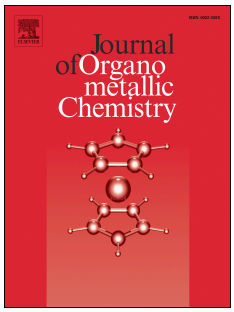

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Double carbonylation of iodoarenes in the presence of a pyridinium SILP-Pd catalyst

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Dedicated to the 65th birthday of Professor László Kollár, in recognition of his contribution to coordination chemistry, homogeneous catalysis and carbonylation reactions

Abstract

The efficiency of a palladium catalyst, immobilised on a supported ionic liquid phase (SILP) with adsorbed 1-butyl-4-methylpyridinium chloride, was investigated in aminocarbonylation reactions. Double carbonylation was found to be the main reaction using different iodoarenes and aliphatic amines as substrates. Application of aniline derivatives as nucleophiles led to the exclusive formation of substituted benzamides. The stabilisation effect of the adsorbed pyridinium ionic liquid was compared to that of imidazolium and phosphonium derivatives. It was proved that the pyridinium SILP-palladium catalyst could be reused in at least 10 cycles. Recyclability was tested in five successive runs for all of the substrates.

Keywords: aminocarbonylation; double carbonylation; heterogeneous catalysis, immobilization; palladium.

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1. Introduction

α-Ketoamides serve as important starting materials in synthetic organic chemistry [1] to produce a great variety of heterocyclic compounds, such as indoles, [2] oxindoles [3], dihydroisoquinolines [4], isatins [5] and imidazolidinones [6]. The α-ketoamide motif is present in many natural and non-natural compounds bearing important biological effects, [7] *e. g.* protease inhibitory activity [8] and as a result, antiviral- [9] and antitumor effect. [10]

Among the great variety of synthetic routes towards α-ketoamides, [7, 11] palladium-catalysed double carbonylation of aryl halides represents a useful strategy mainly due to the ready availability of starting materials with diverse structure and the good functional group tolerance of the reaction. Competing aminocarbonylation, leading to carboxamides, can usually be retarded by carrying out the reactions at lower temperature and higher pressure, especially under homogeneous conditions. As an improvement, several heterogeneous catalytic systems have been developed recently for carbonylation of aryl halides, [12] to facilitate product separation and catalyst recycling and to make the methodology more environmentally friendly. At the same time the application of immobilised catalysts for the carbonylative synthesis of α-ketoamides is a much less explored field compared to other carbonylation methodologies. Heterogeneous catalysts for double carbonylation were obtained by the immobilisation of palladium-phosphine complexes on SBA-15 [13] or on an organic polymer, [14] as well as by the addition of PPh_3 to Pd/C [15] or to a polymer-supported triazine based palladium complex. [16] In phosphine-free systems catalytically active palladium species were deposited on silica-supported polytitazane [17], on covalent triazine- [18] or metal organic frameworks [19] or on different polymers. [20] However, the development of suitable catalysts is still a challenge, as efficiency is highly influenced not only by the nature of the catalyst and the choice of carbonylation conditions, but also by the structure of the reaction partners.

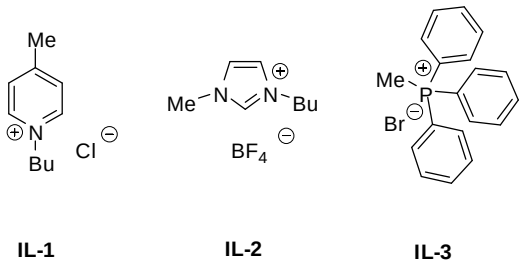
Stabilisation of palladium nanoparticles could also be achieved by the use of supported ionic liquid phases (SILPs). [21-23] Catalysts with the best performance were obtained by the deposition of palladium on SILPs with anchored dicationic moieties. [22,23] At the same time, the preparation of these elaborate supports is cumbersome that might hinder their application. Our previous studies have shown that even simple adsorption of an imidazolium ionic liquid (IL) on silica can increase the efficiency of the Pd-silica system considerably. [21] Although imidazolium salts are by far the most widely explored representatives of ionic liquids, pyridinium derivatives are known to have some favourable properties, such as a better stabilisation effect towards colloidal palladium. [24] In the present report it is shown that a SILP-Pd catalyst, obtained by the simple adsorption of a mixture of a palladium precursor and a pyridinium ionic liquid on silica, can be recycled efficiently in the double carbonylation reaction of aryl iodides and secondary amines as well as in the aminocarbonylation of iodobenzene and aniline derivatives. The stability of the catalysts obtained from SILPs with different adsorbed ionic liquids is also compared.

2. Results and discussion

2.1. Preparation of SILP-Pd catalysts

The catalyst (**CAT-1**) was obtained by a wet impregnation method using a mixture of 1-butyl-4-methylpyridinium chloride (**IL-1**, Figure 1) and the Pd-precursor, $Pd_2(dba)_3.CHCl_3$.

In order to compare the stabilisation effect of the pyridinium IL (**IL-1**) with imidazolium- (**IL-2**) and phosphonium salts (**IL-3**), catalysts supported on other SILPs (**CAT-2** [22] and **CAT-3** [23]), as well as an IL-free version (**CAT-4**) were prepared (Table 1).



IL-1 **IL-2** **IL-3**

Figure 1. Ionic liquids used for the preparation of SILP catalysts **CAT-1 — CAT-3**

Table 1. Supported palladium catalysts used during the carbonylation reactions[a]

Catalyst	Ionic liquid	Pd-content [%][b]
CAT-1	**IL-1**	0.49
CAT-2	**IL-2**	0.40
CAT-3	**IL-3**	0.56
CAT-4	-	0.55

[a]: support: silica, Pd precursor: $Pd_2(dba)_3.CHCl_3$; [b]: (mg Pd/mg catalyst)*100.

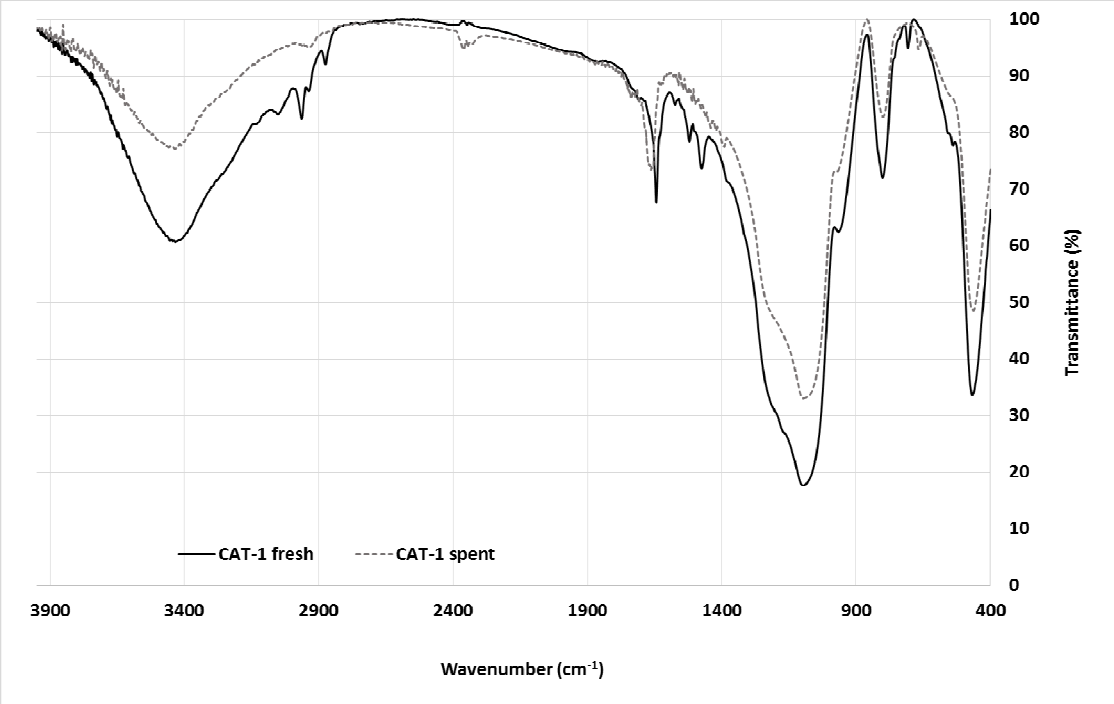
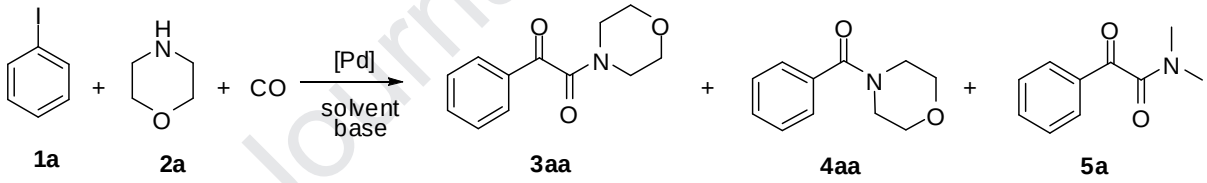


Figure 2. IR spectra of the fresh and spent catalyst **CAT-1**. (Spent catalyst: after two runs in DMF, 30 bar, 100 °C, 3h.)

