Máté Papp, Béla Urbán, Eszter Drotár and Rita Skoda-Földes*

Mono- and double carbonylation of iodobenzene in the presence of reusable supported palladium catalysts

Abstract: Various silica-supported palladium catalysts were prepared and tested in the carbonylation of aryl iodides in the presence of aliphatic amines and aniline. In the former reaction, the main products are the α-ketoamides, whereas monocarbonylation is favoured with aniline. Small modification of the support, of the palladium precursor, or of the conditions of immobilisation were found to affect considerably the outcome of the reactions and recyclability of the catalysts. Under optimum conditions, the phosphine-free palladium catalysts can be reused six to ten times without considerable loss of activity. By the proper selection of the solvent, the leaching of palladium into the reaction mixtures can be reduced considerably.

Keywords: carbonylation; ionic liquid; ketoamide; palladium; silica support.

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1 Introduction

Transition metal catalysed carbonylation and coupling reactions are widely used in synthetic chemistry. Reaction of amines, aryl halides, and carbon monoxide in the presence of a palladium catalyst leads to amides and α-ketoamides, via mono- and double carbonylation processes, respectively. Both types of products have practical importance: the amide functionality is an important motif in a lot of biologically active molecules [1] and some α-ketoamides also show interesting pharmacological properties, such as anti-HIV activity [2] or HCV protease inhibition [3].

In most cases, carbonylations are carried out under homogeneous conditions [1, 4], which hinder industrial applications because of problems in catalyst recovery and recycling. One of the possibilities to overcome these difficulties is the use of catalysts immobilised on solid supports [5].

Synthesis of amides via monocarbonylation by heterogeneous catalysts is usually effected under moderate CO pressure (3–20 bar). A great variety of supported palladium catalysts were tested, such as Pd/C [6], a polymer- [7] or silica-supported palladium-N-heterocyclic carbene- [8], palladium-Schiff base- [9] or palladium-phosphine complex, [10], a palladium-phenantroline derivative encaged in Y-zeolite [11], and Pd nanoparticles immobilised on a zeolitic imidazole framework [12] or on carbon nanotubes [13]. In some cases, carbonylation could be carried out at atmospheric pressure, e.g., in the presence of palladium complexes with bidentate ligands anchored on MCM-41 [14] or on silica [15–17], as well as using palladium nanoparticles supported on a metal-organic framework [18] or on a siliceous mesocellular foam [19]. Whereas an efficient recycling can be achieved in most cases at elevated pressure [7–9, 11–19], under atmospheric conditions a substantial drop of activity was often observed upon the reuse of the catalyst [18, 19].

Double carbonylation reactions catalysed by heterogeneous palladium catalysts are still rare. α-Ketoamides were synthesised under 30–40 bar CO pressure with a silica-supported polytitazane-palladium (Ti-N-Pd) complex [20], a Pd/C+PPh_3 system [21] with palladium nanoparticles supported on a cross-linked functional polymer [22] or with palladium-phosphine complexes grafted onto mesoporous silica (SBA-15) [23]. A commercially available supported $Pd(PPh_3)_4$ catalyst was used efficiently under flow conditions [24]. In all of these double carbonylation reactions, a competing monocarbonylation, leading to amides, was observed. Interestingly, double

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***Corresponding author: Rita Skoda-Földes,** Institute of Chemistry, Department of Organic Chemistry, University of Pannonia, H-8201 Veszprém, P.O.Box 158, Hungary,
e-mail: skodane@almos.uni-pannon.hu
Máté Papp and Béla Urbán: Institute of Chemistry, Department of Organic Chemistry, University of Pannonia, H-8201 Veszprém, P.O.Box 158, Hungary
Eszter Drotár: Research Centre for Natural Sciences, Institute of Materials and Environmental Chemistry, Hungarian Academy of Sciences, H-1519 Budapest, P.O. Box 286, Hungary

carbonylation as a side reaction of monocarbonylation under heterogeneous conditions was reported only in one case [11], in spite of the fact that homogeneous catalytic aminocarbonylation may lead to α-ketoamides in considerable amounts even at atmospheric pressure [25].

Despite the growing number of reports on aminocarbonylation under heterogeneous conditions, little is known about the true nature of the catalysts, and it is difficult to compare the results obtained by different catalytic systems.

Recently, we reported on the excellent recyclability of phosphine-free silica-palladium catalysts stabilised by ionic liquids in double carbonylation reactions [26]. Similar systems supported on silica [8, 27] or a polymer [7] were applied for monocarbonylation by others. However, there was no indication why those particular sets of conditions ($PdCl_2$ precursor immobilised in acetonitrile on silica functionalised by imidazolium chloride [8, 27] and $Pd(OAc)_2$ precursor supported in DMF and aq. Na_2CO_3 on a similarly modified Merrifield resin [7]) were used during the preparation of the heterogeneous catalysts.

According to our own results, modification of the support, of the palladium precursor, or of conditions of immobilisation may affect considerably the selectivity and recyclability of the catalysts. The catalytic systems can really be very complicated, as both palladium nanoparticles and palladium complexes formed under catalytic conditions may play a role in the aminocarbonylation. Moreover, palladium either adsorbed on the surface of the support or dissolved in the reaction mixture (or both) may be involved.

In the present paper, the main emphasis is on the detailed investigation of the influence of immobilisation methodology on the activity, selectivity, and recyclability of the catalysts. In case of the most suitable catalysts, carbonylation conditions are also optimised.

2 Materials and methods

Reagents, solvents and catalyst precursors were purchased from Sigma-Aldrich, Budapest, Hungary ($Pd_2(dba)_3$*$CHCl_3$, $Pd(OAc)_2$, $PdCl_2$, $Pd(PPh_3)_4$, PPh_3, [BMIM]BF_4, aryl iodides, aniline, pyrrolidine, morpholine, DMF, Et_3N); Merck, Budapest, Hungary (piperidine, diethylamine, acetonitrile, THF, ethanol, diethylether), and Messer, Budapest, Hungary (CO).

2.1 Preparation of the supported catalysts

2.1.1 Preparation of CAT-1/1: 200 mg [BMIM][BF_4] and 0.02 mmol (20.7 mg) $Pd_2(dba)_3.CHCl_3$ were dissolved in a mixture of 2 ml acetonitrile and 2 ml THF. The mixture was stirred for 15 min at room temperature. Then, 550 mg silica [Kieselgel 60 (0.040–0.063 mm), Merck, pre-treated by heating for 5 h at 250°C] was added under stirring and the resulting mixture was stirred for 24 h. The solvents were removed *in vacuo*, and the catalyst was dried at 35°C *in vacuo* for 3 h and was stored under argon until use. Palladium content of the catalyst: 0.40% (determined by ICP).

2.1.2 Preparation of CAT-1/2: 200 mg [BMIM][BF_4] and 0.04 mmol (8.7 mg) $Pd(OAc)_2$ were dissolved in a mixture of 2 ml acetonitrile and 2 ml THF. The mixture was stirred for 15 min at room temperature. Then 550 mg silica [Kieselgel 60 (0.040–0.063 mm), Merck, pre-treated by heating for 5 h at 250°C] was added under stirring, and the resulting mixture was stirred for 24 h. The solvents were removed *in vacuo*, and the catalyst was dried at 35°C *in vacuo* for 3 h and was stored under argon until use. The palladium content of the catalyst: 0.49% (determined by ICP).

2.1.3 Preparation of CAT-1/3: 200 mg [BMIM][BF_4] and 0.04 mmol (15.3 mg) dichloro-bis(1-butyl-3-methylimidazol-2-ylidene)palladium-(II), ($Pd(BMIM)_2Cl_2$), prepared by a known method [28]) were dissolved in a mixture of 2 ml acetonitrile and 2 ml THF. The mixture was stirred for 15 min at room temperature. Then 550 mg silica (Kieselgel 60 (0.040-0.063 mm), Merck, pre-treated by heating for 5 h at 250°C) was added under stirring, and the resulting mixture was stirred for 24 h. The solvents were removed *in vacuo*, and the catalyst was dried at 35°C *in vacuo* for 3 h and was stored under argon until use. Palladium content of the catalyst: 0.36% (determined by ICP).

2.1.4 Preparation of CAT-1/4: Two hundred milligrams [BMIM][BF_4] and 0.04 mmol (46.2 mg) $Pd(PPh_3)_4$ were dissolved in a mixture of 2 ml acetonitrile and 2 ml THF. The mixture was stirred for 15 min at room temperature. Then 550 mg silica [Kieselgel 60 (0.040–0.063 mm), Merck, pre-treated by heating for 5 h at 250°C] was added under stirring and the resulting mixture was stirred for 24 h. The solvents were removed *in vacuo*, and the catalyst was dried at 35°C *in vacuo* for 3 h and was stored under argon until use. Palladium content of the catalyst: 0.55% (determined by ICP).

