. Palladium nanoparticles leached from a sulfur-modified Au-supported palladium material (SAPd) <sup>41</sup> and supported over functional polymers (Pd/CFP) <sup>42</sup> have been used. A double carbonylation has been performed with high yield using palladium nanoparticles generated *in situ* in

polyethylene glycol.<sup>43</sup> Despite this development of the double carbonylation reaction, synthesis of  $\alpha$ -ketoamides still needs improvement. Moreover, to the best of our knowledge, the employment of the palladium nanoparticles for the aminocarbonylation in water has not been reported yet.<sup>44-47</sup>

Therefore, our studies focused on the development of a catalytic system suitable for the aminocarbonylation reactions based on palladium nanoparticles generated *in situ* in an aqueous medium. To achieve this purpose, we selected palladium complexes with Ar<sub>2</sub>-BIAN (Ar<sub>2</sub>-BIAN = bis(aryl)acenaphthenequinonediimine) ligands. It was expected that these bulky chelating ligands would be strong enough to efficiently stabilize Pd nanoparticles against agglomeration and thus prevent loss of catalytic activity. Palladium complexes with the Ar<sub>2</sub>-BIAN ligands have been tested with very good results in alkene-CO copolymerization,<sup>48,49</sup> selective hydrogenation of alkynes to alkenes,<sup>50</sup> synthesis of indoles from *ortho*-nitrostyrenes and CO,<sup>51</sup> Suzuki-Miyaura<sup>52</sup> and Heck<sup>53</sup> cross-coupling reactions. However, their application for the aminocarbonylation has not been studied up to now. For this investigation three Ar<sub>2</sub>-BIAN ligands have been selected: the reference compound derived from the simple aniline **1**, and the two molecules obtained from the 2,6-dimethyl- and the 3,5-dimethyl aniline, **2** and **3**, respectively (Figure 1).



**Figure 1.** The investigated Ar<sub>2</sub>-BIAN ligands **1–3**.

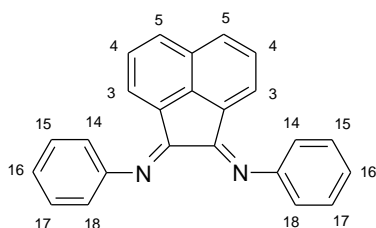
## 2. Experimental

All chemicals were purchased commercially (Sigma Aldrich) and used without further purification. Ar<sub>2</sub>-BIAN ligands were synthesized according to literature procedures by condensation of acenaphthenequinone with the proper aniline.<sup>54-57</sup>

### 2.1. Synthesis of [PdCl<sub>2</sub>(Ar<sub>2</sub>-BIAN)], **1a** - **3a**

All the complexes were synthesized by following a general procedure based on the reaction of [PdCl<sub>2</sub>(cod)] with the proper Ar<sub>2</sub>-BIAN ligand in a 1:1.1 ratio. Complexes **1a** - **3a** were obtained with yields ranging from 80 to 85 %. As an example, the detailed synthesis for complex **3a** is reported below.

Under the nitrogen atmosphere  $[\text{PdCl}_2(\text{cod})]$  (0.035 g, 0.124 mmol) was added to a solution of (3,5- $(\text{CH}_3)_2\text{C}_6\text{H}_3$ )<sub>2</sub>-BIAN (0.050 g, 0.130 mmol) in  $\text{CH}_3\text{CN}$  (10 mL). The reaction mixture was stirred at room temperature for 3 h and then concentrated to half of the volume under reduced pressure. Upon the addition of diethyl ether a red-orange solid precipitate was formed; the precipitate was filtered off, washed with hexane, diethyl ether and dried in vacuum. Yield 0.059 g (82%).



**Scheme 1.** Numbering of C and H atoms in  $\text{Ar}_2$ -BIAN ligands for interpretation of NMR spectra.

$[\text{PdCl}_2(\mathbf{1})]$ , **1a**.- Anal. Calc. for  $\text{C}_{24}\text{H}_{16}\text{Cl}_2\text{N}_2\text{Pd}$  (509.72): C 56.55, H 3.16, N 5.50. Found: C 56.85, H 3.14, N 5.54%.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.10 (d,  $J_{\text{H-H}} = 8.2$  Hz, 2H,  $\text{H}^5$ ), 7.57 (t,  $J_{\text{H-H}} = 7.5$  Hz, 4H,  $\text{H}^{15,17}$ ), 7.51 (t,  $J_{\text{H-H}} = 7.3$  Hz, 2H,  $\text{H}^{16}$ ), 7.47 (dd,  $J_{\text{H-H}} = 8.2$  Hz, 7.6 Hz, 2H,  $\text{H}^4$ ), 7.40 (m, 4H,  $\text{H}^{14,18}$ ), 6.79 (d,  $J_{\text{H-H}} = 7.2$  Hz, 2H,  $\text{H}^3$ ).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  175.3, 147.5, 145.1, 132.6, 131.6, 129.7, 129.2, 129.1, 126.3, 125.0, 122.7. IR ( $\text{cm}^{-1}$ , KBr): 1621  $\nu(\text{C=N})$ , 348  $\nu(\text{Pd-Cl})$ .

$[\text{PdCl}_2(\mathbf{2})]$ , **2a**.- Anal. Calc. for  $\text{C}_{28}\text{H}_{24}\text{Cl}_2\text{N}_2\text{Pd}$  (565.83): C 59.43, H 4.27, N 4.95. Found: C 59.85, H 4.24, N 4.98%.

$^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  8.17 (d,  $J_{\text{H-H}} = 8.3$  Hz, 2H,  $\text{H}^5$ ), 7.53 (dd,  $J_{\text{H-H}} = 8.2$  Hz, 7.4 Hz, 2H,  $\text{H}^4$ ), 7.39 (t,  $J_{\text{H-H}} = 7.5$  Hz, 2H,  $\text{H}^{16}$ ), 7.30 (d,  $J_{\text{H-H}} = 7.5$  Hz, 4H,  $\text{H}^{15,17}$ ), 6.64 (d,  $J_{\text{H-H}} = 7.3$  Hz, 2H,  $\text{H}^3$ ), 2.34 (s, 12H,  $\text{Ar}(\text{CH}_3)_2$ ).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  176.3, 148.0, 143.8, 133.3, 131.9, 130.2, 130.1, 129.3, 129.1, 125.8, 125.0, 18.7. IR ( $\text{cm}^{-1}$ , KBr): 1603  $\nu(\text{C=N})$ , 344  $\nu(\text{Pd-Cl})$ .

$[\text{PdCl}_2(\mathbf{3})]$ , **3a**.- Anal. Calc. for  $\text{C}_{28}\text{H}_{24}\text{Cl}_2\text{N}_2\text{Pd}$  (565.83): C 59.43, H 4.27, N 4.95. Found: C 59.07, H 4.29, N 4.93%.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.09 (d,  $J_{\text{H-H}} = 8.2$  Hz, 2H,  $\text{H}^5$ ), 7.49 (dd,  $J_{\text{H-H}} = 8.2$  Hz, 7.4 Hz, 2H,  $\text{H}^4$ ), 7.11 (s, 2H,  $\text{H}^{16}$ ), 6.97 (s, 4H,  $\text{H}^{14,18}$ ), 6.80 (d,  $J_{\text{H-H}} = 7.3$  Hz, 2H,  $\text{H}^3$ ), 2.39 (s, 12H,  $\text{Ar}(\text{CH}_3)_2$ ).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  175.0, 147.3, 145.2, 139.5, 132.3, 131.6, 130.8, 129.1, 126.3, 125.1, 120.0, 21.7. IR ( $\text{cm}^{-1}$ , KBr): 1611  $\nu(\text{C=N})$ , 346  $\nu(\text{Pd-Cl})$ .