The presence of **IL-1** on the surface of the silica support was proved by elemental analysis and infrared spectroscopy. The IR spectrum of **CAT-1** (Figure 2) reflects the presence of the pyridinium salt. The signals at 2966, 2941 and 2879 cm^{-1} correspond to stretching vibrations of alkyl C-H, while the absorption at 3059 cm^{-1} can be attributed to the presence of aromatic C-H. The bands at 1645, 1522 and 1477 cm^{-1} can be assigned to the vibrations of the pyridinium ring. [25]

*2.2. Carbonylation of iodobenzene (**1a**) and morpholine (**2a**) in the presence of SILP-Pd catalysts*

First, the performance of **CAT-1** was tested under different conditions in the model reaction of iodobenzene (**1a**) and morpholine (**2a**) (Scheme 1). The reaction parameters were chosen according to our previous observations in double carbonylation carried out with SILP catalysts. [21-23]



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

α-Ketoamide **3aa** was formed with good to excellent selectivity in all of the reactions (Table 2.). As it could be expected, some increase in the ratio of amide **4aa** was observed at lower pressures (entries 4, 8, 9), but selectivity for **3aa** remained around 85% even in these cases. The reaction was much slower in acetonitrile (entries 5-9) than in DMF (entries 1-4) or toluene (entries 10,11) and good conversion could be achieved only in eight-hour long reactions (entries 7-9).

Table 2. Aminocarbonylation of iodobenzene (**1a**) and morpholine (**2a**) in the presence of **CAT-1**[a]

Entry	Solvent	Base	Pressure [bar]	Reaction time [h]	Conversion [%][b]	Ratio of products [%][b]	
						3aa	**4aa**
1	DMF	Et_3N	30	0.5	21	100[c]	0
2	DMF	Et_3N	30	1	98	92[c]	8
3	DMF	Et_3N	30	3	100	93[c]	7
4	DMF	Et_3N	5	3	91	85[c]	15
5	acetonitrile	Et_3N	30	0.5	15	100	0
6	acetonitrile	Et_3N	30	1.5	41	93	7
7	acetonitrile	Et_3N	30	8	97	95	5
8	acetonitrile	Et_3N	10	8	96	86	14
9	acetonitrile	Et_3N	5	8	95	86	14
10	toluene	DBU	30	0.5	30	91	9
11	toluene	DBU	30	3	100	93	7

[a]: reaction conditions: 0.2 mmol **1a**, 0.5 mmol **2a**, 0.25 mmol base, catalyst (with 3.2 μmol Pd-content) and 1 ml solvent, 100 °C; [b]: determined by GC; [c]: the presence of side product **5a** could not be detected in the reaction mixtures.

Next, the activity and recyclability of **CAT-1** were compared with those of other heterogeneous catalysts (**CAT-2** — **CAT-4**) under different conditions. The use of all of the catalysts resulted in the formation of α-ketoamide **3aa** with good selectivity in the DMF/Et_3N solvent/base system at high pressure (Figures 3,4). The IL-free catalyst (**CAT-4**) showed a similar performance to the SILP catalyst **CAT-2** in the first runs, but a great loss of activity was observed in the recycling experiments. A much lower decrease could be noticed when the imidazolium catalyst (**CAT-2**) was recycled. Although iodobenzene (**1a**) was totally consumed in all of the experiments carried out with **CAT-3**, the reuse of the catalyst led to a considerable change in the selectivity. While the amide (**4aa**) content of the reaction mixture

dropped appreciably after the first run, a progressive increase in the amount of the side product **5a**, formed due to some decomposition of the solvent DMF, [26] could be detected. The pyridinium-SILP catalyst **CAT-1** exhibited the most stable performance and could be reused efficiently in at least 10 cycles in eight-hour long reactions (Figure 4). It should be mentioned that its selectivity towards the double carbonylation product **3aa** was slightly lower than that of **CAT-2** due to the formation of side product **5a**.

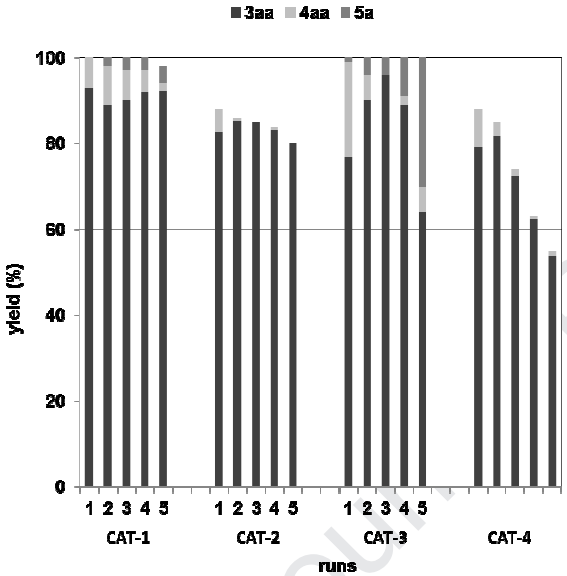


Figure 3. Recirculation experiments with **CAT-1 — CAT-4**. Reaction conditions: 0.2 mmol **1a**, 0.5 mmol **2a**, 0.25 mmol Et_3N, 1 ml DMF, catalyst (Pd-content: **CAT-1**: 3.2 μmol, **CAT-2** and **CAT-4**: 3.6 μmol **CAT-3**: 2.8 μmol), 100 °C, 30 bar, 3h. Yields are determined by GC.

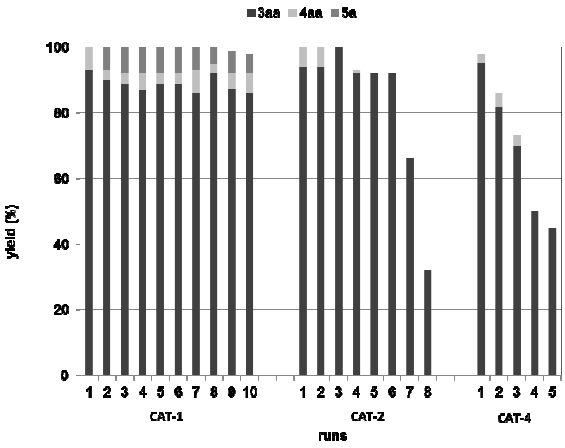


Figure 4. Recirculation experiments with **CAT-1 — CAT-4** in eight-hour long reactions. Reaction conditions: 0.2 mmol **1a**, 0.5 mmol **2a**, 0.25 mmol Et_3N, 1 ml DMF, catalyst (Pd-content: **CAT-1**: 3.2 μmol, **CAT-2** and **CAT-4**: 3.6 μmol **CAT-3**: 2.8 μmol), 100 °C, 30 bar, 8h. Yields are determined by GC.

An even greater difference in the stability of the pyridinium- (**CAT-1**) and imidazolium-type (**CAT-2**) catalysts was observed when carbonylations were carried out at 5 bar CO pressure (Figure 5). While **CAT-1** showed an acceptable stability, **CAT-2** lost its activity very quickly. It should also be mentioned that although at 5 bar the α-ketoamide (**3aa**)/amide (**4aa**) ratio was somewhat lower than at 30 bar CO pressure, the main product **3aa** was still formed with good selectivity in the presence of **CAT-1**. The influence of the reaction conditions applied in the first run is well demonstrated by the fact that in eight-hour long reactions an increased amount of side product **5a** could be detected in the reaction mixtures from the second run on.

At lower pressures, the catalyst **CAT-1** was less stable in acetonitrile than in DMF (Figure 6), but at 30 bar it could be reused with only a small loss of activity. Moreover, it demonstrated a remarkably better recyclability than **CAT-2** under the same conditions.

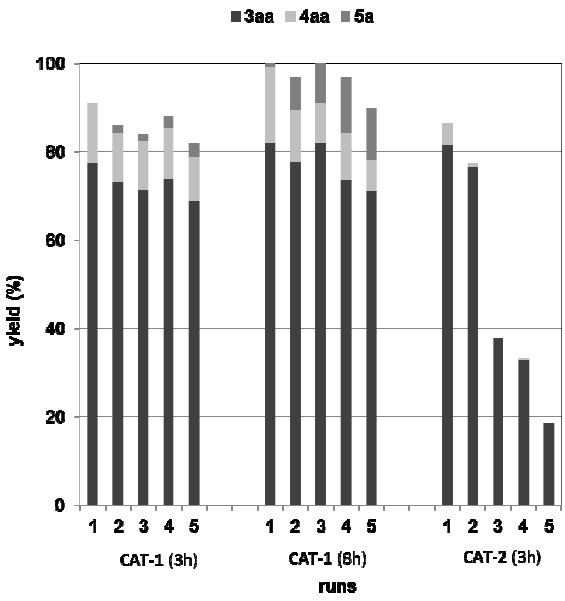


Figure 5. Recirculation experiments with **CAT-1** and **CAT-2** at 5 bar CO pressure. Reaction conditions: 0.2 mmol **1a**, 0.5 mmol **2a**, 0.25 mmol Et_3N, 1 ml DMF, catalyst (Pd-content: 3.2 μmol), 100 °C, 5 bar. Yields are determined by GC.