2.1.5 Preparation of CAT-1/5: Two hundred milligrams [BMIM][BF_4], 0.04 mmol (46.2 mg) $Pd(PPh_3)_4$ and 0.08 mmol (21.0 mg) PPh_3 were dissolved in a mixture of 2 ml acetonitrile and 2 ml THF. The mixture was stirred for 15 min at room temperature. Then 550 mg silica (Kieselgel 60 (0.040-0.063 mm), Merck, pre-treated by heating for 5 h at 250°C) was added under stirring and the resulting mixture was stirred for 24 h. The solvents were removed *in vacuo*, and the catalyst was dried at 35°C *in vacuo* for 3 h and was stored under argon until use. Palladium content of the catalyst: 0.54% (determined by ICP).

2.1.6 Preparation of CAT-2/1: The silica-supported ionic liquid phase **SILP-2** was prepared as described previously [26].

A solution of 8.95 µmol (9.3 mg) $Pd_2(dba)_3.CHCl_3$ in 2 ml acetonitrile, and 2 ml THF was stirred for 15 min. Then, 500 mg of **SILP-2** was added, and the resulting mixture was stirred for 24 h at room temperature. After evaporation of the solvents, the catalyst was dried at 35°C *in vacuo* for 3 h. Palladium content of the catalyst: 0.29% (determined by ICP).

2.1.7 Preparation of CAT-2/2: A solution of 17.9 μmol (4 mg) $Pd(OAc)_2$ in 2 ml EtOH was stirred for 15 min. Then, 500 mg of **SILP-2** was added, and the resulting mixture was stirred for 24 h at room temperature. The catalyst was filtered, washed with ethanol (2 ml) and diethylether (2 ml), and dried at 35°C *in vacuo* for 3 h. Palladium content of the catalyst: 0.77% (determined by ICP).

2.1.8 Preparation of CAT-2/3: A solution of 17.9 μmol (3.2 mg) $PdCl_2$ in 2 ml EtOH was stirred for 15 min. Then, 500 mg of **SILP-2** was added, and the resulting mixture was stirred for 24 h at room temperature. The catalyst was filtered, washed with ethanol (2 ml) and diethylether (2 ml), and dried at 35°C *in vacuo* for 3 h. Palladium content of the catalyst: 0.26% (determined by ICP).

2.1.9 Preparation of CAT-2/4: A solution of 20 μmol (3.5 mg) $PdCl_2$ in 1 ml acetonitrile was refluxed in an inert atmosphere for 2 h. The solvent was evaporated *in vacuo*, and the residue was dissolved in 2 ml EtOH, and the mixture was stirred for 15 min. Then 400 mg of **SILP-2** was added, and the resulting mixture was stirred for 24 h at room temperature. The catalyst was filtered, washed with ethanol (2 ml) and diethylether (2 ml) and dried at 35°C *in vacuo* for 3 h. Palladium content of the catalyst: 0.38% (determined by ICP).

2.1.10 Preparation of CAT-2/5: A solution of 14.8 μmol (15.3 mg) $Pd_2(dba)_3.CHCl_3$ in 2 ml EtOH was stirred for 15 min. Then, 500 mg of **SILP-2** was added, and the resulting mixture was stirred for 5 days at room temperature. The catalyst was filtered, washed with ethanol (2 ml), and diethylether (2 ml) and dried at 35°C *in vacuo* for 3 h. Palladium content of the catalyst: 0.44% (determined by ICP).

2.1.11 Preparation of Pd/silica: A total of 0.02 mmol (20.7 mg) $Pd_2(dba)_3.CHCl_3$ was dissolved in a mixture of 2 ml acetonitrile, and 2 ml THF. The mixture was stirred for 15 min at room temperature. Then 550 mg silica [Kieselgel 60 (0.040-0.063 mm), Merck, pre-treated by heating for 5 h at 250°C] was added and the resulting mixture was stirred for 24 h. The solvents were removed *in vacuo* and the catalyst was dried at 35°C *in vacuo* for 3 h and was stored under argon until use. Palladium content of the catalyst: 0.55% (determined by ICP).

2.2 Catalytic reactions

2.2.1 Catalytic reactions at atmospheric pressure: In a typical experiment, a solution containing the palladium catalyst (with 3.6 μmol Pd-content) was placed in a Schlenk-tube. Under argon, 0.2 mmol (22.5 μl) iodobenzene (**1**), 0.5 mmol (44 μl) morpholine (**2a**), 0.25 mmol (35 μl) triethylamine, and 1 ml DMF was added, and the atmosphere was changed to carbon monoxide. The reaction was conducted for 3 h at 100°C. The reaction mixture was analysed by gas chromatography.

2.2.2 Catalytic reactions at elevated pressure: In a typical experiment, the catalyst (containing 3.6 or 6 μmol Pd) was placed in a stainless steel autoclave. Aryl iodides (**1** and **6a-f**) (0.2 mmol), the amine (**2a-e**) (0.5 mmol), 0.25 mmol (35 μl) or 0.7 mmol (100 μl) triethylamine and solvent (1 ml) were transferred into it under an inert atmosphere. It was charged with carbon monoxide (30 bar or 5 bar) and heated with stirring in an oil bath at 100°C. After cooling to room temperature, the liquid phase was removed with a syringe. The reaction mixture was analysed by gas chromatography and the catalyst was reused.

2.3 Analytical measurements

Reaction mixtures were analysed by gas chromatography (Hewlett Packard 5890) and GC-MS (Hewlett Packard 5971A GC-MSD, HP-1 column). Conversions and selectivities of the reactions were determined by GC using ferrocene as internal standard. Transmission Electron Microscope (TEM) investigations were carried out by a FEI MORGAGNI 268D Transmission Electron Microscope (accelerating voltage: 100kV, W-filament). NMR spectra were recorded in $CDCl_3$ on a Varian Inova 400 spectrometer at 400 MHz. The palladium-content of the catalysts and palladium leaching were determined by ICP on a Perkin Elmer Optima 2000 DV instrument.

The products were identified on the basis of their MS spectra. The main products, **3a**, **3c–e**, **4b** and **7a–f** were also characterised by ^1H NMR. Spectra of **3a**, **3c–e**, **7a** and **7d** correspond well to literature data [29].

3a:^1H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.96–7.93 (m, 2H); 7.67–7.63 (m, 1H); 7.54–7.49 (m, 2H), 3.79–3.77 (m, 4H); 3.65–3.63 (m, 2H); 3.38–3.36 (m, 2H). MS (m/z/rel.int.): 219(M^+)/6; 105/100; 77/54; 51/22

3c:^1H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.92–7.89 (m, 2H); 7.64–7.59 (m, 1H); 7.51–7.47 (m, 2H), 3.71–3.65 (m, 2H); 3.25 (t, J=5.6 Hz, 2H); 1.69–1.63 (m, 4H); 1.53–1.49 (m, 2H). MS (m/z/rel.int.): 217(M^+)/5; 112/100; 105/54; 84/10; 77/33; 69/61; 51/11; 41/29.

3d: ^1H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.99–7.96 (m, 2H); 7.64–7.60 (m, 1H); 7.51–7.47 (m, 2H); 3.64 (t, J=7.0 Hz, 2H); 3.41 (t, J=7.0 Hz, 2H); 1.98–1.90 (m, 4H). MS (m/z/rel.int.): 203(M^+)/3; 202/6; 105/71; 98/100; 77/52; 70/31; 55/56.

3e:^1H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.88–7.85 (m, 2H); 7.62–7.57 (m, 1H), 7.49–7.44 (m, 2H); 3.50 (q, J=7.2 Hz, 2H), 3.19 (q, J=7.2 Hz, 2H); 1.23 (t, J=7.2 Hz, 3H), 1.10 (t, J=7.2 Hz, 3H). MS (m/z/rel.int.): 205(M^+)/5; 105/61; 100/100; 77/42; 72/74; 51/21.

4a: MS(m/z/rel.int.): 191(M^+)/11; 190/34; 176/9; 160/6; 105/100; 86/12; 77/68; 51/24

4b: ^1H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.96–7.94 (brs, 1H);7.89–7.86 (m, 2H); 7.65–7.62 (m, 2H); 7.55–7.51 (m, 1H); 7.48–7.43 (m, 2H); 7.37–7.32 (m, 2H); 7.17–7.11 (m, 1H). MS(m/z/rel.int.): 197(M^+)/42; 105/100; 77/52; 51/14.