## 2.2. Aminocarbonylation reaction

A 50 mL Schlenk flask was charged with iodobenzene (1 mmol), amine (2 mmol),  $K_2CO_3$  (2 mmol) and catalyst ( $5 \cdot 10^{-3}$  mmol). Afterward, 5 mL of distilled water were added. Under balloon pressure of CO, the reaction mixture was stirred at 90 °C for 4 h. Then, the Schlenk flask was cooled down and the organic products were extracted with 3 portions of 7 mL of diethyl ether (3 x 15 min with stirring) and analyzed by GC with mesitylene as the internal standard (0.076 cm<sup>3</sup>, 0.546 mmol). The corresponding amides were isolated by evaporation of the solvents and purification of the crude product by column chromatography on silica gel using hexane and diethyl ether mixture (1:1) as the eluent.

## 2.3. Procedure for catalyst recycling

After the first run, the organic products were separated by extraction (diethyl ether). The aqueous phase containing other reagents was removed to the second vessel by using a stainless steel tube and only the palladium particles were left in the Schlenk flask. Next, the palladium particles were washed with diethyl ether and distilled water. After that, the Schlenk flask was charged again with iodobenzene (1 mmol), amine (2 mmol),  $K_2CO_3$  (2 mmol) and distilled water (5 mL). Under balloon pressure of CO, the reaction mixture was stirred at 90 °C for 4 h. Then, the Schlenk flask was cooled down and the organic products were extracted with 3 portions of 7 mL of diethyl ether or hexane (3 x 15 min with stirring) and then analyzed by GC with mesitylene as the internal standard (0.076 cm<sup>3</sup>, 0.546 mmol).

## 2.4. Analysis of Pd(0) nanoparticles

After the aminocarbonylation reaction of iodobenzene with aniline, the black palladium particles were observed in water and on its surface. The palladium particles were filtered and washed with distilled water, diethyl ether, dried in vacuum and analyzed by elemental analysis.

Found: C 2.77, H 0.30, N 0.19%.

Pd(0) nanoparticles for structural characterization were obtained by reduction of **2a** in water under CO (1 atm) at 90 °C. Under the nitrogen atmosphere **2a** (0.09 g) and  $K_2CO_3$  (0.111 g) were added to water (5 mL). Next, the flask was evacuated and CO was introduced from the balloon (1 atm). The mixture was stirred under CO at 90 °C for 24 h. After that time, the flask was cooled down, the black precipitate was filtered off, dried and analyzed by XPS, XRD and SEM/EDS methods.

## 2.5. X-ray structure determination

Single crystals of **2a** and **3a** suitable for X-ray measurements were obtained by slow evaporation of  $\text{CDCl}_3$  solution.

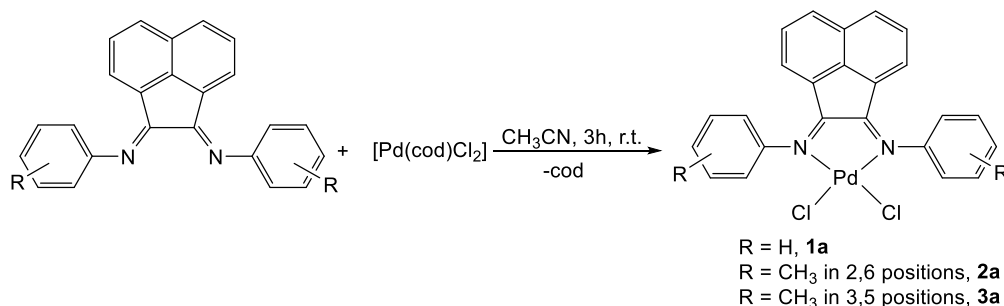
The single crystals were mounted on glass fibers and the diffraction data collected on a KM-4 CCD diffractometer with graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The structures were subsequently solved using direct methods and developed by full least-squares refinement on  $F^2$ . Structural solution and refinement were carried out using SHELX suite of programs.<sup>58</sup> Analytical absorption corrections were performed with CrysAlis RED.<sup>59</sup> C, N, O, Cl and Pd atoms were refined anisotropically. All H atoms were positioned geometrically and refined isotropically using a riding model with a common fixed isotropic thermal parameter. The molecular structure plots were prepared using ORTEP-3 program.<sup>60</sup>

The supplementary crystallographic data for this paper can be obtained from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). CCDC reference codes: 1474030 for **2a** and 1474031 for **3a**.

### 3. Results and discussion

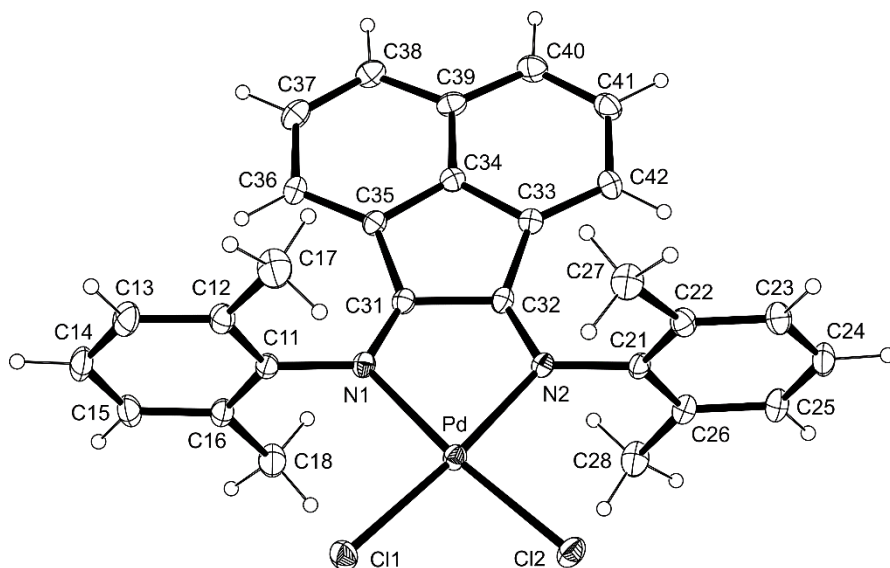
#### 3.1. Synthesis and X-ray structure of $[\text{PdCl}_2(\text{Ar}_2\text{-BIAN})]$ complexes

The three palladium complexes of the general formula  $[\text{PdCl}_2(\text{Ar}_2\text{-BIAN})]$ , **1a** – **3a**, were obtained by substitution of the weakly coordinated 1,5-*cis,cis*-cyclooctadiene (**cod**) of the precursor  $[\text{PdCl}_2(\text{cod})]$  in  $\text{CH}_3\text{CN}$  solution, at room temperature, with the desired  $\text{Ar}_2\text{-BIAN}$  (Scheme 2). Two of these compounds were synthesized earlier by a similar procedure.<sup>61,62</sup> The presence of the  $\text{Ar}_2\text{-BIAN}$  ligands in the palladium coordination sphere was confirmed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy.