In order to avoid dissolution of the ionic liquid film by the solvent, the applicability of the toluene/DBU solvent/base system was also tested. In spite of the fact that these conditions were proved to be suitable for double carbonylations carried out with SILPs decorated with imidazolium-type dicationic moieties, [22] no formation of carbonylated products could be observed with **CAT-2** prepared from the SILP with adsorbed **IL-2**. On the contrary, good conversions could be achieved in the presence of either **CAT-1** or **CAT-3** (Figure 7). Unfortunately, reuse of **CAT-1** led to a noticeable increase in the ratio of the amide product **4aa**.

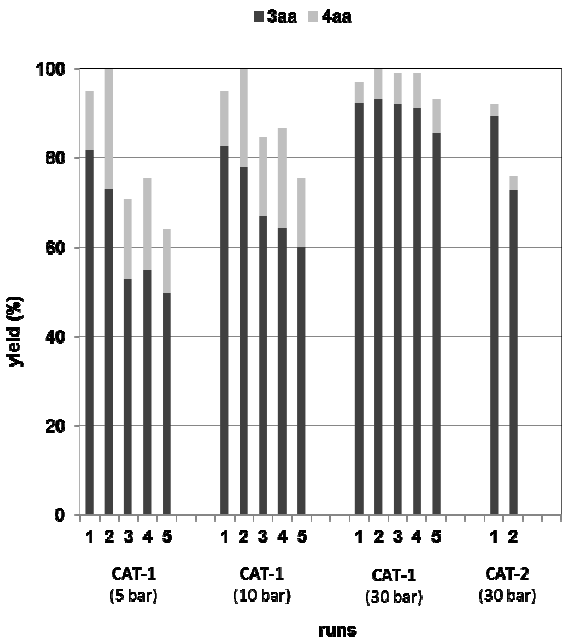


Figure 6. Recirculation experiments with **CAT-1** and **CAT-2** in acetonitrile. Reaction conditions: 0.2 mmol **1a**, 0.5 mmol **2a**, 0.25 mmol Et_3N, 1 ml acetonitrile, catalyst (Pd-content: 3.2 μmol), 100 °C, 8h. Yields are determined by GC.

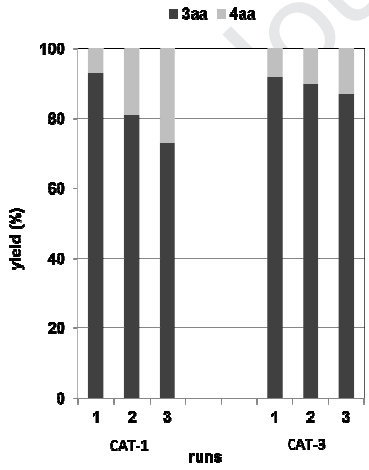


Figure 7. Recirculation experiments with **CAT-1** and **CAT-3** in toluene. Reaction conditions: 0.2 mmol **1a**, 0.5 mmol **2a**, 0.25 mmol DBU, 1 ml toluene, catalyst (Pd-content: 3.2 μmol), 100 °C, 3h. Yields are determined by GC.

2.3. Palladium leaching

Partial loss of immobilised palladium may have a decisive effect on the stability of heterogeneous catalysts, so the next investigations were aimed at the determination of the palladium content of the liquid phase of the reaction mixtures. Similarly to the results obtained earlier with the catalyst on the imidazolum SILP **CAT-2**, [21] a considerable amount of palladium leached into the reaction mixtures in the first experiments. However, in case of **CAT-2**, the drop in the loss of palladium was observed already after the first run (from 23.7 % of the original load, to a total of 8.1% in the 5 successive runs). [21] Palladium leaching of **CAT-1** was smaller in the three-hour long reaction (Table 3, entry 3), but approximately the same loss of palladium was measured in the recycling experiment (entry 4). The palladium-content of the reaction mixture decreased noticeable only from the third run (entries 5, 6). These observations are in good accordance with the differences in the dissolution of the two different ionic liquids, **IL-1** and **IL-2**. The ^{1}H NMR investigations of the reaction mixtures indicated that while in case of **IL-1** almost the total amount of the adsorbed ionic liquid was dissolved in the reaction mixture already in the first run, only circa half of **IL-2** was removed in the first cycle, and the other half was lost in the second one. That means that the initial loss of palladium is mainly due to the increased solubility of palladium complexes/nanoparticles in the ionic liquid/organic solvent mixture.

The absence of the bands corresponding to the alkyl-pyridinium moiety in the IR spectrum of the spent catalyst (Figure 2) also supports the loss of the majority of the IL. (The signal at 1668 cm^{-1} can be attributed to some residual DMF that could not be completely removed after the catalytic reaction.) These changes could also be followed by comparing the differences between the composition of the fresh and spent catalyst. The decrease in the carbon content from 18.8% to 7.73% indicated the loss of some organic moieties. The relatively high N

content (1.92%), can be attributed to residual DMF, and is in accordance with the IR results. ^{1}H NMR investigations showed a similar behaviour in acetonitrile but the presence of **IL-2** could not be detected in the reaction mixture obtained in toluene.

Examining the leaching data of experiments carried out with different reaction times in DMF (Table 3, entries 1-3), an appreciable decrease in the palladium-content of the reaction mixture could be detected in the three-hour long reaction (Table 3, entries 2 and 3). This supports the assumption that after the completion of the reaction after one hour (see Table 2, entry 2), a part of the leached palladium was redeposited on the support. So it can be concluded that similarly to the reactions carried out with **CAT-2**, [21] a dissolution-reprecipitation mechanism [27] may also operate here. While 5.1% of the original load of palladium was lost in acetonitrile (entry 7), the metal content of the reaction mixture in toluene was much lower (entry 8).

Table 3. Leaching of palladium during recirculation experiments for aminocarbonylation of iodobenzene (**1a**) with morpholine (**2a**) in different solvents[a]

Entry	Solvent	Base	Reaction time [h]	Pd-leaching [%]
1	DMF	Et_3N	0.5	6.4
2	DMF	Et_3N	1	11.7
3	DMF	Et_3N	3	8.8
4	DMF	Et_3N	3 (2^{nd} run)	10.4
5	DMF	Et_3N	3 (3^{rd} run)	3.2
6	DMF	Et_3N	3 (4^{th} run)	<2
7	acetonitrile	Et_3N	8	5.1
8	toluene	DBU	3	<1

[a]: reaction conditions: 0.2 mmol **1a**, 0.5 mmol **2a**, 0.25 mmol base, catalyst **CAT-1** (with 3.2 μmol Pd-content) in 1 ml solvent, 30 bar CO pressure, 100 °C; [b]: determined by ICP-AES.

To obtain information about the homogeneous or heterogeneous nature of the catalytic reactions in the presence of **CAT-1**, hot filtration and mercury poising tests were also carried out (Table 4). In a typical experiment the catalytic mixture was filtered after half an hour . One half of the mixture was heated further under CO pressure and the other was treated similarly but in the presence of mercury.

A considerable conversion of **1a** was detected after the removal of the solid material using either a fresh supply (entry 1) or a spent catalyst (entry 3) in DMF. This is in accordance with the amount of leached palladium in the first two cycles. The reaction could be stopped almost completely in the presence of mercury in case of the spent catalyst (entry 4) indicating that the catalytically active species that have leached to the reaction mixture are mainly nanoparticles. On the contrary, some further reaction of iodobenzene (**1a**) was observed in the filtrate of the first reaction even when mercury was added. This can be due to an initial loss of palladium complexes together with palladium nanoparticles in the first run experiment. In acetonitrile (Table 4, entry 6) the complete lack of catalytic activity in the presence of mercury shows the presence of nanoparticles only. According to the tests in toluene (entries 7, 8), both complexes and nanoparticles contribute to the catalytic activity of the filtrate after a half an hour long reaction.

In a summary of catalytic and leaching data, it can be stated that although the toluene/DBU system was proved to be superior in terms of the dissolution of the ionic liquid as well as the loss of the metal, a better selectivity towards α-ketoamide **3aa** could be achieved in DMF or acetonitrile. Comparing the latter solvents, better recyclability of the catalyst could be achieved in DMF.