4c: MS(m/z/rel.int.): 189(M^+)/36; 188/100; 105/97; 84/9; 77/56; 51/12.

4d: MS(m/z/rel.int.): 175(M^+)/46; 174/35; 146/19; 105/100; 77/58; 51/16.

4e: MS(m/z/rel.int.): 177(M^+)/13; 176/36; 105/100; 77/39; 51/11.

5: ^1H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.78–7.75 (m, 2H); 7.54–7.49 (m, 1H); 7.40–7.36 (m, 2H); 2.97 (s, 3H); 2.81 (s, 3H). MS(m/z/rel.int.): 177 (M^+)/6; 106/6; 105/100; 77/44; 72/48; 51/17; 50/6

7a: ^1H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.82 (d, J=8.8 Hz, 2H); 7.66 (d, J=8.8 Hz, 2H); 3.80–3.75 (m, 4H); 3.66–3.64 (m, 2H); 3.38–3.53 (m, 2H). MS(m/z/rel.int.): 299(M^+)/6; 297(M^+)/6; 185/100; 183/100; 157/20; 155/20; 114/93; 86/31; 76/22; 75/19; 70/83; 42/27.

7b: ^1H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.10 (ddd, J=0.3 Hz, 1.6 Hz, 1.9 Hz, 1H); 7.88 (ddd, J=1.1 Hz, 1.6 Hz, 7.8 Hz, 1H); 7.77 (ddd (J=1.1 Hz, 1.9 Hz, 8.0 Hz, 1H); 7.40 (ddd, J=0.3 Hz, 7.8 Hz, 8.0 Hz, 1H);

3.80–3.76 (m, 4H); 3.67–3.65 (m, 2H); 3.39–3.36 (m, 2H). MS(m/z/rel. int.): 299(M^+)/5; 297(M^+)/5; 185/28; 183/28; 157/11; 155/11; 114/100; 86/14; 76/15; 75/12; 70/63; 42/20.

7c: ^{1}H NMR (400 MHz, CDCl$_3$), δ (ppm): 7.94 (ddd, J=0.4 Hz, 1.8 Hz, 2.1 Hz, 1H); 7.84 (ddd, J=1.1 Hz, 1.8 Hz, 7.8 Hz, 1H); 7.62 (ddd, J=1.1 Hz, 2.1 Hz, 8.0 Hz, 1H); 7.47 (ddd, J=0.4 Hz, 7.8 Hz, 8.0 Hz, 1H); 3.80–3.78 (m, 4H); 3.67–3.66 (m, 2H); 3.40–3.37 (m, 2H). MS(m/z/rel.int.): 255(M^+)/3; 253(M^+)/9; 141/20; 139/61; 114/100; 111/26; 86/13; 75/16; 70/69; 42/20.

7d: ^{1}H NMR (400 MHz, CDCl$_3$), δ (ppm): 7.74 (ddd, J=1.0 Hz, 1.5 Hz, 7.7 Hz, 1H); 7.66 (dddd, J=0.4 Hz, 1.5 Hz, 2.6 Hz, 8.9 Hz, 1H); 7.51 (dddd, J=0.4 Hz, 5.3 Hz, 7.7 Hz, 8.2 Hz, 1H); 7.35 (dddd, J=1.0 Hz, 2.6 Hz, 8.1 Hz, 8.2Hz, 1H); 3.80–3.78 (m, 4H); 3.67–3.65 (m, 2H); 3.39–3.37 (m, 2H). MS(m/z/rel.int.): 237(M^+)/9; 123/70; 114/100; 95/39; 86/12; 75/15; 70/77; 42/22.

7e: ^{1}H NMR (400 MHz, CDCl$_3$), δ (ppm): 7.91 (d, J=9.0 Hz, 2H); 6.97 (d, J=9.0 Hz, 2H); 3.88 (s, 3H); 3.77–3.76 (m, 4H); 3.65–3.62 (m, 2H); 3.38–3.35 (m, 2H). MS(m/z/rel.int.): 249(M^+)/3; 135/100; 92/10; 77/15; 70/8.

7f: ^{1}H NMR (400 MHz, CDCl$_3$), δ (ppm): 7.71–7.69 (brs, 1H); 7.66 (dd, J= 1.9 Hz, 7.8 Hz, 1H); 7.26 (d, J=7.8 Hz, 1H); 3.78–3.76 (m, 4H); 3.64–3.61 (m, 2H); 3.36–3.33 (m, 2H); 2.33 (s, 3H); 2.31 (s, 3H). MS(m/z/rel.int.): 247(M^+)/3; 133/100; 105/24; 79/9; 77/9; 70/9.

8a: MS(m/z/rel.int.): 271(M^+)/17; 270/41; 269(M^+)/17; 268/42; 185/99; 183/100; 157/28; 155/28; 104/12; 86/41; 76/34; 75/26; 72/11; 56/54; 50/18; 42/12.

8b: MS(m/z/rel.int.): 271(M^+)/26; 270/55; 269(M^+)/26; 268/55; 256/16; 254/16; 185/92; 183/92; 157/42; 155/42; 104/14; 86/74; 77/12; 76/63; 75/42; 74/11; 72/16; 1; 56/100; 55/11; 50/30; 42/24.

8c: MS(m/z/rel.int.): 227(M^+)/5; 226/13; 225(M^+)/16; 224/36; 212/4; 210/12; 141/32; 139/100; 113/16; 111/48; 86/36; 75/26; 56/50; 42/9.

8d: MS(m/z/rel.int.): 209(M^+)/14; 208/28; 123/100; 95/53; 86/24; 75/18; 56/41; 42/6.

8e: MS(m/z/rel.int.): 221(M^+)/10; 220/16; 135/100; 92/10; 77/15.

8f: MS(m/z/rel.int.): 219(M^+)/11; 218/17; 133/100; 105/20; 79/11; 77/12.

3 Results and discussion

Catalysts (Table 1) were prepared either by physisorption of the ionic liquid on silica gel (**SILP-1**, Figure 1) or by anchoring the ionic liquid covalently to the support (grafting, **SILP-2**).

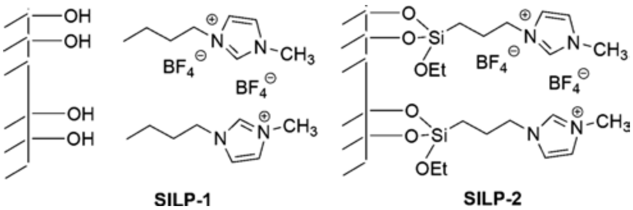


Figure 1: SILP phases used for the preparation of supported catalysts.

Table 1: Supported palladium catalysts used during the carbonylation reactions.

Catalyst	Support	Pd-precursor	Solvent	Pd-content (%)^a
Pd/silica	Silica	Pd$_2$(dba)$_3$.CHCl$_3$	THF, CH$_3$CN	0.55
CAT-1/1	**SILP-1**	Pd$_2$(dba)$_3$.CHCl$_3$	THF, CH$_3$CN	0.40
CAT-1/2	**SILP-1**	Pd(OAc)$_2$	THF, CH$_3$CN	0.49
CAT-1/3	**SILP-1**	Pd(BMIM)$_2$Cl$_2$	THF, CH$_3$CN	0.36
CAT-1/4	**SILP-1**	Pd(PPh$_3$)$_4$	THF, CH$_3$CN	0.55
CAT-1/5	**SILP-1**	Pd(PPh$_3$)$_4$ ^{b}	THF, CH$_3$CN	0.54
CAT-2/1	**SILP-2**	Pd$_2$(dba)$_3$.CHCl$_3$	THF, CH$_3$CN	0.29
CAT-2/2	**SILP-2**	Pd(OAc)$_2$	EtOH	0.77
CAT-2/3	**SILP-2**	PdCl$_2$	EtOH	0.26
CAT-2/4	**SILP-2**	Pd(CH$_3$CN)$_2$Cl$_2$	EtOH	0.38
CAT-2/5	**SILP-2**	Pd$_2$(dba)$_3$.CHCl$_3$	EtOH	0.44

^{a}(Mg Pd/mg catalyst)*100. ^{b}With additional two eq. PPh$_3$.