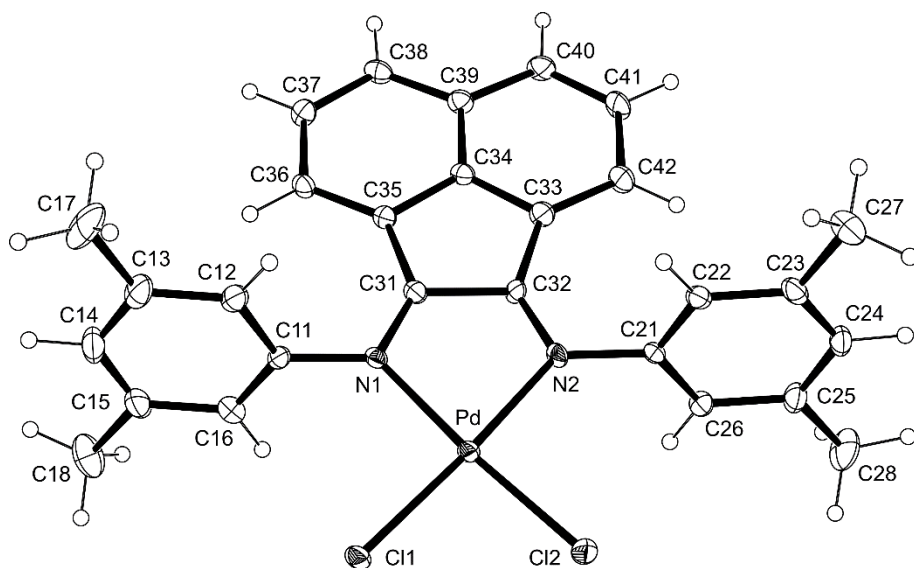


**Scheme 2.** Synthesis of complexes **1a** – **3a**.

Single crystal X-ray analysis revealed that in **2a** and **3a** (Figure 2 and 3, respectively) palladium is coordinated in distorted square-planar geometry (selected bond lengths and angles are reported in the caption of the figures). The N1–C11 and N2–C21 bond lengths in **2a** are slightly longer than the corresponding distances in **3a**. The plane defined by atoms: N1, C11 to C18 and N2, C21 to C28 is perpendicular to the palladium coordination plane in **2a**, while in **3a** this dihedral angle is about 80°.



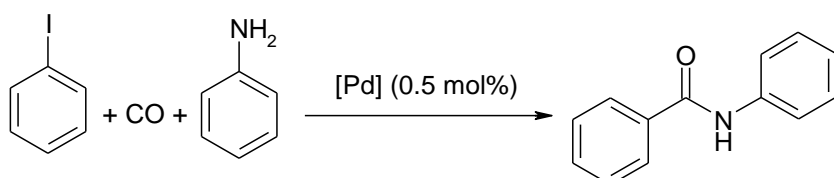
**Figure 2.** Molecular structure of **2a**. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. For clarity, solvent molecules (chloroform and acetone) have been omitted. Selected bond lengths (Å) and angles (°): Pd–Cl1 2.2790(11), Pd–Cl2 2.2757(11), Pd–N1 2.033(3), Pd–N2 2.054(3), N1–C11 1.438(5), N2–C21 1.438(5), C11–Pd–Cl2 92.51(5), C11–Pd–N1 92.44(9), C11–Pd–N2 173.74(9), Cl2–Pd–N2 93.75(10), Cl2–Pd–N1 175.05(9), N1–Pd–N2 81.30(13).



**Figure 3.** Molecular structure of **3a**. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. For clarity, solvent molecules (chloroform) have been omitted. Selected bond lengths (Å) and angles (°): Pd–Cl1 2.2789(16), Pd–Cl2 2.2661(18), Pd–N1 2.039(5), Pd–N2 2.036(5), N1–C11 1.426(8), N2–C21 1.430(8), Cl1–Pd–Cl2 91.44(6), Cl1–Pd–N1 93.74(14), Cl1–Pd–N2 174.70(16), Cl2–Pd–N2 92.98(16), Cl2–Pd–N1 174.26(15), N1–Pd–N2 81.7(2).

### 3.2. Catalytic activity of the palladium complexes, **1a** – **3a**, in the aminocarbonylation reaction

The obtained palladium complexes, **1a** – **3a** were tested as the catalysts in the aminocarbonylation reaction of iodobenzene with aniline, under the optimized reaction conditions (Scheme 3, Table 1).



**Scheme 3.** The model aminocarbonylation reaction.

**Table 1.** Aminocarbonylation reaction of iodobenzene with aniline.<sup>a</sup>

Run	Precatalyst	Pre-treatment time (h) (r.t., P <sub>CO</sub> = 1 atm)	Reaction time (h)	Yield of benzanilide (%) <sup>b</sup>
1	<b>1a</b>	-	1.5	50
2	<b>2a</b>	-	1.5	54
3	<b>3a</b>	-	1.5	55
4	<b>1a</b>	-	4	89
5	<b>2a</b>	-	4	92
6	<b>3a</b>	-	4	94
7	[PdCl <sub>2</sub> (cod)]	-	4	66
8	[PdCl <sub>2</sub> (cod)] + <b>3</b>	-	4	85
9	[PdCl <sub>2</sub> ]	-	4	43
10	[PdCl <sub>2</sub> ] + <b>3</b>	-	4	75
11	<b>3a</b>	-	1	38
12	<b>3a</b>	0.5	1	44
13	<b>3a</b>	3	1	56

<sup>a</sup>Reaction conditions: PhI (1 mmol), aniline (2 mmol), [Pd] 0.5 mol%, CO (1 atm), K<sub>2</sub>CO<sub>3</sub> (2 mmol), water (5 mL), 90 °C. <sup>b</sup> Yield was determined by GC using mesitylene as internal standard.



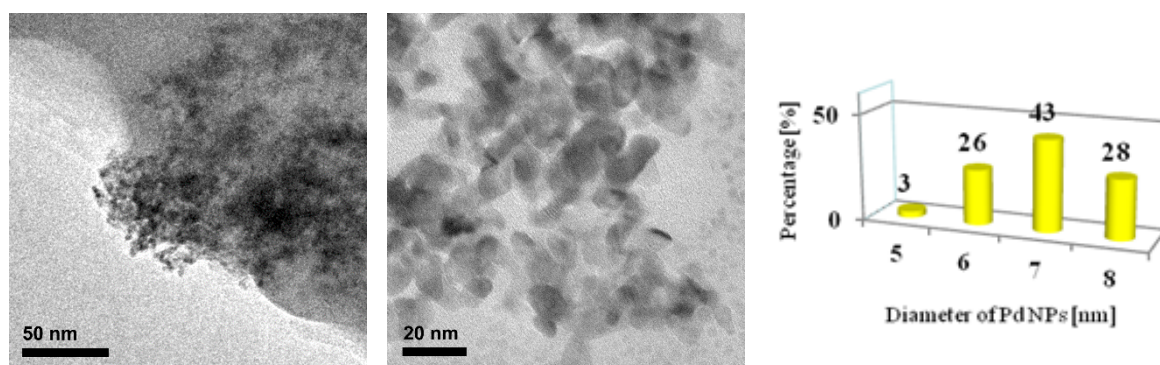
In all cases, the substrates were converted into the desired benzanilide, while no side products were observed, thus the yield of benzanilide corresponds to the conversion of the substrates.