Table 4. Hot filtration and mercury poisoning tests in the aminocarbonylation of iodobenzene (**1a**) with morpholine (**2a**) in different solvents[a]

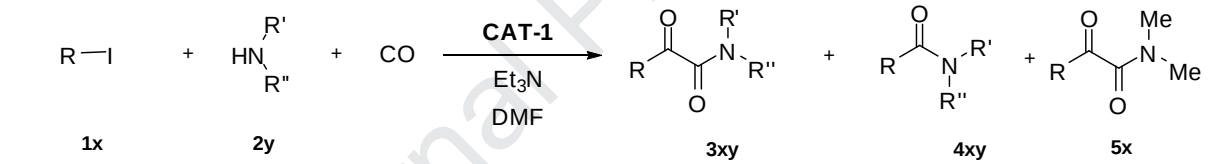
Entry	Solvent	Base	First step[b]		Second step[c]		
			Conv. of **1a** (%)[d]	Ratio of **3aa**:**4aa**[d]	Hg	Conv. of **1a** (%)[d]	Ratio of **3aa**:**4aa**[d]
1	DMF	Et_3N	21	100:0	-	57	95:5
2					+	31	98:2
3[e]	DMF	Et_3N	18	100:0	-	50	98:2
4					+	19	100:0
5	acetonitrile	Et_3N	41[f]	93:7	-	55	93:7
6					+	41	93:7
7	toluene	DBU	30	91:9	-	50	92:8
8					+	35	91:9

[a]: reaction conditions: 0.2 mmol **1a**, 0.5 mmol **2a**, 0.25 mmol base, catalyst **CAT-1** (with 3.2 μmol Pd-content), 1 ml solvent, 30 bar CO, 100 °C; [b]: reaction time: 0.5h; [c]: reaction time: 3h; [d]: determined by GC; [e]: recycled catalyst after a three hour-long first run; [f]: reaction time: 1.5h.

*2.4. Carbonylation of other substrates in the presence of **CAT-1***

The efficiency of **CAT-1** in the carbonylation of other substrates, aryl halides (**1a-1f**) and aliphatic amines (**2a-2f**) (Schemes 2-5) as well as iodobenzene (**1a**) and aniline derivatives (**2g-2k**) (Scheme 6), was also explored (Table 5). Because of the relatively high loss of palladium in the first two cycles, the catalyst was used in five successive runs in each case to prove recyclability. Good conversions could be achieved in most of the reactions with the exception of the use of the sterically hindered amine **2d** (entry 3). The α-ketoamides were the main products in the reactions of secondary aliphatic amines **2a-c** and **2e** (entries 1, 2, 4, 11-

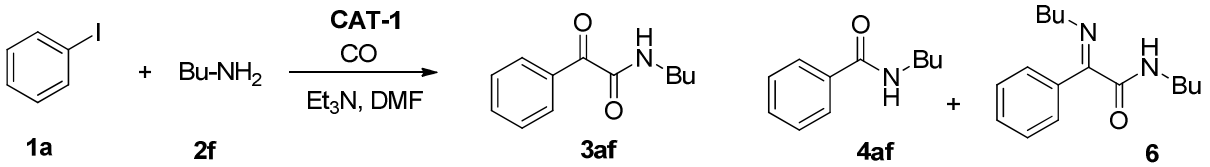
17). Poor selectivity was observed with 2-ethylpiperidine (**2d**) with the amide derivative **4ad** as the prevailing product (entry 3). It should be mentioned, that a similar difference between the distribution of mono- and double carbonylated products was observed before in the reactions of piperidine (**2c**) and 2-ethylpiperidine (**2d**) under homogeneous conditions. [28] The application of *N*,*N*-diethylamine (**2e**) resulted in some change in the product distribution towards the amide (**4ae**) when the catalyst was recycled (entry 4). In most of the reactions with morpholine (**2a**) (entries 11-17) or pyrrolidine (**2b**) (entry 1) as the nucleophile, a slow but noticeable increase in the amount of side product **5** could be detected in the consecutive experiments. The imine derivative (**6**, Scheme 3) was the main product in the carbonylation of the primary amine **2f**, due to the reaction of ketoamide **1af** with the excess of amine (entry 5).



a: R=Ph
b: R=4-MeO-C_6H_4
c: R=3,4-Me_2-C_6H_3
d: R=3-F-C_6H_4
e: R=4-Cl-C_6H_4
f: R=1-naphthyl

a: R'R''=$(CH_2)_2$-O-$(CH_2)_2$
b: R'R''=$(CH_2)_4$
c: R'R''=$(CH_2)_5$
d: R'R''=CH(Et)-$(CH_2)_4$
e: R'=R''=Et

Scheme 2. Carbonylation products formed from aryl iodides **1a-1f** and secondary amines **2a-2e**



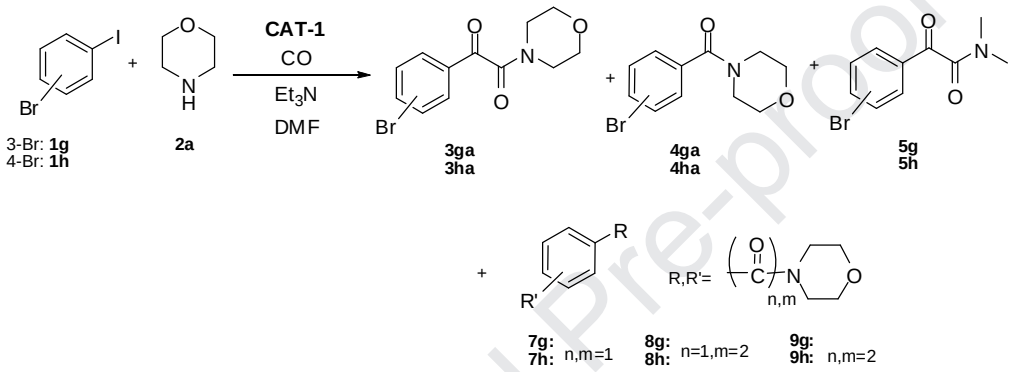
Scheme 3. Carbonylation of iodobenzene (**1a**) and *n*-butylamine (**2f**)

Table 5. Carbonylation of aryl iodides **1a-1i** and amines **2a-2k** in the presence of **CAT-1**[a]

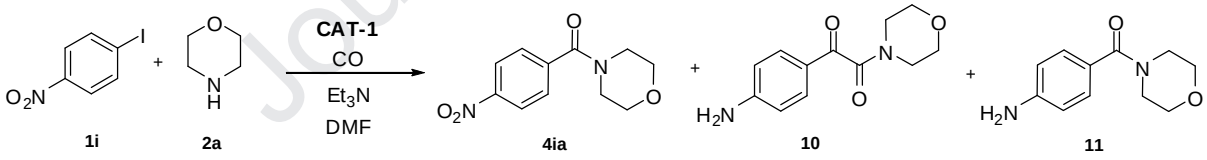
entry	**1**	**2**	run 1		run 2		run 3		run 4		run 5	
			conv. (%)[b]	ratio of **3/4/5**[b]	conv. (%)[b]	ratio of **3/4/5**[b]	conv. (%)[b]	ratio of **3/4/5**[b]	conv. (%)[b]	ratio of **3/4/5**[b]	conv. (%)[b]	ratio of **3/4/5**[b]
1	**1a**	**2b**	100	70/27/3	100	70/22/8	100	70/17/13	99	57/26/17	98	57/26/18
2	**1a**	**2c**	100	85/11/4	97	88/6/6	100	88/6/6	96	88/6/6	100	87/6/7
3	**1a**	**2d**	100	27/64/9	88	43/55/2	82	45/52/3	78	45/55/0	72	46/54/0
4	**1a**	**2e**	100	84/14/2	100	83/14/3	100	81/17/2	100	73/27/0	95	65/35/0
5	**1a**	**2f**	100	15/5/0[c]	100	10/12/2[c]	100	7/16/1[c]	100	13/19/3[c]	100	10/24/4[c]
6	**1a**	**2g**	100	0/100/0	100	0/100/0	100	0/100/0	100	0/100/0	100	0/100/0
7	**1a**	**2h**	100	0/100/0	90	0/100/0	96	0/100/0	96	0/100/0	90	0/100/0
8	**1a**	**2i**	100	0/100/0	100	0/100/0	100	0/100/0	100	0/100/0	96	0/100/0
9	**1a**	**2j**	100	0/100/0	100	0/100/0	100	0/100/0	100	0/100/0	100	0/100/0
10	**1a**	**2k**	100	0/100/0	97	0/100/0	100	0/100/0	100	0/100/0	98	0/100/0
11	**1b**	**2a**	100	91/9/0	100	87/5/8	100	84/5/11	98	84/5/11	92	84/4/12
12	**1c**	**2a**	100	91/7/2	100	86/7/7	98	82/6/12	97	82/6/12	100	77/7/16
13	**1d**	**2a**	100	96/4/0	100	81/9/10	100	78/9/13	100	76/8/16	100	79/8/13
14	**1e**	**2a**	100	69/27/4	98	76/14/8	97	72/14/11	96	75/12/13	96	72/13/15
15	**1f**	**2a**	100	68/32/0	100	74/22/4	98	68/24/6	100	73/18/9	99	71/18/11
16	**1g**	**2a**	100	66/21/1[d]	100	79/10/7[d]	100	79/8/10[d]	100	72/8/17[d]	100	71/8/21
17	**1h**	**2a**	100	74/5/6[e]	100	72/6/9[e]	100	73/6/10[e]	100	75/6/9[e]	100	74/6/9[e]
18	**1i**	**2a**	100	(6[f])/30(64[g])/0	100	(5[f])/19(76[g])/0	100	(4[f])/17(79[g])/0	100	(3[f])/13(84[g])/0	100	(3[f])/9(88[g])/0

[a] : reaction conditions: 0.2 mmol **1**, 0.5 mmol **2**, 0.25 mmol Et_3N, **CAT-1** (3.2 μmol Pd, 1.6 mol%), 1 ml DMF, 100 °C, 30 bar, 8 h. [b] : determined by GC. [c]: main product: **6** (Scheme 2), formed in 85%, 86%, 86%, 75% and 72% yield in runs 1-5, respectively (GC). [d]: side products: **7g**, **8g** and **9g** (Scheme 3), formed with a total yield of 12%, 4%, 3% and 3% (GC) in runs 1-4, respectively. [e]: side products: **7h**, **8h** and **9h** (Scheme 3), formed with a total yield of 15%, 13%, 11%, 10% and 11% (GC) in in runs 1-5, respectively. [f]: in parenthesis: ratio of 4-amino derivative **10**, Scheme 4). [g]: in parenthesis: ratio of 4-amino derivative **11**, Scheme 4).