Palladium was immobilised using different precursors (Table 1) and solvents. Pd(II) compounds may be reduced to catalytically active Pd(0) during the aminocarbonylation reaction with the help of CO [30], Et$_3$N [31], or by the solvent (e.g., DMF [32]). In the case of **CAT-2/2** – **CAT-2/4** heterogenisation was carried out in EtOH to facilitate reduction of Pd(II) to Pd(0) [33] prior to carbonylation.

Aminocarbonylation of iodobenzene (**1**) with morpholine (**2a**) as the nucleophilic reaction partner was chosen as the model reaction (Scheme 1) to test the selectivity and recyclability of the catalysts.

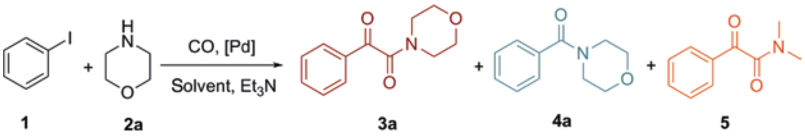
3.1 Aminocarbonylation of iodobenzene (1) with morpholine (2a) as the nucleophilic reagent

In this carbonylation reaction only the awaited α-ketomide (**3a**) and amide (**4a**) products were formed in the presence of most of the catalysts prepared in the THF/acetonitrile solvent mixture (**CAT-1/1**, **CAT-1/2**, **CAT-1/3**, **CAT-1/4,** and **CAT-2/1**). At the same time, ketoamide **5** as a side product was detected in the reaction mixtures obtained with catalysts **CAT-1/3**, **CAT-2/2** – **CAT-2/5** when aminocarbonylation was carried out in DMF that could serve as a source of dimethylamine [34].

As some of the catalysts reported before were shown to be active in apolar solvents, such as toluene [8, 9, 13, 19, 22], whereas others gave good results only in polar media [11, 24], the catalysts were tested in aminocarbonylation using DMF, acetonitrile and toluene as solvent.

3.1.1 Aminocarbonylation in DMF

In case of catalysts obtained with physically adsorbed ionic liquid (**SILP-1**), a substantial loss of [BMIM][BF$_4$] (>95% of the original amount, based on the ^{1}H NMR



Scheme 1: Aminocarbonylation of iodobenzene (**1**) with morpholine (**2a**) as the nucleophile.

analysis of the reaction mixtures) was observed in the first runs of aminocarbonylations carried out in DMF.

Interestingly, phosphine-free palladium-catalysts (**CAT-1/1** – **CAT-1/3**) showed better performance than Pd/silica (Figure 2) especially concerning recyclability, despite the greater loss of palladium observed in the reactions of the former catalysts (Table 2, entries 1, 2, and 4). The beneficial effect of the ionic liquid might be due to a stabilisation of the initially formed palladium nanoparticles at the beginning of the reaction. Imidazolium ionic liquids are frequently used as template, stabiliser, and immobilising agent for catalytic transition-metal nanoparticles to prevent aggregation [35]. TEM image (Figure 3) of spent **CAT-1/1** proves the presence of palladium nanoparticles and shows some residual ionic liquid despite the great loss of [BMIM][BF_4] in the first cycle.

When comparing the performance of catalysts obtained from different precursors, [$Pd_2(dba)_3$.$CHCl_3$ (**CAT-1/1**), $Pd(OAc)_2$ (**CAT-1/2**) and $Pd(BMIM)_2Cl_2$ (**CAT-1/3**)], **CAT-1/1** showed the lowest activity. The application of the Pd-NHC precursor led to a catalyst (**CAT-1/3**) with high activity but lower selectivity to the α-ketomide (**3a**). In addition, a considerable amount of side product **5** was formed when the catalyst was reused.

In our group, an enhanced activity of palladium catalysts with excess phosphine ligands, with a P/Pd ratio of 6–10, was observed before in aminocarbonylations using ionic liquids as solvents [36]. As a consequence, the efficiency of $Pd(PPh_3)_4$ was also tested (**CAT-1/4**). After initial high activity, a great decrease in product yields was observed. The latter could be reduced to some extent by an increase in the phosphine/palladium ratio (Figure 2, **CAT-1/5**). The loss of activity may be caused by the leaching of PPh_3 into the reaction mixture (90% of the original amount in the first run, according to ^1H NMR measurements). It should be mentioned however, that the great loss of ligand was not accompanied by an unusually high loss of palladium (Table 2, entry 5), that was found to be almost the same as in case of **CAT-1/1**. The great drop of activity after the first run may be explained by the formation of inactive palladium complexes after the loss of phosphine ligands.

All of the catalysts obtained from silica or **SILP-1** showed high selectivity towards the α-ketoamide (**3a**),

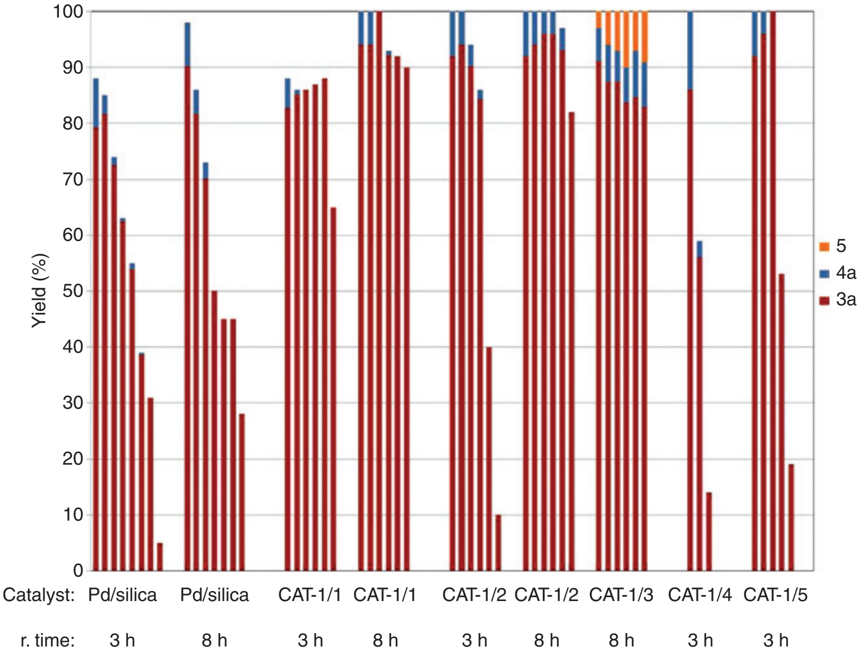


Figure 2: Selectivity and recyclability of catalysts immobilised on silica or **SILP-1** in aminocarbonylation carried out in DMF [0.2 mmol **1**, 0.5 mmol **2a**, 0.25 mmol Et_3N, catalyst (with 3.6 µmol Pd-content), 1 ml DMF, 30 bar CO, 100°C].

Table 2: Leaching of palladium during recirculation experiments for the aminocarbonylation of iodobenzene (**1**) with morpholine (**2**)[a].

Entry	Catalyst	R. time (h)	Pd leaching (%)[b]
1	Pd/silica	3	4.3
2	**CAT-1/1**	3	5.3
3	**CAT-1/1**	8	3.9
4	**CAT-1/2**	3	8.7
5	**CAT-1/4**[c]	3	5.4
6	**CAT-2/1**	3	3.9
7	**CAT-2/1**	8	3.1
8	**CAT-2/5**[d]	8	1.5

[a]Reaction conditions: 0.2 mmol **1**, 0.5 mmol **2a**, 0.25 mmol Et_3N, catalyst (with 3.6 µmol Pd-content) in 1 ml DMF, 30 bar CO pressure, 100°C. [b]An average of six runs, determined by ICP [(mmol Pd in the reaction mixture/ mmol Pd on the fresh catalyst)x100]. [c]An average of three runs. [d]In acetonitrile.

which even increased in the recycling experiments with the exception of **CAT-1/3**. A similar phenomenon was observed before by Li and Yuan [11] in double carbonylation with palladium supported on a cross-linked functional polymer.

A higher activity and better recyclability of the catalyst (**CAT-2/1**), prepared by a similar method but immobilised on the support with grafted ionic liquid (**SILP-2**), was observed both in experiments with shorter and longer reaction times (Figure 4). Selectivity towards the α-ketoamide (**3a**) was found to be a bit lower in the first five runs but it was improved during recycling and complete conversion of iodobenzene (**1**) to product **3a** was observed in the 9th and 10th cycles (reaction time: 8 h). Better performance upon reuse may be partly due to a lower loss of palladium (Table 2, entries 6, 7) compared to **CAT-1/1** and **CAT-1/2**.