The catalytic activity of the three palladium complexes with the Ar<sub>2</sub>-BIAN ligands, differed only slightly and the yield of benzanilide varied from 50 to 55% after 1.5h and values of 89 to 94% were obtained when prolonging the reaction time up to 4 h, with the catalyst **3a** leading to the best results at both reaction times (Table 1, runs 1 - 6). On the other hand, when [PdCl<sub>2</sub>(cod)] was applied, the activity was significantly lower, with the yield of benzanilide only 66%. However, upon addition of a ligand to the palladium precursor the yield of benzanilide increased to 85% (Table 1, runs 7 and 8). Even stronger effect of the ligand was observed when PdCl<sub>2</sub> was used. In this case, the yield of benzanilide increased from 43 to 75% after introduction of the ligand (Table 1, runs 9 and 10), thus indicating its very positive role on the catalytic activity of the system. It is straightforward to note that the application of the pre-synthesized complexes led to the best results, when compared to the *in situ* formed system.

Two more experiments were carried out in order to evaluate the effect of precatalyst pre-treatment with CO for 0.5 and 3 h before running the catalytic reaction (Table 1, runs 11 - 13). In both cases, the conversion increased and longer pre-treatment resulted in higher yields. This trend suggested that the catalytically active species were formed at the presence of CO and longer exposure resulted in more efficient activation of the precatalyst.

### 3.3. TEM experiment

During the aminocarbonylation reaction, the color of the solution changed from orange, characteristic to the precatalysts, to gray-black, suggesting reduction of Pd(II) to Pd(0). In order to confirm this hypothesis, the post-catalytic reaction mixture was analyzed by TEM. The collected images confirmed that Pd(0) NPs with an average diameter of ca. 7 nm were formed (Figure 4).



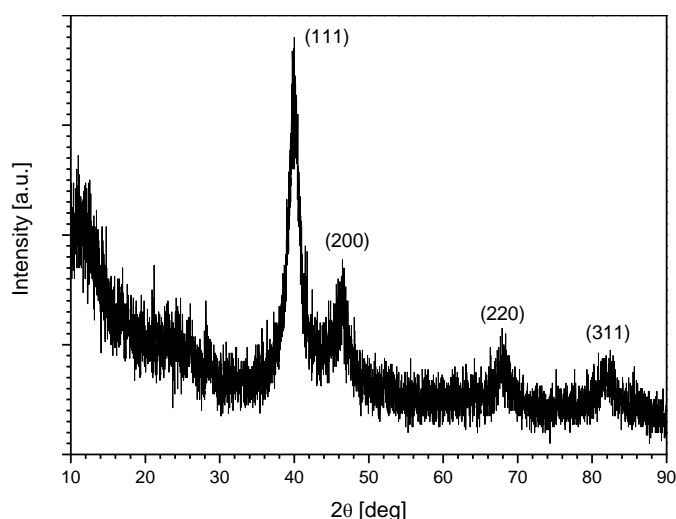
**Figure 4.** TEM images of Pd(0) NPs formed during the aminocarbonylation reaction with **2a** and particle size distribution.

Black Pd(0) particles were also observed on the surface of the aqueous phase during extraction of the products. These particles were collected by filtration, washed with water, **diethyl ether** and dried under vacuum. Elemental analysis of this residue evidenced the presence of carbon (2.77%), hydrogen (0.30%) and nitrogen (0.19%), indicating the presence of an organic material along with palladium. These results suggest that during the catalytic reaction, the formed Pd(0) NPs are surrounded by Ar<sub>2</sub>-BIAN ligand, which plays an important role as a stabilizing agent preventing their agglomeration.

### 3.4. Characterization of palladium nanoparticles

In order to get deeper knowledge about Pd(0) nanoparticles formed from [PdCl<sub>2</sub>(Ar<sub>2</sub>-BIAN)] complexes, reduction of **2a** was performed under the CO atmosphere in aqueous solution containing K<sub>2</sub>CO<sub>3</sub>.

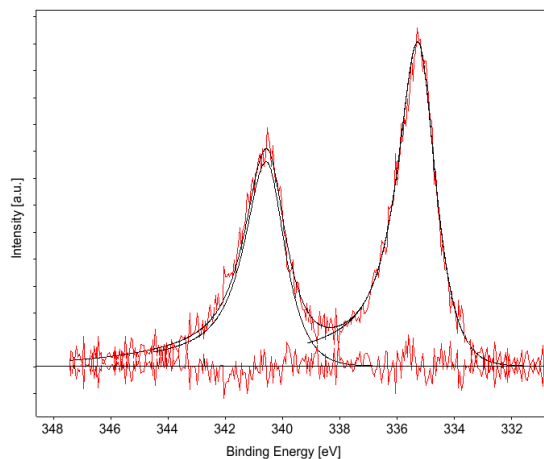
The phase composition of the obtained precipitate was determined by X-ray powder diffraction (XRD). A typical diffractogram reveals several characteristic well-defined peaks (Figure 5), which are attributed to Pd(0) crystallizing in *Fm3m* space group (JCPDS card number 5-681). Broadening of the diffraction lines confirms nanocrystalline nature of the material.



**Figure 5.** X-ray diffraction pattern of Pd(0) nanoparticles obtained by reduction of **2a**.

According to the XPS analysis the sample contained only Pd(0), which was evidenced by the presence of signals at 335.3 eV (Pd 3d<sup>5/2</sup>) and 340.6 eV (Pd 3d<sup>3/2</sup>) (Figure 6). The XPS spectrum

of **2a** measured for the comparison showed signals typical for Pd(II) at 338.0 eV and 343.3 eV. Interestingly, when the amount of  $K_2CO_3$  was decreased by three times, the reduction was not complete and 66% of Pd(0) was found.



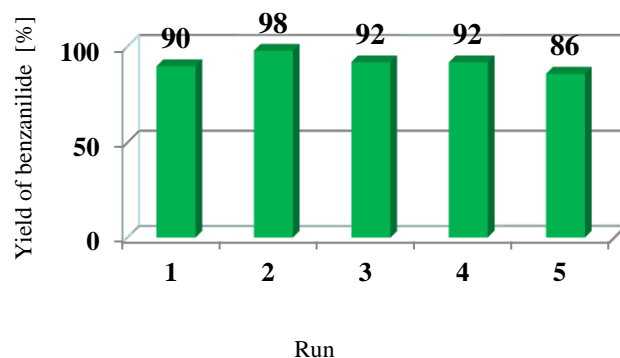
**Figure 6.** XPS spectrum of Pd(0) nanoparticles obtained by reduction of **2a**.