A partial substitution of the bromo functionalities of bromo-iodobenzenes **1g** and **1h** was observed (Scheme 4), especially in the first experiments (entries 16, 17). Unfortunately, no conversion of bromobenzene, or activated bromobenzene derivatives, such as 4-nitro-bromobenzene could be effected under similar conditions. Carbonylation of 4-nitro-iodobenzene led to the 4-amino compounds (**10** and **11**, Scheme 5) as the main products (entry 18).

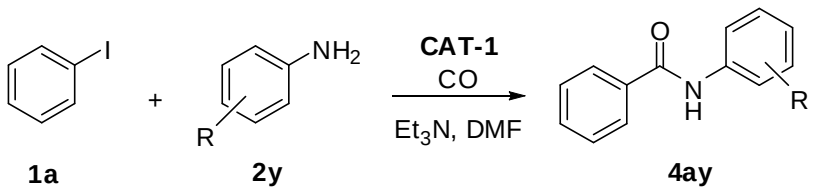


Scheme 4. Carbonylation products of aryl iodides **1g** and **1h**



Scheme 5. Carbonylation products of 4-nitro-iodobenzene (**1i**)

Excellent recyclability together with a complete selectivity towards the amides **4ag-4ak** were achieved in the reactions of the aniline derivatives **2g-2k** (Table 5, entries 6-10).



1a **2y** **4ay**

g: R=H
h: R=4-Bu
i: R=4-OMe
j: R=4-NO_2
k: R=4-C(O)CH_3

Scheme 6. Carbonylation of iodobenzene (**1a**) and aniline derivatives **2g-2k**

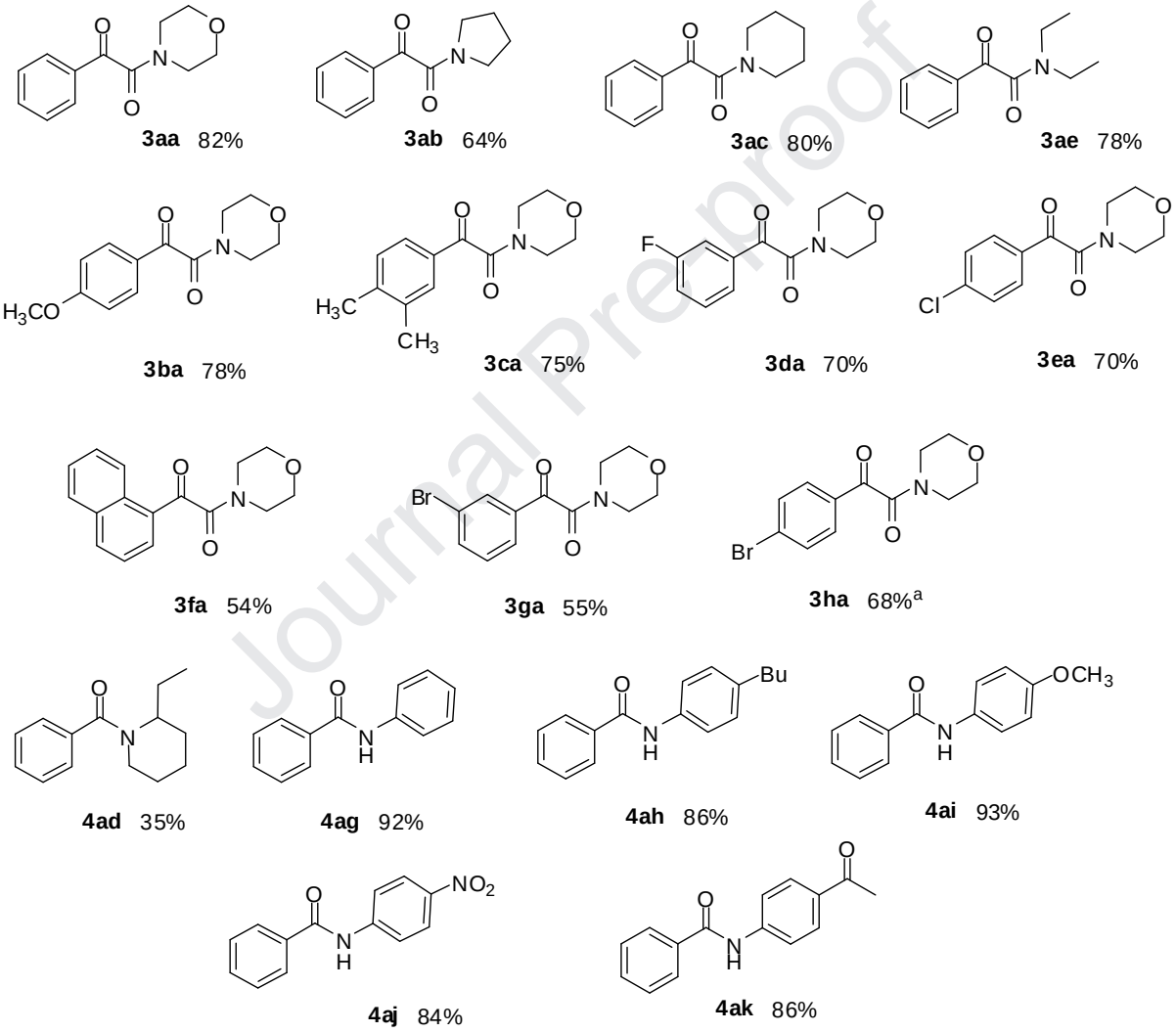


Figure 8. Yields of the main products after chromatographic separation of the combined mixtures of runs 1-3. (Reaction conditions: 0.2 mmol **1a**, 0.5 mmol **2a**, 0.25 mmol Et_3N, 1 ml DMF, catalyst **CAT-1** (Pd-content: 3.2 μmol), 100 °C, 30 bar, 8h. ([a]: Isolated from the combined mixtures of runs 2-4)

The main products could be isolated by column chromatography in acceptable to good yields (Figure 8).

3. Experimental

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.

The palladium-content of the catalysts and palladium leaching were determined by ICP-AES.

^{1}H and ^{13}C NMR spectra of the products were recorded in $CDCl_3$ or DMSO-d_6 on a Bruker Avance 500 spectrometer at 500.15 MHz and 125.78 MHz, or on a Bruker Avance 400 spectrometer at 400.13 MHz and 100.62 MHz, respectively. Chemical shifts (δ) are reported in ppm relative to $CHCl_3$ (7.26 and 77.16 ppm for ^{1}H and ^{13}C, respectively). NMR spectra of isolated products correspond well to those reported previously. [22] Other components were characterised using GC-MS. IR spectra were made using a Thermo Nicolet Avatar 330 FT-IR instrument. Samples were prepared as KBr pellets.

3.1.Preparation of supported catalysts

Catalysts **CAT-2**, [21] **CAT-3** [22] and **CAT-4** [21] were prepared as reported previously.

*Preparation of **CAT-1***

200 mg 1-butyl-4-methylpyridinium chloride (**IL-1**) 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 40 °C in vacuo for 3 h and was stored under argon until use. Palladium content

of the catalyst: 0.49% (determined by ICP). Ionic liquid content: 1.33 mmol/ g modified silica (determined from the weight increase after heating the material to constant weight at 150 °C in vacuo, as well from the N-content of the solid material (elemental analysis: C: 18.8%; H: 2.84%; N: 1.90%).

3.2. Catalytic reactions

In a typical experiment the catalyst (containing 3.2 μmol Pd) was placed in a stainless steel autoclave. The aryl iodide (0.2 mmol), amine (0.5 mmol), base (0.25 mmol) and solvent (1 ml) were transferred into it under an inert atmosphere. It was charged with carbon monoxide (5 bar or 30 bar) and heated with stirring in an oil bath at 100 °C. After cooling to room temperature the catalyst was removed by filtration and was reused without further purification. The reaction mixture was analysed by gas chromatography.