Also, an increase in the reaction time resulted in an excellent recyclability and led to a 100% yield of product **3a,** even in the 10th run. A better conversion can be achieved in longer reaction times, and this can be explained by a dissolution/reprecipitation mechanism proposed by Köhler [37]. Even if soluble palladium complexes or palladium nanoparticles are involved in the catalytic cycle, they can return to the surface of the support in the form of nanoparticles after the reaction is completed. The reprecipitation of palladium is supported by the smaller leaching of the catalysts in longer reactions (Table 2). The higher activity of the recycled catalyst (**CAT-2/1**) in the longer experiments can also be proved. Mixtures obtained after a 1-h reaction time in the second run with spent catalysts of the 3-h and 8-h experiments showed 38% and 47% conversions, respectively (Table 3, entries 1, 2). A smaller difference in the results was observed in the second runs of a similar experiment performed in the presence of **CAT-2/5** in acetonitrile (entries 3,4).

The TEM image of the spent catalyst again shows the presence of palladium nanoparticles (Figure 3). To obtain information about the homogeneous or heterogeneous nature of the catalytic reaction, hot filtration and mercury poisoning tests were carried out in the reaction of **CAT-2/1** (Table 4). The catalytic mixture was filtered after 30 min. One half of the mixture was heated further in a CO atmosphere, and the other half was treated similarly but in the presence of mercury.

According to the results, a low conversion of iodobenzene (**1**) could be observed after the removal of the heterogeneous catalyst, and the reaction could be

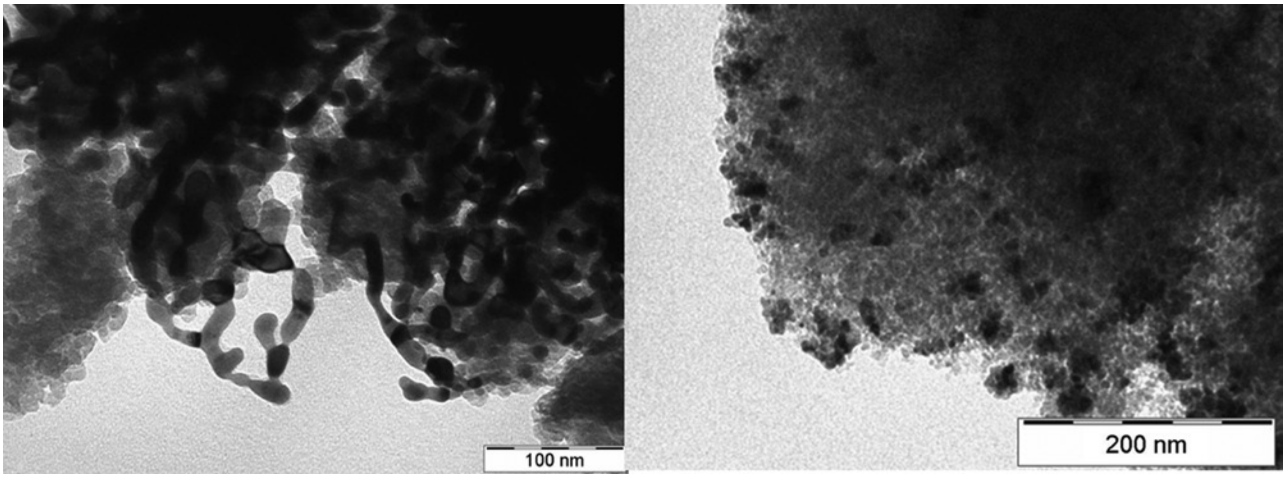


Figure 3: TEM images of spent **CAT-1/1** (left) and **CAT-2/1** (right) after two runs (with 8-h reaction time).

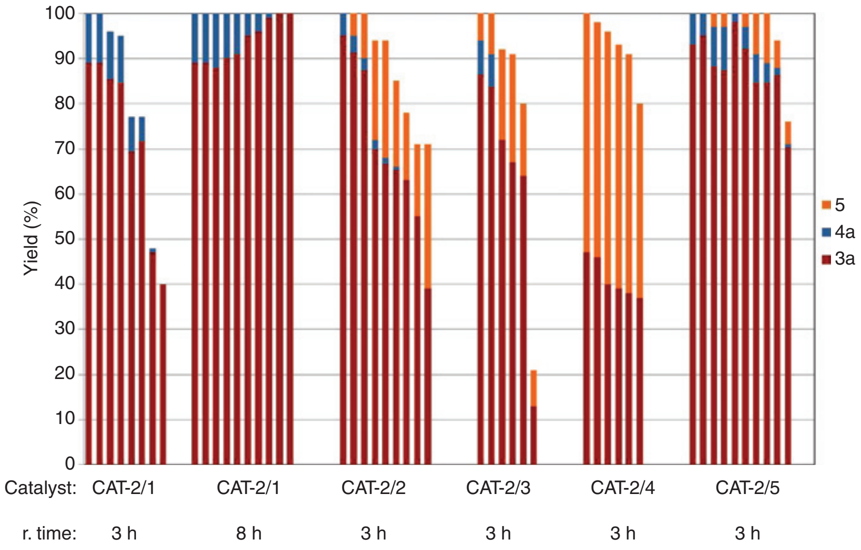


Figure 4: Selectivity and recyclability of catalysts immobilised on **SILP-2** in aminocarbonylation carried out in DMF [0.2 mmol **1**, 0.5 mmol **2a**, 0.25 mmol Et_3N, catalyst (with 3.6 µmol Pd-content], 1 ml DMF, 30 bar CO, 100°C).

Table 3: Recirculation tests[a].

Entry	Catalyst	Solvent	First run		Second run[b]	
			R. time (h)	Conv. of 1 (%)[c]	R. time (h)	Conv. of 1 (%)[c]
1	**CAT-2/1**	DMF	3	100	1	38
2			8	100	1	47
3	**CAT-2/5**	CH_3CN	3	85	1	26
4			8	100	1	29

[a] Reaction conditions: 0.2 mmol **1**, 0.5 mmol **2a**, 0.25 mmol Et_3N, catalyst (with 3.6 µmol Pd-content), 1 ml solvent, 30 bar CO, 100°C. [b] Spent catalyst and fresh reaction mixture: 0.2 mmol **1**, 0.5 mmol **2a**, 0.25 mmol Et_3N, 1 ml solvent, 30 bar CO, 100°C. [c] Determined by GC.

completely stopped by the addition of mercury (Table 4, entries 3, 4). This shows that a small amount of catalytically active palladium nanoparticles had leached to the reaction mixture.

For comparison, a similar experiment was carried out with catalyst **CAT-1/3** obtained from a Pd-NHC precursor (Table 4, entries 1, 2). Although in this case some further reaction could be observed in the filtrate, even in the presence of mercury, conversion was much lower than without the addition of the catalyst poison. This supports the presence of some complexes and nanoparticles in the reaction mixture.

Table 4: Hot filtration and mercury poisoning tests[a].

Entry	Catalyst	Solvent	First step			Second step			
			R. time (h)	Conv. of 1 (%)[b]	Ratio of 3a:4a[b]	Hg	R. time (h)	Conv. of 1 (%)[b]	Ratio of 3a:4a[b]
1	**CAT-1/3**	DMF	0.5	61	96:4	-	4	78	96:4
2						+	4	65	93:7
3	**CAT-2/1**	DMF	0.5	12	74:26	-	4	30	88:12
4						+	4	12	74:26
5	**CAT-2/5**	CH_3CN	0.5	36	95:5	-	4	43	93:7
6						+	4	37	94:6

[a] Reaction conditions: 0.2 mmol **1**, 0.5 mmol **2a**, 0.25 mmol Et_3N, catalyst (with 3.6 µmol Pd-content), 1 ml solvent, 30 bar CO, 100°C. [b]: determined by GC.