EDS studies undertaken along with the SEM measurements enabled to estimate the distribution of the elements on the Pd(0) nanoparticles surface. Interestingly, in all points nitrogen was found in amounts higher than 6 atom% indicating the presence of  $Ar_2$ -BIAN ligand. Analysis of the chloride content evidenced its presence only in few points in amounts of 0.62-3.09 atom%, considerably smaller than palladium (1.68-23.06 atom%). As expected, chlorides were removed during formation of the Pd NPs.

### 3.5. Recycling of palladium catalyst

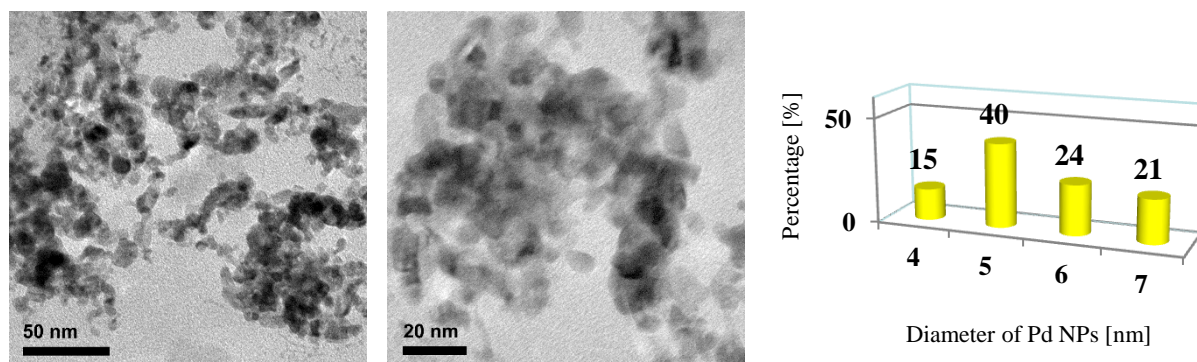
In order to estimate the stability of the Pd nanoparticles formed from **3a** during the catalytic reaction, attempts of their recycling have been undertaken. To achieve this aim, the aminocarbonylation reaction was carried out with **3a**, yielding 90% of benzanilide. The organic products were extracted with diethyl ether and the organic phase was separated from the aqueous phase. The Pd nanoparticles were observed as suspended in the aqueous phase. Water was then transferred to another flask by using a stainless steel tube (catheter tubing). Next, fresh reactants and the solvent were added to the Pd nanoparticles left in the Schlenk flask and the reaction was carried out again for 4 h. This process was repeated 4 times with unexpectedly high efficiency of the catalytic system in each run, with the yield of the desired product always higher than 90%, and the highest value of 98% achieved at the first recycling test. In the fifth run, the activity slightly

decreased, although still 86% of benzanilide was formed (Figure 7). It should be pointed out that these results were obtained without any additional stabilizing agent.



**Figure 7.** Recycling of the **3a** catalyst in aminocarbonylation of iodobenzene with aniline. Reaction conditions: see Table 1.

The TEM analysis of the palladium residue recovered at the end of this experiment evidenced non-agglomerated Pd nanoparticles of the average diameter of 5 nm, slightly smaller as compared to the first catalytic run (Figure 8).



**Figure 8.** TEM images of Pd(0) nanoparticles after five catalytic runs and particle size distribution.

### 3.6. Poisoning tests

With the aim to determine whether the Pd nanoparticles are responsible for the catalytic reaction, the mercury test was performed.<sup>63-66</sup> According to the literature, the addition of Hg(0) to the reaction mixture should result in retarding of the catalytic process due to the formation of

inactive Pd/Hg amalgam. On the other hand, when soluble palladium species are involved in the catalytic process, the catalytic activity should not be effected by the addition of Hg(0).

For the studied reaction, two mercury tests were carried out, differing in the time when Hg(0) was added. When Hg(0) was added to the catalytic system together with the substrates, the conversion of iodobenzene was as low as 24%, while when Hg(0) was added after 60 minutes from the beginning of the catalytic run, the reaction stopped at 35% conversion of iodobenzene (Table 2, Figure 9). Therefore, it is reasonable to conclude that in this reaction palladium nanoparticles are involved in the catalytic process taking place on their **surface**. **Similar heterogeneous mechanism of the aminocarbonylation was suggested for the system based on Pd nanoparticles immobilized on MOF-5,<sup>34</sup> or ZIF-8,<sup>35</sup> on mesocellular foam<sup>36</sup> and binaphthyl-supported<sup>37</sup>.**

An additional indication of the heterogeneous reaction pathway was obtained from the studies of the solution activity after the separation of the Pd nanoparticles. Thus, the catalytic reaction with **2a** was stopped after 1.5 h and the catalyst was removed by filtration. The remaining liquid phase was re-heated under CO (1 atm) for 4 h at **90 °C**. After that time the GC analysis showed 60% conversion of iodobenzene, which corresponds to the yield of benzanilide. The obtained yield was comparable to that obtained after 1.5 h (54%, Table 1) and significantly lower than that noted after 4h (92%, Table 1) of the catalytic reaction.

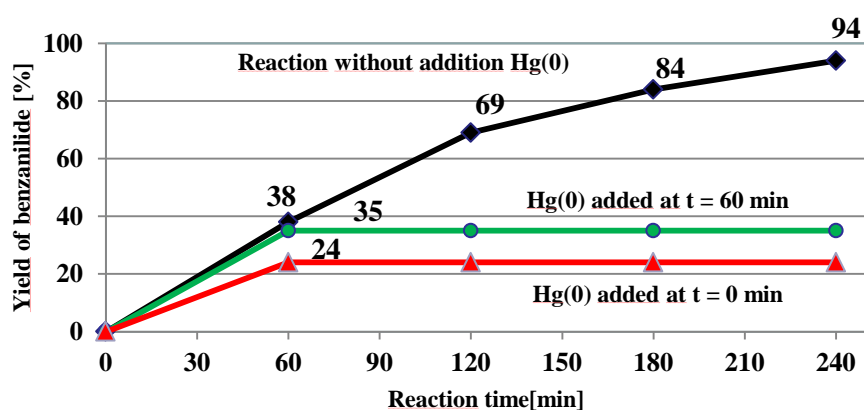
Although recently a new protocol based on a quantitative partial poisoning with tetramethylthiourea has been introduced to distinguish between well-defined molecular and nanoparticle-based catalysts<sup>67</sup>, in addition to the mercury test we applied the standard method based on the use of CS<sub>2</sub> **poison**.<sup>64</sup> Thus, the decrease of the yield of benzanilide at the presence of CS<sub>2</sub> indicated on the limited access of the substrates to the palladium surface covered by CS<sub>2</sub>.

**Table 2.** Aminocarbonylation reaction of iodobenzene catalyzed by Pd-(Ar<sub>2</sub>-BIAN) -effect of Hg, CS<sub>2</sub> and TBAB<sup>a</sup>

Poison additive	Yield of benzanilide (%)
None	94
Hg added at the beginning of the reaction	24
Hg added after 60 min	35
CS <sub>2</sub> , 0.65 mol%	77
CS <sub>2</sub> , 1 mol%	67
CS <sub>2</sub> , 1.5 mol%	62
TBAB, 5 mol%	89
TBAB, 10 mol%	77

TBAB, 15 mol%	66
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<sup>a</sup> Reaction conditions: 90 °C, **3a** 0.5 mol%, PhI (1 mmol), aniline (2 mmol), CO (1 atm), K<sub>2</sub>CO<sub>3</sub> (2 mmol), water 5 mL, 4 h, [Hg]/[Pd] = 300.