After the evaporation of the solvent of the reaction mixture, the products were purified by column chromatography (silica, eluent: ethyl acetate (**3aa**, **4ag**), toluene:ethyl acetate = 3:2 (**3ae**, **3ba**, **3ca**, **3ea**), toluene: ethyl acetate = 5:2 (**4ah**, **4ai**, **4aj**, **4ak**), toluene: acetone = 4:1 (**3ab**, **3ac**, **3da**, **3fa**, **3ga**, **3ha**, **4ad**)).

3.3. Characterisation of the products

1-Morpholino-2-phenylethane-1,2-dione (3aa): ^{1}H NMR (500.15 MHz, $CDCl_3$): 7.95-7.99 (m, 2H), 7.63-7.69 (m, 1H), 7.50-7.55 (m, 2H), 3.78-3.82 (m, 4H), 3.65-3.67 (m, 2H), 3.37-3.41 (m, 2H). ^{13}C NMR (125.78 MHz, $CDCl_3$): 191.3, 165.6, 135.1, 133.3, 129.8, 129.3, 66.9, 66.8, 46.4, 41.8..MS (m/z/rel.int.): 219 (M^+)/6; 114/11; 105/100; 86/4; 77/54; 70/26; 51/22. Yield: 82%.

1-Phenyl-2-(pyrrolidin-1-yl)ethane-1,2-dione (3ab): ^{1}H NMR (400.13 MHz, $CDCl_3$): 7.97-8.01 (m, 2H), 7.60-7.66 (m, 1H), 7.47-7.52 (m, 2H), 3.63-3.68 (m, 2H), 3.40-3.45 (m, 2H),

1.90-2.00 (m, 4H). ^{13}C NMR (100.62 MHz, $CDCl_3$): 191.7, 165.1, 134.7, 133.1, 130.0, 129.0, 46.8, 45.4, 26.1, 24.2. MS (m/z/rel.int.): 203(M^+)/3; 202/6; 105/71; 98/100; 77/52; 70/31; 55/56. Yield: 82%. Yield: 64%.

1-Phenyl-2-(piperidin-1-yl)ethane-1,2-dione (3ac): ^{1}H NMR (500.15 MHz, $CDCl_3$): 7.89-7.96 (m, 2H), 7.57-7.64 (m, 1H), 7.43-7.52 (m, 2H), 3.65-3.71 (m, 2H), 3.23-3.29 (m, 2H), 1.62-1.71 (m, 4H), 1.48-1.55 (m, 2H). ^{13}C NMR (125.78 MHz, $CDCl_3$): 192.0, 165.5, 134.7, 133.4, 129.6, 129.1, 47.1, 42.2, 26.3, 25.5, 24.4. MS (m/z/rel.int.): 217(M^+)/5; 112/100; 105/54; 84/10; 77/33; 69/61. Yield: 80%.

1-Phenyl-2-(2-ethylpiperidin-1-yl)ethane-1,2-dione (3ad): MS (m/z/rel.int.): 245(M^+)/2; 140/100; 105/60; 77/55; 55/45.

N,N-Diethyl-2-oxo-2-phenylacetamide (3ae): ^{1}H NMR (500.15 MHz, $CDCl_3$): 7.92-7.95 (m, 2H), .7.60-7.65 (m, 1H), 7.47-7.52 (m, 2H), 3.56 (q, J = 7.1 Hz, 2H), 3.24 (q, J = 7.1 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H), 1.15 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125.78 MHz, $CDCl_3$): 191.7, 166.9, 134.7, 133.5, 129.8, 129.1, 42.2, 39.0, 14.2, 13.0. MS (m/z/rel.int.): 205(M^+)/5; 105/61; 100/100; 77/42; 72/74; 51/21. Yield: 78%.

N-Butyl-2-oxo-2-phenylacetamide (3af): MS (m/z/rel.int.): 205(M^+)/13; 105/100; 77/34; 57/29; 51/10; 41/10.

1-Morpholino-2-(4-methoxyphenyl)ethane-1,2-dione (3ba): ^{1}H NMR (500.15 MHz, $CDCl_3$): 7.91-7.95 (m, 2H), 6.95-7.02 (m, 2H), 3.90 (s, 3H), 3.76-3.81 (m, 4H), 3.63-3.67 (m, 2H), 3.36-3.40 (m, 2H). ^{13}C NMR (125.78 MHz, $CDCl_3$): 190.0, 166.0, 165.2, 132.3, 126.4, 114.6, 67.0, 66.9, 55.8, 46.5, 41.7. MS (m/z/rel.int.): 249(M^+)/3; 136/12; 135/100; 114/3; 107/11; 92/10; 77/14; 70/8; 64/5. Yield: 78%.

1-(3,4-Dimethylphenyl)-2-morpholinoethane-1,2-dione (3ca): ^{1}H NMR (500.15 MHz, $CDCl_3$): 7.74 (brs, 1H), 7.69 (d, J=8.7Hz, 1H), 7.28 (d, J=8.7Hz, 1H), 3.76-3.83 (m, 4H), 3.62-3.67 (m, 2H), 3.35-3.39 (m, 2H), 2.35 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (125.78 MHz,

$CDCl_3$): 191.3, 165.9, 145.2, 137.8, 131.1, 130.5, 130.4, 127.6, 66.8, 66.7, 46.3, 41.6, 20.4, 19.8. MS (m/z/rel.int.): 247(M^+)/3; 133/100; 105/24; 79/9; 77/9; 70/9. Yield: 75%.

1-(3-Fluorophenyl)-2-morpholinoethane-1,2-dione (3da): ^{1}H NMR (500.15 MHz, $CDCl_3$): 7.72-7.75 (m, 1H), 7.67-7.63 (m, 1H), 7.48-7.52 (m, 1H), 7.32-7.37 (m, 1H), 3.75-3.81 (m, 4H), 3.63-3.67 (m, 2H) 3.35-3.40 (m, 2H). ^{13}C NMR (125.78 MHz, $CDCl_3$): 189.8 (d, J = 2.0 Hz), 164.9, 163.0 (d, J = 242.0 Hz), 135.3 (d, J = 6.0 Hz), 131.0 (d, J = 8.5 Hz), 125.9 (d, J = 3.6 Hz), 122.1 (d, J = 22.2 Hz), 116.1 (d, J = 22.5 Hz), 66.8 (2C), 46.4, 41.9. MS (m/z/rel.int.): 237(M^+)/9; 123/70; 114/100; 95/39; 86/12; 75/15; 70/77; 56/7; 45/6; 42/22. Yield: 70%.

1-(4-Chlorophenyl)-2-morpholinoethane-1,2-dione (3ea): ^{1}H NMR (500.15 MHz, $CDCl_3$): 7.89-7.94 (m, 2H), 7.48.7.52 (m, 2H), 3.76-3.83 (m, 4H), 3.64-3.69 (m, 2H), 3.36.3.41 (m, 2H). ^{13}C NMR (125.78 MHz, $CDCl_3$): 189.8, 165.1, 141.8, 131.7, 131.2, 129.7, 66.9, 66.8, 46.5, 41.9.MS (m/z/rel.int.): 253(M^+)/3; 141/33; 140/8; 139/100; 114/53; 113/9; 111/29; 86/14; 76/6; 75/22; 70/70; 56/8; 50/8; 42/29. Yield: 70%.

1-(Naphth-1-yl)-2-morpholinoethane-1,2-dione (3fa): ^{1}H NMR (500.15 MHz, $CDCl_3$): 9.24 (d, J = 8.6 Hz, 1H), 8.14 (d, J = 7.9 Hz, 1H), 8.04 (dd, J = 7.1, J = 0.9 Hz, 1H), 7.93 (d, J = 7.9 Hz, 1H), 7.69-7.75(m, 1H), 7.55.7.63 (m, 2H), 3.82.3.85 (m, 4H), 3.65-3.70 (m, 2H), 3.42-3.47 (m, 2H). ^{13}C NMR (125.78 MHz, $CDCl_3$): 193.7, 166.2, 136.3, 134.6, 134.3, 131.1, 129.6, 128.9, 128.6, 127.3, 125.9, 124.7, 66.9 (2C), 46.6, 41.9. MS (m/z/rel.int.): 269(M^+)/10; 156/12; 155/100; 128/6; 127/53; 126/8; 77/5; 70/10; 42/5. Yield: 54%.

1-(3-Bromophenyl)-2-morpholinoethane-1,2-dione (3ga): ^{1}H NMR (500.15 MHz, $CDCl_3$): 8.07-8.11 (m, 1H), 7.86-7.90 (m, 1H), 7.75-7.79 (m, 1H), 7.40 (td, J = 8.0 Hz, 1.9 Hz, 1H), 3.76-3.82 (m, 4H), 3.64-3.69 (m, 2H), 3.36-3.40 (m, 2H). ^{13}C NMR (125.78 MHz, $CDCl_3$): 189.6, 164.8, 137.8, 135.0, 132.5, 130.8, 128.5, 123.5, 66.9, 66.8, 46.4, 41.9.