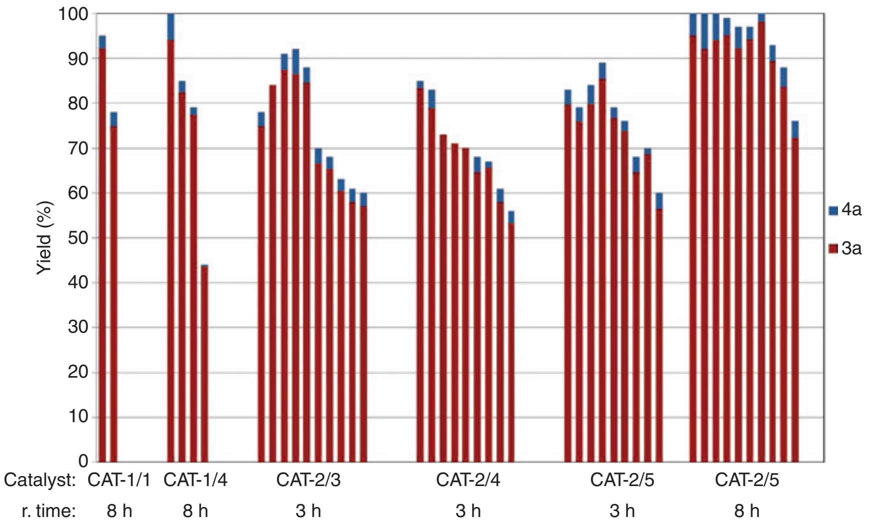


Figure 5: Selectivity and recyclability of catalysts in aminocarbonylation carried out in acetonitrile [0.2 mmol **1**, 0.5 mmol **2a**, 0.25 mmol Et_3N, catalyst (with 3.6 µmol Pd-content), 1 ml acetonitrile, 30 bar CO, 100°C].

According to previous reports, although the presence of palladium-carbene complexes was observed in 1,3-dialkylimidazolium-chloride solutions of Pd(II) salts, ionic liquids with $[BF_4]^-$ or $[PF_6]^-$ anions facilitated the formation of palladium nanoparticles [38]. In addition, palladium nanoparticles were shown to be formed in ionic liquids under thermal decomposition conditions without the addition of a reducing agent, starting from $Pd(dba)_2$ and $Pd(OAc)_{2,}$ as well as from palladium-carbene complexes [39]. Therefore, although the role of palladium-carbene complexes as catalysts cannot be excluded, they may also serve as reservoirs for catalytically active palladium nanoparticles under carbonylation conditions.

Catalysts obtained from **SILP-2** in EtOH (**CAT-2/2** – **CAT-2/5**) exerted high activity in the conversion of iodobenzene. Acceptable results were obtained upon recycling, but a considerable amount of side-product **5** was formed in DMF in each case.

3.1.2 Aminocarbonylation in acetonitrile

The efficiency of another polar solvent, acetonitrile, was also investigated in reactions with some of the catalysts immobilised either on **SILP-1** (**CAT-1/1**, **CAT-1/5**) or **SILP-2** (**CAT-2/3**, **CAT-2/4**, **CAT-2/5**). Good conversion of iodobenzene (**1**) was achieved with the first group of catalysts in the first runs, but unfortunately, a great loss of activity was observed upon recycling, even carrying out the carbonylation for a longer reaction time. **CAT-2/3**, **CAT-2/4** and **CAT-2/5** showed lower activity in acetonitrile than in DMF (Figure 5) but compounds **3a** and **4a** were the only products in the reaction mixtures, and the catalysts could be reused with only a small loss of activity. When the reaction time was increased to 8 h, the conversion of iodobenzene dropped below 90%, but only in the 9th run in the presence of **CAT-2/5**. Contrary to the reactions in DMF, there is no appreciable change in the selectivity of aminocarbonylation in the recycling experiments. As another advantage, the amount of leached palladium is considerably lower here than in case of reactions carried out in DMF (Table 2, entry 8).

Hot filtration and mercury poisoning tests (Table 4, entries 5, 6) showed that the conversion of iodobenzene (**1**) was very slow after the removal of the heterogeneous catalyst, and it could be completely stopped by the addition of mercury. These results are in good accordance with the small amount of leached palladium detected during aminocarbonylation of this catalyst (Table 2, entry 8).

3.1.3 Aminocarbonylation in toluene

Some previous reports show the excellent activity of immobilised palladium catalysts in toluene [8, 9, 13, 19, 22], so the possibility of the use of this solvent was also taken into account. As it was observed before in the case of **CAT-1/1** and **CAT-2/1** [26], the use of an apolar solvent

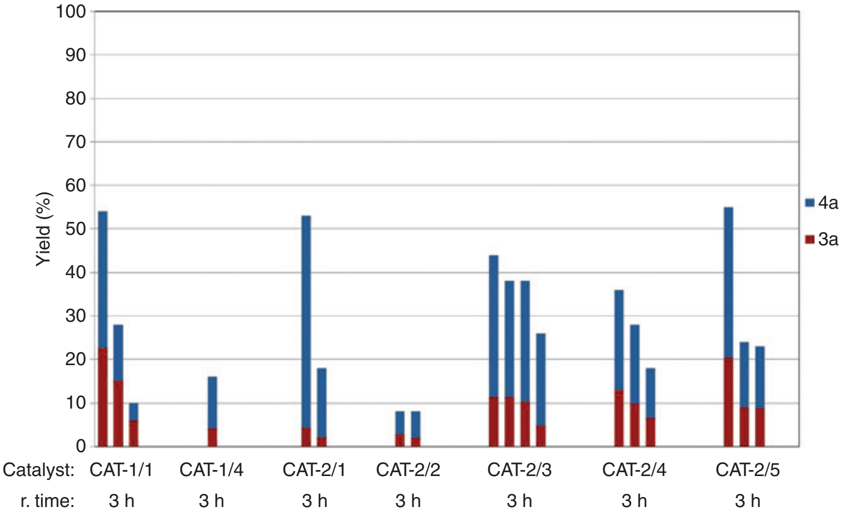


Figure 6: Selectivity and recyclability of catalysts in aminocarbonylation carried out in toluene [0.2 mmol **1a**, 0.5 mmol **2a**, 0.25 mmol Et_3N, catalyst (with 3.6 µmol Pd-content), 1 ml toluene, 30 bar CO, 100°C].

reduced catalytic efficiency considerably in all of the catalysts investigated (Figure 6). At the same time, under these conditions, the main product was amide **4a** despite the use of a high CO pressure (30 bar). This probably can be explained by the fact that, although the formation of amides is thought to occur via neutral complexes, ionic species are involved in the catalytic cycle of double carbonylation. As a consequence, polar solvents may enhance the rate of the latter reaction by stabilisation of the ionic intermediates in the presence of apolar ones, and monocarbonylation is favoured.

Despite the fact that no loss of ionic liquid was observed, even when catalysts were prepared with **SILP-1**, recyclability is poor with the exception of **CAT-2/3**, where there is only a moderate loss of activity in the first three runs.

3.1.4 Aminocarbonylation at lower pressure

Aminocarbonylation of iodobenzene (**1**) with morpholine (**2a**) was attempted using lower carbon monoxide pressure [5 bar (Figure 7) and 1 bar (Figure 8)]. A good selectivity towards the α-ketoamide (**3a**) was observed at 5 bar, and double carbonylation was found to take place even under atmospheric conditions. The catalysts could be recycled with some loss of activity when moderate pressure was used, but a great drop of activity was observed in the atmospheric reactions when catalyst recycling was attempted. The formation of side-product **5** could be detected in reaction mixtures obtained with catalysts prepared in EtOH.

3.2 Aminocarbonylation of iodobenzene (1) with aniline (2b) as the nucleophilic reagent

Some of the heterogeneous catalysts were tested in another model reaction using an aromatic amine, aniline (**2b**), as the nucleophile. In contrast to the reaction of morpholine,

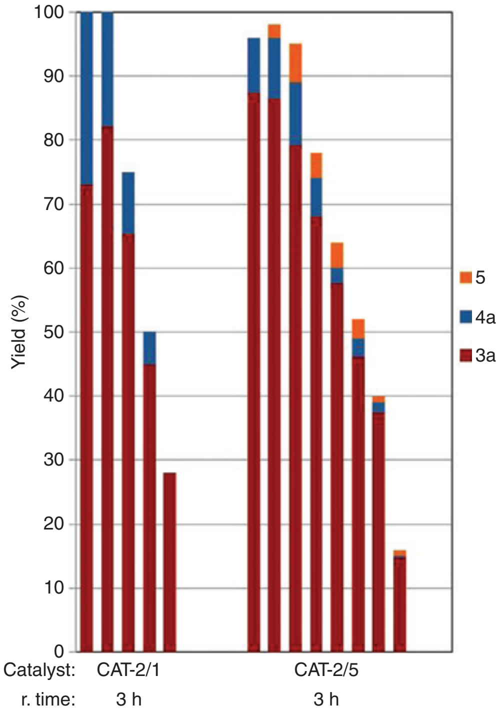


Figure 7: Selectivity and recyclability of catalysts in aminocarbonylation carried out in DMF at 5 bar [0.2 mmol **1**, 0.5 mmol **2a**, 0.25 mmol Et_3N, catalyst (with 3.6 µmol Pd-content), 1 ml DMF, 5 bar CO, 100°C].