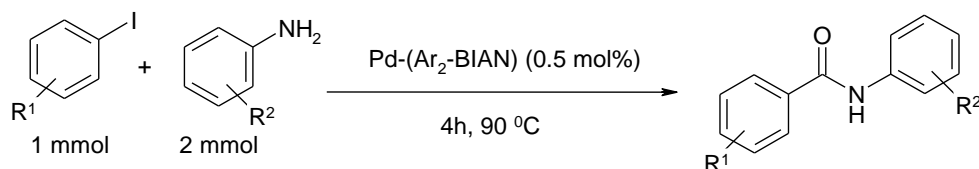
**Figure 9.** Aminocarbonylation reaction of iodobenzene at the presence of Hg(0). Reaction conditions see Table 2.

Next, the effect of TBAB (tetrabutylammonium bromide) on the reaction course was studied. It can be expected that stabilization of Pd nanoparticles would increase at the presence of ammonium salt, resulting in the reactivity **increase**.<sup>68</sup> However, another effect should also be considered, namely intensive dissolution of Pd NPs while heating with PhI at the presence of TBAB<sup>69</sup>. Thus, we decided to test the effect of TBAB by adding it to the reaction mixture in 10- to 30-fold excess with respect to palladium. As a result, the yield of benzanilide decreased (Table 2). Considering the fact that formation of the soluble palladium species was very plausible under the applied conditions, it can be concluded that their activity was remarkably lower than that of Pd NPs.

Interestingly, in a similar reaction, such as carbonylative Suzuki coupling, soluble palladium species that leached from the Pd nanoparticles during the catalytic process were considered to be catalytically active.<sup>70, 71</sup>

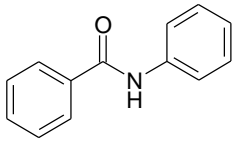
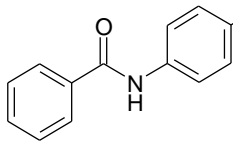
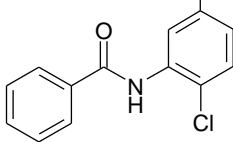
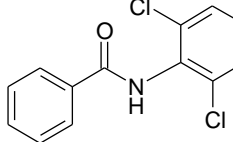
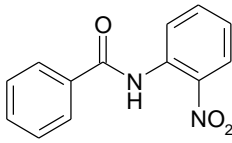
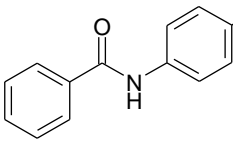
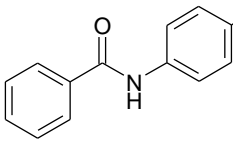
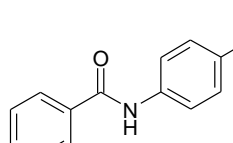
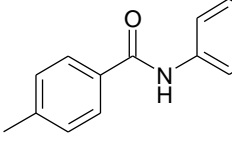
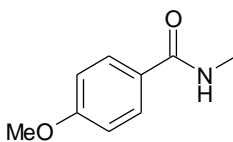
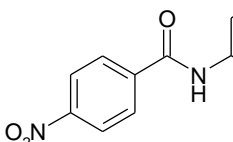
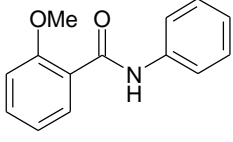
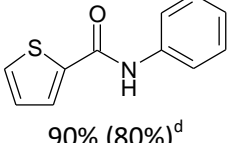
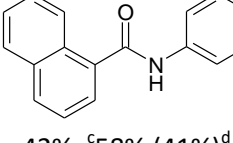
### 3.7. Aminocarbonylation reactions of iodobenzene with substituted anilines

The scope of the reaction was expanded by using substituted anilines (Scheme 4) under the optimized reaction conditions and using **2a** as the precatalyst (Table 3).



**Scheme 4.** Aminocarbonylation reaction of aryl iodides with substituted anilines.

**Table 3.** Aminocarbonylation reaction of aryl iodides with substituted anilines. <sup>a,b</sup>

 92% (84%) <sup>c</sup>	 81%, (73%) <sup>c</sup>	 98%, (90%) <sup>c</sup>	 47%, (40%) <sup>c</sup>
 53%, (45%) <sup>c</sup>	 72%, (67%) <sup>c</sup>	 86%, (80%) <sup>c</sup>	 98%, (91%) <sup>c</sup>
 74% (65%) <sup>d</sup>	 60%, <sup>c</sup> 81% (73%) <sup>d</sup>	 31%, <sup>c</sup> 46% (33%) <sup>d</sup>	 70%, <sup>c</sup> 100% (88%) <sup>d</sup>
	 90% (80%) <sup>d</sup>	 42%, <sup>c</sup> 58% (41%) <sup>d</sup>	

<sup>a</sup> **2a** (0.5 mol%), K<sub>2</sub>CO<sub>3</sub> (2 mmol), water (5 mL), aryl iodide (1 mmol), substituted aniline (2 mmol), CO (1 atm), 90 °C, 4 h. <sup>b</sup> Conversions were determined by GC using mesitylene as internal standard. <sup>c</sup> 6h. <sup>d</sup> Isolated yield.

It is worth to **note that** in these reactions only one kind of product (secondary amide) was obtained, thus indicating that even with substituted anilines or substituted iodobenzenes the catalyst is extremely selective.

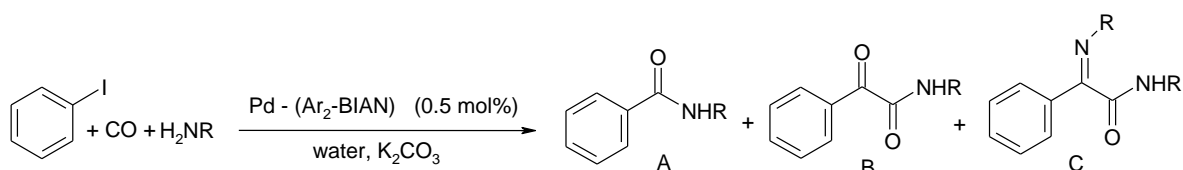
On the other hand, a remarkable effect of the substituents of the aniline on the activity of the catalyst was observed. The best results were obtained with the 2,5-dichloroaniline and 4-acetylaniline, which led to almost complete conversion to the corresponding benzanilides. For all the other substrates conversions lower than that of the simple aniline were observed. Indeed, the presence of either electron withdrawing or electron repulsing substituents in *para* position resulted in a decrease of the **activity**. That was even more pronounced when the substituents were in *ortho*

position. These data suggest that both the electronic and steric effect remarkably affect in a negative way the activity of the catalyst.