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. Yield: 55%.

1-(4-Bromophenyl)-2-morpholinoethane-1,2-dione (3ha): ^{1}H NMR (500.15 MHz, $CDCl_3$): 7.81-7.85 (m, 2H), 7.65-7.69 (m, 2H), 3.76-3.82 (m, 4H), 3.64-3.68 (m, 2H), 3.36-3.40 (m, 2H). ^{13}C NMR (125.78 MHz, $CDCl_3$): 190.0, 165.0, 132.7, 132.1, 131.2, 130.7, 66.9, 66.8, 46.5, 41.9. 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. Yield: 68%.

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

Phenyl(pyrrolidin-1-yl)methanone (4ab): MS (m/z/rel.int.): 175 (M^+)/44; 174/28; 146/28; 105/100; 77/57; 51/16.

Phenyl(piperidin-1-yl)methanone (4ac): MS (m/z/rel.int.): 189 (M^+)/36; 188/100; 106/10; 105/98; 84/9; 77/56; 51/12.

Phenyl(2-ethylpiperidin-1-yl)methanone (4ad): ^{1}H NMR (500.15 MHz, $CDCl_3$): 7.35-7.42 (m, 5H), 4.52-4.92 (m, 1H), 3.42-3.83 (m, 1H), 2.74-3.33 (m, 1H), 1.44-1.88 (m, 8H), 0.66-1.05 (m, 3H). ^{13}C NMR (125.78 MHz, $CDCl_3$): 170.8, 137.2, 129.1, 128.4, 126.5, 55.8/49.7, 43.2/37.2, 28.3, 26.0, 22.6, 19.1, 10.7. MS (m/z/rel.int.): 217(M^+)/7; 188/38; 105/100; 77/43; 51/10. Yield: 35%.

***N,N*-Diethylbenzamide (4ae)**: MS (m/z/rel.int.): 177(M^+)/13; 176/36; 105/100; 77/39; 51/11.

***N*-Butylbenzamide (4af)**: 177(M^+)/7; 149/2; 105/100; 77/41; 72/48; 51/17.

***N*-Phenylbenzamide (4ag)**: ^{1}H NMR (400.13 MHz, $CDCl_3$): 7.86-7.90 (m, 2H), 7.78-7.86 (brs, 1H), 7.32-7.67 (m, 2H), 7.54-7.58 (m, 1H), 7.47-7.52 (m, 2H), 7.35-7.40 (m, 2H), 7.13-7.19 (m, 1H). ^{13}C NMR (100.62 MHz, $CDCl_3$): 166.0, 138.1, 135.1, 132.0, 129.2, 129.0, 127.2, 124.8, 120.4. MS (m/z/rel.int.): 197(M^+)/42; 105/100; 77/52; 51/14. Yield: 92%.

***N*-(4-Butylphenyl)benzamide (4ah)**: ^{1}H NMR (500.15 MHz, $CDCl_3$): 7.84-7.89 (m, 2H), 7.76-7.81 (brs, 1H), 7.52-7.56 (m, 3H), 7.45-7.52 (m, 2H), 7.16-7.20 (m, 2H), 2.60 (t, J = 7.6 Hz, 2H), 1.60 (qui, J=7.6 Hz, 2H), 1.35 (sext, J=7.6 Hz, 2H), 0.93 (t, J = 7.6 Hz, 3H). ^{13}C NMR (125.78 MHz, $CDCl_3$): 165.8, 139.6, 135.7, 135.3, 131.9, 129.1, 129.0, 127.1, 120.4, 35.2, 33.8, 22.4, 14.1. MS (m/z/rel.int.): 253(M^+)/57; 210/32; 105/100; 77/46; 51/5. Yield: 86%.

***N*-(4-Methoxyphenyl)benzamide (4ai)**: ^{1}H NMR (500.15 MHz, $CDCl_3$): 7.85 (d, J=6.6 Hz, 2H), 7.78-7.83 (brs, 1H), 7.51-7.57 (m, 3H), 7.47 (t, J=7.5 Hz, 2H), 6.90 (d, J=6.6 Hz, 2H), 3.81 (s, 3H). ^{13}C NMR (125.78 MHz, $CDCl_3$): 165.8, 156.8, 135.2, 131.8, 131.2, 128.9, 127.1, 122.3, 114.4, 55.7.MS (m/z/rel.int.): 227(M^+)/51; 122/5; 105/100; 95/4; 77/38; 51/6. Yield: 93%.

***N*-(4-Nitrophenyl)benzamide (4aj)**: ^{1}H NMR (500.15 MHz, DMSO-d_6): 10.80 (s, 1H), 8.25-8.29 (m, 2H), 8.05-8.09 (m, 2H), 7.97-8.00 (m, 2H), 7.62-7.66 (m, 1H), 7.7.54-7.59 (m, 2H). ^{13}C NMR (125.78 MHz, DMSO-d_6): 166.2, 145.5, 142.5, 134.2, 132.1, 128.5, 127.9, 124.7, 119.8. MS (m/z/rel.int.): 242(M^+)/7; 105/100; 77/51; 51/8. Yield: 84%.

***N*-(4-Acetylphenyl)benzamide (4ak)**: **)**: ^{1}H NMR (500.15 MHz, $CDCl_3$): 8.03-8.07 (brs, 1H), 7.97-8.01 (m, 2H), 7.87-7.90 (m, 2H), 7.75-7.79 (m, 2H), 7.56-7.60 (m, 1H), 7.49-7.53 (m, 2H), 2.60 (s, 3H). ^{13}C NMR (125.78 MHz, $CDCl_3$): 165.9, 142.5, 134.7, 133.3, 132.4, 130.0, 129.1, 127.2, 119.4, 26.6. MS (m/z/rel.int.): 239(M^+)/25; 105/100; 77/39; 51/6; 43/35. Yield: 86%.

Morpholino(4-methoxyphenyl)methanone (4ba): MS (m/z/rel.int.): 221(M^+)/10; 220/16; 135/100; 107/8; 92/9; 77/15; 64/5; 56/3.

Morpholino(3,4-dimethylphenyl)methanone (4ca): MS (m/z/rel.int.): 219(M^+)/11; 218/17; 133/100; 105/20; 79/11; 77/12.

Morpholino(3-fluorophenyl)methanone (4da): MS (m/z/rel.int.): 209(M^+)/15; 208/28; 194/12; 178/5; 166/3; 123/100; 95/53; 86/24; 75/18; 56/41; 42/6.

Morpholino(4-chlorophenyl)methanone (4ea): MS(m/z/rel.int.): 227(M^+)/3; 226/4; 225(M^+)/10, 224/20;141/32; 140/8; 139/100; 113/13; 111/36; 86/23; 76/7; 75/29; 56/34; 44/29.

Morpholino(naphth-1-yl)methanone (4fa): MS (m/z/rel.int.): 241(M^+)/38; 240/23; 156/23; 155/100; 127/81; 86/8; 77/8.

Morpholino(3-bromophenyl)methanone (4ga): 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; 55/42; 104/14; 86/74; 77/12; 76/63; 75/42; 74/11; 72/16; 56/100; 55/11; 50/30; 42/24.

Morpholino(4-bromophenyl)methanone (4ha): MS (m/z/rel.int.): 271(M^+)/17; 269(M^+)/17; 268/42; 185/99; 183/100; 157/28; 155/22; 104/12; 86/41; 76/34; 75/26; 72/11; 56/54; 50/18; 42/12.

Morpholino(4-nitrophenyl)methanone (4ia): MS (m/z/rel.int.): 236(M^+)/10; 235/14; 150/40; 86/37; 76/43; 56/100.

***N,N*-Dimethyl-2-oxo-2-phenylacetamide (5a)**: MS (m/z/rel.int.): 177(M^+)/6; 105/100; 77/46; 72/54; 51/19.

***N,N*-Dimethyl-2-oxo-2-(4-methoxyphenyl)acetamide (5b)**: MS (m/z/rel. int.): 207(M^+)/3; 137/100; 107/9; 92/9; 77615; 72/10

***N,N*-Dimethyl-2-oxo-2-(3,4-dimethylphenyl)acetamide (5c)**: MS (m/z/rel. int.): 205(M^+)/3; 133/100; 105/26; 79/10; 77/11; 72/11.

***N,N*-Dimethyl-2-oxo-2-(3-fluorophenyl)acetamide (5d)**: MS (m/z/rel. int.): 195(M+)/8; 123/38; 95/25; 75/13; 72/100; 44/13.

***N,N*-Dimethyl-2-oxo-2-(4-chlorophenyl)acetamide (5e)**: MS (m/z/rel. int.): 213(M^+)/2; 211(M^+)/7; 141/13; 139/41; 113/6; 111/19; 75/15; 72/100.