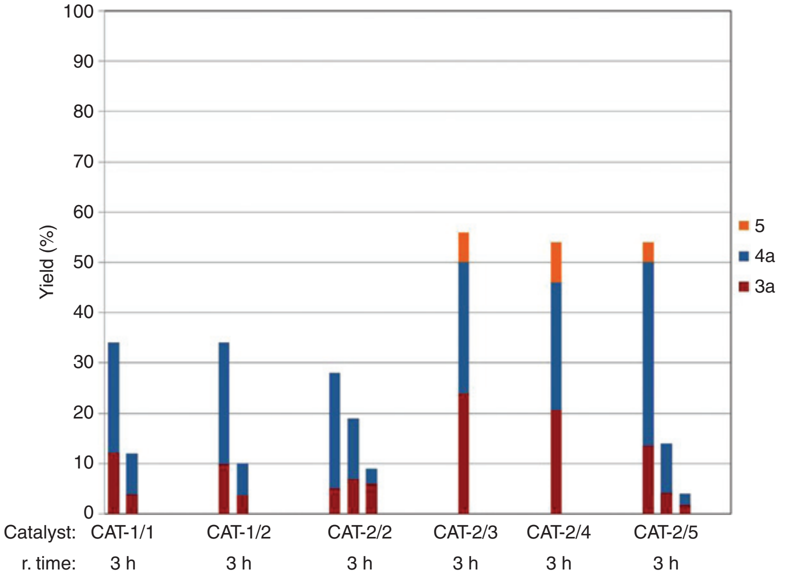
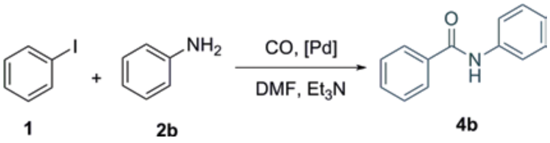


Figure 8: Selectivity and recyclability of catalysts in aminocarbonylation carried out in DMF at atmospheric pressure [0.2 mmol **1**, 0.5 mmol **2a**, 0.25 mmol Et_3N, catalyst (with 3.6 µmol Pd-content), 1 ml DMF, 1 bar CO, 100°C].

in this case a selective monocarbonylation was observed in each case, and amide **4b** was the only product that could be detected in the reaction mixture (Scheme 2).



Scheme 2: Aminocarbonylation of iodobenzene (**1**) with aniline (**2b**) as the nucleophile.

Efficient recycling of the catalysts can be achieved by the use of either **CAT-1/1** or **CAT-2/4** even in relatively short reaction times (Figure 9). Surprisingly, **CAT-2/1** gave excellent results in the aminocarbonylation with morpholine, but showed lower activity and could be reused only with a considerable loss of activity. As another interesting feature, no side product formation was observed, even with catalysts prepared in EtOH (**CAT-2/2** – **CAT-2/4**). It should be mentioned that at atmospheric pressure, only a low conversion of iodobenzene was achieved (26% conversion in 4 h in the presence of **CAT-2/2**).

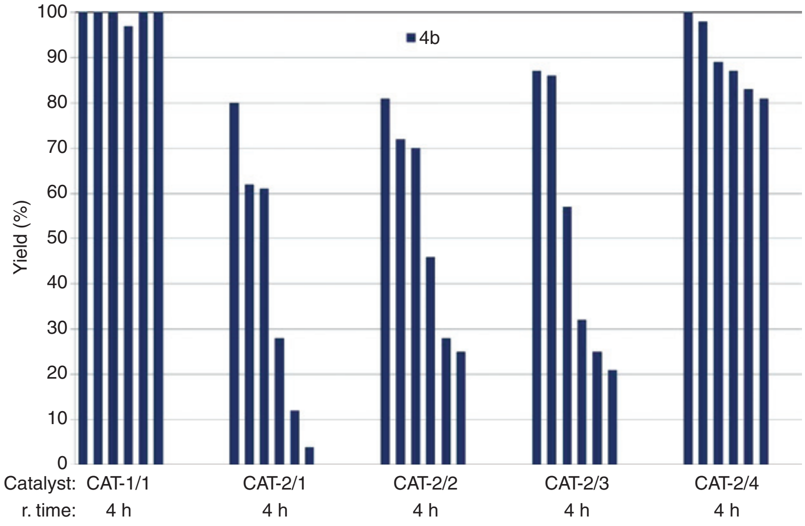
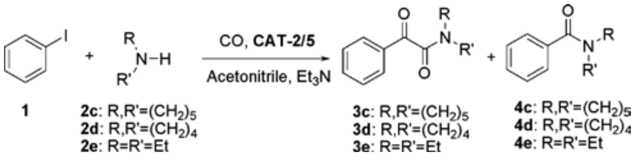


Figure 9: Recyclability of catalysts in aminocarbonylation of iodobenzene (**1**) with aniline (**2b**) at 30 bar [0.2 mmol **1**, 0.5 mmol **2b**, 0.7 mmol Et_3N, catalyst (with 6 µmol Pd-content), 1 ml DMF, 30 bar CO, 100°C].



Scheme 3: Aminocarbonylation of iodobenzene (**1**) with aliphatic amines (**2c–e**).

3.3 Aminocarbonylation of other substrates

To show the efficiency of the heterogeneous catalysts, aminocarbonylation of iodobenzene (**1**) in the presence of other aliphatic amines (**2c–2e**, Scheme 3) as well as the reactions of other aryl iodides (**6a–6f**, Scheme 4) with morpholine (**2a**) was investigated in the presence of **CAT-2/5** (Table 5). A total conversion of the aryl iodides and good selectivity towards ketoamide products (**3c–e**, **7a–f**) were observed in each case, even after catalyst recycling.

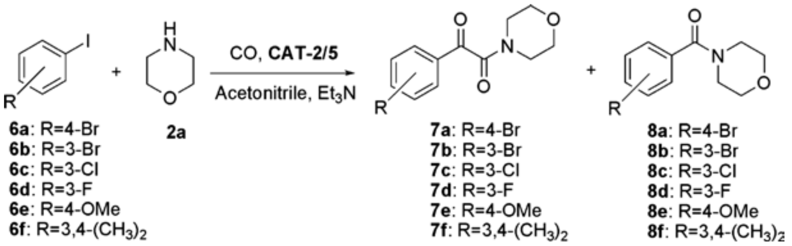
4 Conclusions

Various silica-supported palladium catalysts were prepared and tested in the double carbonylation of iodobenzene (**1**) in the presence of morpholine (**2a**) or aniline (**2b**) as nucleophilic reagents.

It was shown that small alterations in the immobilisation procedure may greatly affect the efficiency of the catalysts.

Modification of the support with ionic liquids, even by physisorption, results in more active catalysts than that obtained from silica itself. **CAT-2/1** and **CAT-2/5**, prepared by silica-grafted ionic liquid as support, were found to be the most efficient catalysts with excellent recyclability. With the first catalyst, total conversion of iodobenzene to ketoamide **3a** was achieved even in the 10th run. At the same time, good recycling results, together with a considerably lower loss of palladium, were obtained in carbonylations with the latter catalyst. This shows the efficiency of the application of EtOH as solvent during palladium-immobilisation. As another advantage, no change in the selectivity of the reaction in the subsequent runs could be observed with **CAT-2/5**.

The use of catalysts with higher activity leads to the formation of a by-product when carbonylation is carried out in DMF due to the decomposition of the solvent. As the presence of polar solvents were proved to be essential to obtaining optimum results, acetonitrile was found to be the solvent of choice in these cases.



Scheme 4: Aminocarbonylation of aryl iodides (**6a-f**) with morpholine (**2a**).

Table 5: Aminocarbonylation of other substrates[a].