An effect of the substituents of the iodobenzene was also noted. The presence of electron withdrawing group (1-iodo-4-nitrobenzene) in *para* position led to lower conversion than that obtained for electron repulsing substituents (4-iodoanisole and 4-iodotoluene). On the other hand, methoxy substituent in *ortho* position increased conversion to the corresponding benzanilide compared to methoxy substituent in *para* position. Very good result, 90% conversion to the corresponding benzanilide, was obtained for 2-iodothiophene.

### 3.8. Aminocarbonylation reactions of iodobenzene with aliphatic amines

As far as aliphatic amines are concerned, it is well known that with these substrates the aminocarbonylation is less selective than with aromatic ones<sup>72</sup>. Except the expected amide,  $\alpha$ -ketoamide and  $\alpha$ -iminoamide may also be formed in these reactions (Scheme 5). Various additives have been used to improve the selectivity and very good results have been obtained when DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) was used.<sup>73,74</sup>



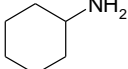
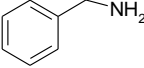
**Scheme 5.** The aminocarbonylation reaction of iodobenzene with aliphatic amines.

We decided to test our catalytic system in the aminocarbonylation reaction of four aliphatic amines without any additional agents (Table 4). Initially, the catalytic reactions were run for 4 h leading to moderate conversions which increased to more than 90% with prolonging the reaction time up to 6 h.

Table 4. Results of aminocarbonylation of iodobenzene with aliphatic amines.<sup>a, b</sup>

Amine	Entry	Amount of amine [mmol]	T [°C]	Time [h]	CO [atm]	Conv. C <sub>6</sub> H <sub>5</sub> I [%] <sup>b</sup>	Yield A [%]	Yield B [%]	Yield C [%]
H <sub>2</sub> N(C <sub>6</sub> H <sub>13</sub> )	1	2	60	4	1	67	57	1	9
	2	2	60	6	1	91	60	4	27
	3	1.1	60	6	1	85	40	26	16
	4	3	60	6	1	93	63	11	19
	5	5	60	6	1	94	76 (64) <sup>c</sup>	3	15
	6	1.1	60	6	10	80	29	36 (25) <sup>c</sup>	15
	7	1.1	90	4	10	91	20	54	17



H <sub>2</sub> N(C <sub>4</sub> H <sub>9</sub> )	9	2	60	4	1	61	25	17	19
	10	2	60	6	1	95	22	35	36
	11	1.1	60	6	1	78	16	44	14
	12	5	60	6	1	90	69 (56) <sup>c</sup>	3	18
	13	1.1	60	6	10	74	8	54 (40) <sup>c</sup>	12
	14	1.1	90	4	10	94	8	70	16
	15	2	60	4	1	79	23	38	17
	16	2	60	6	1	82	24	24	30
	17	1.1	60	6	1	75	13	45	14
	18	5	60	6	1	90	31 (19) <sup>c</sup>	7	52
	19	1.1	60	6	10	70	9	50 (35) <sup>c</sup>	11
	20	1.1	90	4	10	94	7	75	12
	21	2	90	4	1	97	63	15	0
	22	1.1	60	6	1	61	23	36	0
	23	5	60	6	1	64	57 (43) <sup>c</sup>	7	0
	24	1.1	60	6	10	81	11	70 (60) <sup>c</sup>	0
	25	1.1	90	4	10	100	10	90	0

<sup>a</sup>Reaction conditions: **2a** (0.5 mol%), PhI (1 mmol), water (5 mL), K<sub>2</sub>CO<sub>3</sub> (2 mmol),

<sup>b</sup> Conversion was determined by GC using mesitylene as internal standard.

<sup>c</sup> Isolated yield

The obtained data indicated that the reaction selectivity into the specified product was influenced mainly by the [RNH<sub>2</sub>]/[PhI] ratio. In general, an increase of the amine amount favored formation of the amide, while at lower concentration of the amine, [RNH<sub>2</sub>]/[PhI] = 1/1, the yield of  $\alpha$ -ketoamide was higher.

On increasing the CO pressure from 1 to 10 atm a remarkable decrease in the selectivity into amide in favor of the double carbonylated adduct, the  $\alpha$ -ketoamide, was observed. Further improvement of the yield of  $\alpha$ -ketoamide was achieved after temperature increase to 90 °C. Under these conditions 90% of  $\alpha$ -ketoamide was formed in the reaction with benzylamine (Table 4, entry 25).

In the reactions with n-hexylamine the amount of the amide increased from 40 to 76% when [RNH<sub>2</sub>]/[PhI] ratio was changed from 1.1 to 5 (Table 4, entry 3 and 5). The highest yield of the  $\alpha$ -ketoamide, 54%, was obtained at 10 atm of CO and 90 °C (Table 4, entry 7).

Similarly reacted n-butylamine, which formed 69% of the amide at a 5-fold excess of the amine to PhI (Table 4, entry 12). On the other hand, formation of the  $\alpha$ -ketoamide was preferred at [RNH<sub>2</sub>]/[PhI] ratio equal to 1.1, enabling to obtain 44% of this product at 1 atm of CO (Table 4, entry 11) and 70% at 10 atm of CO and 90 °C (Table 4, entry 14).

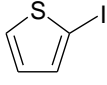
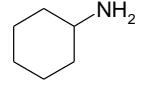
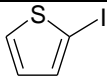
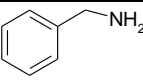
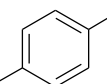
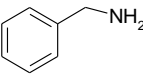
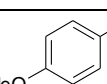
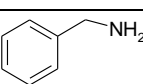
The reaction with cyclohexylamine was less selective and the highest yield of the amide was 31% (Table 4, entry 18), whereas 50% of the  $\alpha$ -ketoamide was obtained after using CO at the

pressure of 10 atm at 60 °C (Table 4, entry 19). At 90 °C the yield of  $\alpha$ -ketoamide increased to 75% (Table 4, entry 20).

In all these reactions the high basicity of the amine ( $pK_b = 3.31 - 3.43$ ) facilitated formation of the  $\alpha$ -iminoamide side-product in amount between 11 and 56%. In contrast, less basic benzylamine ( $pK_b = 4.94$ ) provided more selective reaction conditions, without formation of the  $\alpha$ -iminoamide. At the  $[RNH_2]/[PhI]$  ratio equal to 2 the reaction produced 63% of the amide (Table 4, entry 21). The best conditions for the  $\alpha$ -ketoamide were found with equimolar amounts of the amine and PhI employed at 10 atm of CO (Table 4, entry 24 and 25 ).

In further studies the aminocarbonylation reaction of three iodoaromatic substrates with aliphatic amines under conditions optimized for iodobenzene were performed (Table 5).