***N,N*-Dimethyl-2-oxo-2-(naphth-1-yl)acetamide (5f)**: MS (m/z/rel. int.): 227 (M^+)/9; 155/100; 127/66; 101/5; 77/8; 72/20.

***N,N*-Dimethyl-2-oxo-2-(3-bromophenyl)acetamide (5g)**: MS (m/z/rel. int.): 257(M+)/4; 255(M+)/4; 185/48; 183/50; 157/13; 155/13; 76/20; 75/19; 72/100; 50/15.

***N,N*-Dimethyl-2-oxo-2-(4-bromophenyl)acetamide (5h)**: MS (m/z/rel. int.): 257(M^+)/4; 255(M^+)/4; 185/19; 183/20; 157/9; 155/8; 76/13; 75/11; 72/100; 44/7.

***N*-Butyl-benzoylformamide N'-butylimine (6)**: MS (m/z/rel.int.): 260(M^+)/3; 217/18; 160/3; 130/4; 117/3; 104/100; 77/9; 57/8; 41/10.

1,3-Phenylenebis(morpholinomethanone) (7g): MS (m/z/rel.int.): 304(M^+)/26; 303/18; 219/16; 218/100; 189/11; 160/10; 133/33; 114/10; 105/12; 104/27; 86/86; 77/11; 76/37; 70/18; 56/42; 42/15.

1,4-Phenylenebis(morpholinomethanone) (7h): MS (m/z/rel.int.): 304(M^+)/6; 191/11; 190/100; 91/5; 77/6.

1-(3-Morpholinocarbonyl)phenyl-2-morpholinoethane-1,2-dione (8g): MS (m/z/rel.int.): 332(M^+)/22; 304/14; 218/100; 133/35; 114/86; 104/24; 86/12; 76/27; 70/67; 56/16; 42/25.

1-(4-Morpholinocarbonyl)phenyl-2-morpholinoethane-1,2-dione (8h): MS (m/z/rel.int.): 332(M^+)/8; 304/10; 219/13; 218/100; 208/7; 114/31; 104/17; 76/9; 70/26; 56/6; 42/10.

1,3-Phenylenebis(2-morpholinoethane-1,2-dione) (9g): MS (m/z/rel.int.): 360(M^+)/14; 246/100; 133/12; 114/96; 104/17; 78/13; 76/20; 70/84; 45/11; 42/32.

1,4-Phenylenebis(2-morpholinoethane-1,2-dione) (9h): MS (m/z/rel.int.): 360(M^+)/16; 332/12; 247/14; 246/100; 218/8; 114/98; 104/21; 76/12; 70/71; 45/5; 42/22.

1-Morpholino-2-(4-aminophenyl)ethane-1,2-dione (10): MS (m/z/rel.int.): 234(M^+)/3; 120/100; 92/17; 70/6; 65/16.

4-Aminophenyl(morpholino)methanone (11): MS (m/z/rel.int.): 206(M^+)/13; 205/9; 121/8; 120/100; 93/2; 92/18; 91/2; 66/2; 65/17; 64/2; 56/2; 39/5.

4. Conclusions

A supported ionic liquid phase with adsorbed pyridinium ionic liquid was proved to exert efficient stabilising effect toward the immobilised palladium catalyst. Detailed investigations revealed that in spite of the loss of the majority of the ionic liquid in the first two cycles, the catalyst can be used effectively in at least 10 consecutive runs. The importance of the choice of the ionic liquid was demonstrated by the comparison of the catalytic performance of pyridinium- (**CAT-1**) and imidazolium (**CAT-2**) SILP-Pd catalysts. Although very similar leaching data could be measured for the two catalysts, the former showed higher activity and better recyclability. The heterogeneous catalyst **CAT-1** could be reused during the carbonylation of a wide scope of substrates, but the structure of the reaction partners has a decisive effect both on the recyclability of the catalyst and the selectivity of the carbonylation reaction.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://

References

[1] A. Muthukumar, S. Sangeetha, G. Sekar, Org. Biomol. Chem. 16 (2018) 7068–7083.

[2] (a) Y.X. Jia, D. Katayev, E. P. Kündig, Chem. Commun. 46 (2010) 130–132. (b) A. Muthukumar, G. N. Rao, G. Sekar, Org. Biomol. Chem. 17 (2019) 3921-3933.

[3] J. X. Hu, H. Wu, C. Y. Li, W. J. Sheng, Y. X. Jia, J. R. Gao, Chem. Eur. J. 17 (2011) 5234–5237.

[4] H. Masui, N. Ishizawa, S. Fuse, T. Takahashi Tetrahedron 71 (2015) 6354–6360.

[5] S. R. Laursen, M. T. Jensen, A. T. Lindhardt, M. F. Jacobsen, T. Skrydstrup, Eur. J. Org. Chem. (2016) 1881–1885.

[6] Z. Zhu, X. Lv, J. E. Anesini, D. Seidel, Org. Lett. 19 (2017) 6424−6427.

[7] C. De Risi, G. P. Pollini, V. Zanirato, Chem. Rev. 116 (2016) 3241−3305.

[8] L. Kaysser, Nat. Prod. Rep. 36 (2019) 1654−1686.

[9] (a) C. Steuer, C. Gege, W. Fischl, K. H. Heinonen, R. Bartenschlager, C. D. Klein, Bioorg. Med. Chem. 19 (2011) 4067–4074. (b) K. O. Chang, Y. Kim, S. Lovell, A. D. Rathnayake, W. C. Groutas, Viruses 11 (2019) 197.

[10] S. Pacifico, V. Ferretti, V. Albanese, A. Fantinati, E. Gallerani, F. Nicoli, R. Gavioli, F. Zamberlan, D. Preti, M. Marastoni, ACS Med. Chem. Lett. 10 (2019) 1086−1092.

[11] D. Kumar, S. R. Vemula, G. R. Cook, ACS Catal. 6 (2016) 4920−4945.

[12] B. Urbán, M. Papp, R. Skoda-Földes, Curr. Green Chem. 6 (2019) 78−95.

[13] M. Genelot, N. Villandier, A. Bendjeriou, P. Jaithong, L. Djakovitch, V. Dufaud, Catal. Sci. Technol. 2 (2012) 1886−1893.

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

[15] L. Liu, S. Zheng, W. Sun, C. Xia, Chin. J. Chem. 27 (2009) 623−627.

[16] S. S. Islam, R. A. Molla, S. Ta, N. Yasmin, D. Das, S. M. Islam, J. Organomet. Chem. 882 (2019) 18−25.

[17] Y. Yan, H. Zuo, Z. Jin, 1997. React. Funct. Polym. 32 (1997) 1−24.

[18] Z. Wang, C. Liu, Y. Huang, Y. Hu, B. Zhang, Chem.l Commun. 52 (2016) 2960−2963.

[19] V. M. Solano, G. G. Miera, V. Pascanu, A. K. Inge, B. Martín-Matute, ChemCatChem 10 (2017) 1−7.

[20] (a) R. A. Molla, M. A. Iqubal, K. Ghosh, A. S. Roy, Kamaluddin, S. M. Islam, RSC Adv. 4 (2014) 48177−48190. (b) B. Chen, F. Li, Z. Huang, T. Lua, G. Yuan, 2014. Appl. Catal. A 481 (2014) 54–63. (c) S. S. Islam, S. Riyajuddin, R. A. Molla, N. Yasmin, K Ghosh, S. M. Islam, New J. Chem. 44, (2020) 1979−1987. /

[21] M. Papp, R. Skoda-Földes, J. Mol. Catal. A 378 (2013) 193−199.

[22] M. Papp, P. Szabó, D. Srankó, G. Sáfrán, L. Kollár, R. Skoda-Földes, RSC Adv. 7 (2017) 44587−44597.

[23] B. Urbán, P. Szabó, D. Srankó, G. Sáfrán, L. Kollár, R. Skoda-Földes, Mol. Catal. 445 (2018) 195–205.

[24] W. Wojtków, A. M. Trzeciak, R. Choukroun, J. L. Pellegatta, J. Mol. Catal. A. 224 (2004) 81–86.

[25] (a) D. Cook, Can. J. Chem. 39 (1961) 2009-2024. (b) C. Pichon, P. Mialane, J. Marrot, C. Binet, A. Vimont, A. Travert, J. C. Lavalley, Phys. Chem. Chem. Phys. 13 (2011) 322–327.

[26] M. Papp, B. Urbán, E. Drotár and R. Skoda-Földes, Green Proc. Synth. 4 (2015) 103–115.

[27] R. G. Heidenreich, J. G. E. Krauter, J. Pietsch, K. Köhler, J. Mol. Catal. A 182–183 (2002) 499-509.

[28] Z. Szarka, R. Skoda-Földes, Á. Kuik, Z. Berente, L. Kollár, Synthesis (2003) 545–550.

Pd was supported on the surface of silica modified with adsorbed pyridinium ions > The catalyst was tested in carbonylation of iodoarenes and aliphatic/aromatic amines < Enhanced activity and recyclability was observed compared to other SILPs > The catalyst was recycled 5 times for a wide range of substrates

Declaration of Interest Statement

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.