Entry	Aryl iodide	Amine	Run 1		Run 2	
			Conv. (%)[b]	Ratio of products (%)[b]	Conv. (%)[b]	Ratio of products (%)[b]
1	**1a**	**2c**	100	92 (**3c**)/8 (**4c**)	98	94 (**3c**)/6 (**4c**)
2	**1a**	**2d**	100	84 (**3d**)/16 (**4d**)	100	88 (**3d**)/12 (**4d**)
3	**1a**	**2e**	100	93 (**3e**)/7 (**4e**)	100	94 (**3e**)/6 (**4e**)
4	**6a**	**2a**	100	90 (**7a**)/10(**8a**)	100	88 (**7a**)/12 (**8a**)
5	**6b**	**2a**	100	88 (**7b**)/12(**8b**)	100	90 (**7b**)/10 (**8b**)
6	**6c**	**2a**	100	87 (**7c**)/13 (**8c**)	100	88 (**7c**)/12 (**8c**)
7	**6d**	**2a**	100	92 (**7d**)/8(**8d**)	100	92 (**7d**)/8 (**8d**)
8	**6e**	**2a**	100	96 (**7e**)/4 (**8e**)	100	96 (**7e**)/4 (**8e**)
9	**6f**	**2a**	100	92 (**7f**)/8 (**8f**)	100	94 (**7f**)/6 (**8f**)

[a]Reaction conditions: 0.2 mmol aryl iodide, 0.5 mmol amine, 0.25 mmol Et$_3$N, **CAT-2/5** (with 3.6 μmol Pd-content) in 1 ml acetontirile, 30 bar CO pressure, 100°C. [b]Determined by GC using ferrocene as internal standard.

The catalysts were effective when reactions were performed under CO pressure, but the application of 30 bar of pressure was necessary for efficient recycling. Under these conditions, α-ketoamide **3a** was obtained as the main product in the reaction of iodobenzene (**1**) with morpholine (**2a**) in all cases. Although at atmospheric pressure amide **4a** was the main product, the formation of a considerable amount of double carbonylation product **3a** could also be observed in each case. **CAT-2/5** could be used efficiently for the synthesis of a number of α-ketoamides, starting from other aliphatic amines, as well as substituted aryl iodides.

Contrary to the reaction of aliphatic amines, selective monocarbonylation was obtained in the presence of aniline (**2b**) as the nucleophile, even under CO pressure. Also, in this reaction **CAT-1/1** was found to be the catalyst with best activity and recyclability that shows that the composition of the catalyst should be fine-tuned according to the nature of the substrates.

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References

[1] Roy S, Roy S, Gribble GW. *Tetrahedron* 2012, 68, 9867–9923.

[2] Wang T, Zhang Z, Wallace OB, Deshpande M, Fang H, Yang Z, Zadjura LM, Tweedie DL, Huang S, Zhao F, Ranadive S, Robinson BS, Gong YF, Ricarrdi K, Spicer TP, Deminie C, Rose R, Wang HH, Blair WS, Shi PY, Lin PF, Colonno RJ, Meanwell NA. *J. Med. Chem.* 2003, 46, 4236–4239.

[3] Chatel-Chaix L, Baril M, Lamarre D. *Viruses* 2010, 2, 1752–1765.

[4] Brennführer A, Neumann H, Beller M. *Angew. Chem. Int. Ed.* 2009, 48, 4114–4133.

[5] Gadge ST, Bhanage BM. *RSC Adv.* 2014, 4, 10367–10389.

[6] Salvadori J, Balducci E, Zaza S, Petricci E, Taddei M. *J. Org. Chem.* 2010, 75, 1841–1847.

[7] Qureshi ZS, Revankar SA, Khedkar MV, Bhanage BM. *Catal. Today* 2012, 198, 148–153.

[8] Khedkar MV, Sasaki T, Bhanage BM. *ACS Catal.* 2013, 3, 287–293.

[9] Islam SM, Ghosh K, Roy AS, Molla RA. *RSC Adv.* 2014, 4, 38986–38999.

[10] Mansour A, Portnoy M. *J. Mol. Catal. A* 2006, 250, 40–43.

[11] Mei H, Hu J, Xiao S, Lei Y, Li G. *Appl. Catal. A* 2014, 475, 40–47.

[12] Dang TT, Zhu Y, Ngiam JSY, Ghosh SC, Chen A, Seayad AM. *ACS Catal.* 2013, 3, 1406–1410.

[13] Biying AO, Yuanting KT, Hosmane NS, Yinghuai Z. *J. Organomet. Chem.* 2013, 747, 184–188.

[14] Hao W, Sha J, Sheng S, Cai M. *Catal. Comm.* 2008, 10, 257–260.

[15] Cai M, Huang Y, Hu R, Song C. *J. Mol. Catal. A* 2004, 208, 17–20.

[16] Cai M, Huang Y, Hu R, Song C. *J. Mol. Catal. A 2004*, 212, 151–154.

[17] Cai M, Zhao H, Huang Y. *J. Mol. Catal. A* 2005, 238, 41–45.

[18] Dang TT, Zhu Y, Ghosh SC, Chen A, Chai CLL, Seayad AM. *Chem. Commun.* 2012, 48, 1805–1807.

[19] Tinnis F, Verho O, Gustafson KPJ, Tai CW, Bäckvall JE, Adolfsson H. *Chem. Eur. J.* 2014, 20, 5885–5889.

[20] Yan YY, Zuo HP, Jin ZL. *React. Func. Polym.* 1997, 32, 21–24.

[21] Liu J, Zheng S, Su W, Xia C. *Chin. J. Chem.* 2009, 27, 623–627.

[22] Chen B, Li F, Huang Z, Lu T, Yuan G. *Appl. Catal. A* 2014, 481, 54–63.

[23] Genelot M, Villandier N, Bendjeriou A, Jaithong P, Djakovitch L, Dufaudz V. *Catal. Sci. Technol.* 2012, 2, 1886–1893.

[24] Balogh J, Kuik Á, Ürge L, Darvas F, Bakos J, Skoda-Földes R. *J. Mol. Catal. A.* 2009, 302, 76–79.

[25] Takács E, Varga C, Skoda-Földes R, Kollár L. *Tetrahedron Lett.* 2007, 48, 2453–2456.

[26] Papp M, Skoda-Földes R. *J. Mol. Catal. A*, 2013, 378, 193–199.

[27] Khedkar MV, Shinde AR, Sasaki T, Bhanage BM. *J. Mol. Catal. A* 2014, 385, 91–97.

[28] özdemir I, Demir S, Gök Y, Çetinkaya E, Çetinkaya B. *J. Mol. Catal. A* 2004, 222, 97–102.

[29] Liu J, Zhang R, Wang S, Sun W, Xia C. *Org. Lett.* 2009, 11, 1321–1324.

[30] Negishi E, Ed., *Handbook of Organopalladium Chemistry for Organic Synthesis*, Wiley: New York, 2002, pp. 47–65.

[31] Trzeciak AM, Ciunik Z, Ziółkowski JJ. *Organometallics* 2002, 21, 132–137.

[32] Serp P, Hernandez M, Richard B, Kalck P. *Eur. J. Inorg. Chem.* 2001, 2327–2336.

[33] Kume Y, Qiao K, Tomida D, Yokoyama C. *Catal. Commun.* 2008, 9, 369–375.

[34] Muzart J. *Tetrahedron* 2009, 65, 8313–8323.

[35] Astruc D. *Inorg. Chem.* 2007, 46, 1884–1894.

[36] Skoda-Földes R, Takács E, Horváth J, Tuba Z, Kollár L. *Green Chem.* 2003, 5, 643–645.

[37] Heidenreich RG, Krauter JGE, Pietsch J, Köhler K. *J. Mol. Catal. A* 2002, 182–183, 499–509.

[38] Hamill NA, Hardacre C, McMath SEJ. *Green Chem.* 2002, 4, 139–142.

[39] Prechtl MHG, Scholten JD, Dupont J. *Molecules* 2010, 15, 3441–3461.

Bionotes

Máté Papp

Máté Papp is currently an undergraduate student of Chemistry at the University of Pannonia. He is a member of the research group of Professor Rita Skoda-Földes. His research topic is the investigation of aminocarbonylation reactions with recyclable heterogeneous catalysts.

Béla Urbán

Béla Urbán is currently a graduate student in the Doctoral School of Chemistry and Environmental Sciences at the University of Pannonia. He is a member of the research group of Professor Rita Skoda-Földes. His research topic is the investigation of aminocarbonylation reactions with recyclable heterogeneous catalysts.

Eszter Drotár

Eszter Drotár has worked since 2010 for the Research Centre for Natural Sciences as a geologist and recently as a research fellow. Their laboratory contains a transmission electron microscope (FEI MORGAGNI 268D type) and a scanning electron microscope(ZEISS EVO 40XVP type).

Rita Skoda-Földes

Rita Skoda-Földes obtained her PhD from the University of Pannonia in 1996. Since 2009, she has been a Professor of Chemistry there. Her current research interests include the investigation of palladium-catalysed reactions under homogeneous and heterogeneous conditions, synthesis of steroid derivatives, and ferrocene-labelled molecules.