**Table 5.** Results of aminocarbonylation of aryl iodides with aliphatic amines.<sup>a, b</sup>

Aryl iodide	Amine	Entry	Amount of amine [mmol]	T [°C]	Time [h]	CO [atm]	Conv. C <sub>6</sub> H <sub>5</sub> I [%] <sup>b</sup>	Yield A [%]	Yield B [%]	Yield C [%]
		1	1.1	90	4	10	100	34	60 (45) <sup>c</sup>	6
		2	5	60	6	1	58	53 (44) <sup>c</sup>	3	2
		3	1.1	90	4	10	100	39	61 (48) <sup>c</sup>	0
		4	5	60	6	1	53	51 (40) <sup>c</sup>	2	0
		5	1.1	90	4	10	100	8	92 (80) <sup>c</sup>	0
		6	5	60	6	1	47	32 (18) <sup>c</sup>	15	0
		7	1.1	90	4	10	100	4	96 (85) <sup>c</sup>	0
		8	5	60	6	1	42	12	30	0

<sup>a</sup>Reaction conditions: **2a** (0.5 mol%), PhI (1 mmol), water (5 mL), K<sub>2</sub>CO<sub>3</sub> (2 mmol),

<sup>b</sup> Conversion was determined by GC using mesitylene as internal standard. <sup>c</sup> Isolated yield

2-Iodothiophene reacted with cyclohexylamine forming 60%  $\alpha$ -ketoamide at 10 atm of CO and 90 °C (Table 5, entry 1). At 1 atm of CO amide was predominantly formed with the yield 53% (Table 5, entry 2). In this reactions was small amount of  $\alpha$ -iminoamide was also formed.

Similar yield of  $\alpha$ -ketoamide (61%) and amide (51%) were obtained in aminocarbonylation of 2-iodothiophene with less basic benzylamine (Table 5, entry 3 and 4). In these reactions side-product was not found.

Very good selectivity to  $\alpha$ -ketoamide was noted in reactions of 4-iodotoluene and 4-iodoanisole with benzylamine at 10 atm of CO (Table 5, entry 5 and 7). The corresponding  $\alpha$ -ketoamides were obtained in amount 92% and 96%, slightly higher when compare with iodobenzene. On decreasing of the CO pressure from 10 atm to 1 atm the yield of amides increased for both substrates to 32% and 12% (Table 5, entry 6 and 8). Interestingly, 4-iodoanisole reacted mainly to the  $\alpha$ -ketoamide even at 1 atm of CO and 60 °C.

### 3.9. Plausible mechanism of aminocarbonylation.

Considering the results of the performed poisoning tests and composition of the obtained products, a plausible mechanism for the studied reaction can be proposed (Figure 10). Initially, the Pd(II) precursor is converted *in situ* into Pd-(Ar<sub>2</sub>-BIAN) nanoparticles that is the catalytically active form. Subsequent steps of the reaction occur on the surface of Pd-(Ar<sub>2</sub>-BIAN) NPs and are similar to those proposed in the literature.<sup>74, 75</sup> Thus, oxidative addition of iodobenzene followed by migratory insertion of CO lead to the acyl intermediate 2.

Nucleophilic attack of the amine on the acyl ligand results in formation of the amide (pathway 1). Alternatively, the amine coordinates to the intermediate 2, which is transformed into the acyl-amide intermediate 4 at the presence of CO (pathway 2). Formation of the C-C bond on the species 4 followed by reductive elimination leads to the dicarbonylation product,  $\alpha$ -ketoamide. Preference of the pathway 1 over 2 is determined by the basicity of the used amine. Less basic, aromatic amines, reacted exclusively according to pathway 1, while increased basicity of amine favored the dicarbonylation pathway 2.

The intermediate 4 can also react with a second molecule of the amine by its nucleophilic attack on the acyl group. In this case, the side product,  $\alpha$ -iminoamide is formed. Formation of this product is preferred for strong Lewis bases, such as cyclohexylamine.

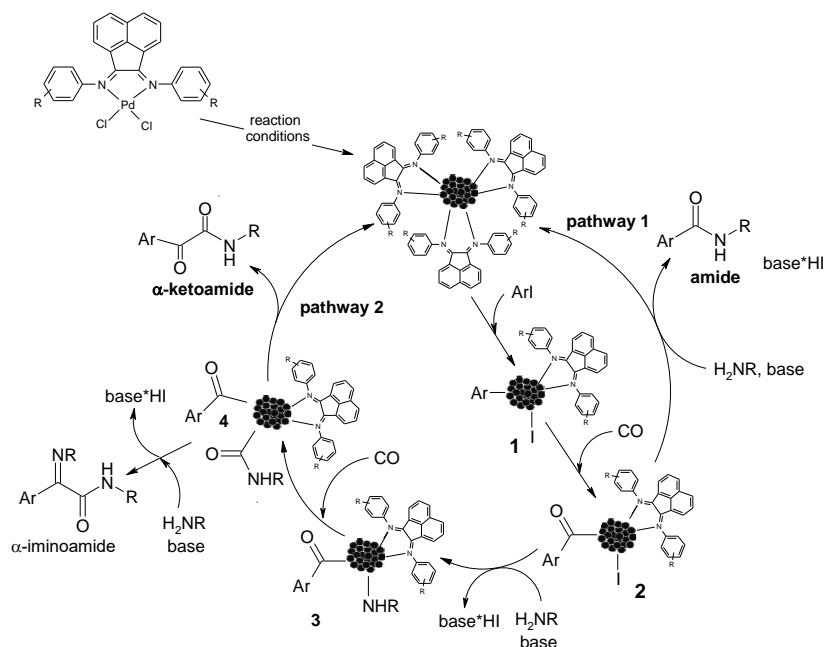


Figure10. Plausible reaction mechanism.

## Conclusions

In summary, we have developed novel nanosized palladium catalysts for the aminocarbonylation of iodobenzene with either aromatic or aliphatic amines in aqueous medium. The catalysts, formed *in situ* from  $[\text{PdCl}_2(\text{Ar}_2\text{-BIAN})]$  complexes, comprises of the Pd(0) nanoparticles stabilized with  $\text{Ar}_2\text{-BIAN}$  ligands. They can be easily recovered and reused in several catalytic runs with high activity. In reaction with aromatic amines, amides were formed as the only products. In contrast, in the reaction with aliphatic amines,  $\alpha$ -ketoamides were also formed. The yield of  $\alpha$ -ketoamides increased at lower concentration of the amine and at higher CO pressure (10 atm).

The carbonylation reactions of iodobenzene with aromatic amines studied by us proceed under milder conditions than the aminocarbonylation reactions in water presented so far in the literature.<sup>15, 50-52</sup> For example, according to the previous papers, benzanilide has been obtained in 8 hours at 2-14 atm of CO and with the amount of the catalyst 1-2 mol%. The aminocarbonylation reactions catalyzed by the commercially available catalyst Pd/C also required more harsh conditions than applied by us. In the reactions catalyzed by Pd/C the authors used higher amounts of the catalyst (minimum 2 mol%), CO pressure higher than 1 atm and the temperature in the range 100-140 °C.<sup>18, 19</sup> Our catalytic system works efficiently under more attractive reaction conditions.

Advantageously, the reaction conditions used by us for the double carbonylation are more attractive than these reported till now for this process. Our reactions were performed in 4 h whereas in most cases longer time, 8-24 h<sup>14, 38, 41, 42 47, 76, 77</sup> was needed to reach the high conversion. The CO pressure equal 10 atm was significantly lower than used by other authors (20-40 atm).<sup>14, 38-40, 42, 47, 73, 78</sup> Finally, the amount of the catalyst, 0.5 mol%, was smaller than in other systems.<sup>38-40, 42, 73, 77</sup>

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