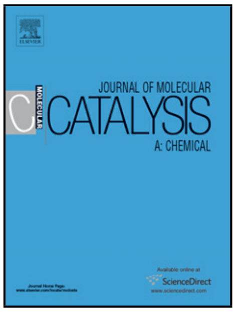

Title: Phosphine-free atmospheric carbonylation of aryl iodides with aniline derivatives in the presence of a reusable silica-supported palladium catalyst

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PII: S1381-1169(14)00495-6
DOI: http://dx.doi.org/doi:10.1016/j.molcata.2014.11.008
Reference: MOLCAA 9342

To appear in: *Journal of Molecular Catalysis A: Chemical*

Received date: 24-6-2014
Revised date: 3-11-2014
Accepted date: 9-11-2014

Please cite this article as: B. Urbán, M. Papp, D. Srankó, R. Skoda-Földes, Phosphine-free atmospheric carbonylation of aryl iodides with aniline derivatives in the presence of a reusable silica-supported palladium catalyst, *Journal of Molecular Catalysis A: Chemical* (2014), http://dx.doi.org/10.1016/j.molcata.2014.11.008

Highlights

Phosphine-free silica supported palladium catalysts were prepared

Silica support was modified with grafted imidazolium chloride

Optimisation of immobilisation was carried out

Selective synthesis of N-arylamides was achieved under atmospheric conditions

The catalyst was reused with small loss of activity

Phosphine-free atmospheric carbonylation of aryl iodides with aniline derivatives in the presence of a reusable silica-supported palladium catalyst

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Abstract

Various palladium catalysts were obtained by the immobilisation of palladium on silica, modified with imidazolium salts. The efficiency of the catalysts was greatly dependent on the choice of the anion of the imidazolium salt, the palladium precursor and on the conditions of heterogenisation. Palladium acetate immobilised on silica with grafted imidazolium chloride moieties was shown to be a selective and recyclable catalyst for atmospheric aminocarbonylation of aryl iodides with aromatic amines in DMF. It was proved that the greater loss of palladium in DMSO can be explained by the formation of soluble palladium complexes.

Keywords: aminocarbonylation, N-aryl amides, grafted imidazolium ions, palladium, silica support

1. Introduction

Palladium catalysed carbonylation in the presence of amine nucleophiles [1] serves as a powerful tool for the construction of the amide functionality, an important structural motif in pharmacologically active molecules, agrochemicals and peptides [2]. Although amides can be prepared under mild reaction conditions by the use of homogeneous palladium catalysts,

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difficulties in separation of the products and catalyst recycling make this methodology less attractive from the industrial point of view.

In the past 10 years, several efficient immobilised palladium-catalysts were developed, primarily for C-C coupling reactions [3]. At the same time, only a few examples have been reported for the use of supported catalysts in aminocarbonylations [4]. Moreover, most of these reactions were carried out under CO pressure that required the use of high pressure techniques. Alkoxycarbonylation [5] and microwave induced aminocarbonylation of aryl iodides [6] as well as the synthesis of *N*-substituted phthalimides [7] were performed in the presence of Pd/C under 5-9 bar CO pressure. A polymer supported palladium-*N*-heterocyclic carbene complex was shown to be a recyclable catalyst in aminocarbonylations under 6.9 bar CO [8]. A palladium catalyst, immobilised by a bidentate phosphine ligand grafted on Merrifield resin, was reported to convert bromoarenes to amides at 4.8 bar CO [9]. Pd nanoparticles supported on a zeolitic imidazole framework (ZIF-8) were described as an efficient heterogeneous catalyst for the aminocarbonylation of bromoarenes in the presence of phosphines and iodoarenes under phosphine-free conditions using a CO pressure of 4 bar [10].

The use of higher pressures (30-40 bar) usually led to selective double carbonylation leading to α-ketoamides. A silica-supported polytitazane–palladium (Ti–N–Pd) complex [11], Pd/C used together with PPh_3 as ligand [12] or palladium-phosphine complexes grafted onto mesoporous silica (SBA-15) [13] were proved to be active catalysts in such reactions.

In most cases, atmospheric aminocarbonylations were performed with catalysts obtained by the immobilisation of special, bidentate ligands on solid supports. Cai's group reported on the application of palladium-catalysts with bidentate phosphine [14], arsine [15] and mixed sulphur-phosphine ligands [16] as well as monodentate selenium ligands [17] grafted on silica [15-17] or MCM-41 [14].

Recently, Seayad disclosed results on atmospheric pressure carbonylation of aryl iodides in the presence of palladium nanoparticles supported on a metal-organic framework [18]. At the same time, 2 bar CO pressure had to be used for an efficient recycling of the catalyst and long reaction time, 24 h in most cases, was necessary with aromatic amines as nucleophiles. Moreover, it was admitted that this catalyst needed special handling because MOF-5 was moisture-sensitive, and structural changes occurred that negatively affected the catalytic performance [10]. The synthesis of isoindole-1,3-diones by a carbonylative cyclisation reaction was reported by Bhanage using $PdCl_2$ immobilised on a supported ionic liquid phase (SILP) [19].

In our group, heterogeneous palladium catalysts were prepared using a SILP with grafted imidazolium-tetrafluoroborate moieties for the immobilisation of palladium [20]. Under pressure, excellent yields of α-ketoamides, formed by double carbonylation, were obtained. At the same time, under atmospheric conditions only low conversion of the aryl iodide was observed.

In this paper our results concerning carbonylation of aryl iodides with aromatic amines, carried out in the presence of SILP palladium catalysts, are presented. It is shown that the outcome of the reaction depends greatly on several factors, such as the choice of the IL phase, palladium precursor and conditions of immobilisation.

2. Experimental

*2.1.Preparation of the supported ionic liquid phases **SILP-1** and **SILP-2***

SILP-1 was obtained as described in our previous paper by grafting 1-methyl-3-(3-triethoxysilylpropyl)imidazolium tetrafluoroborate on silica (Kieselgel 60 (0.040-0.063 mm)) [20]. Ionic liquid loading: 0.63 mmol/g silica (determined by measuring the weight increase after heating the material to constant weight at 150 ^oC in vacuo).

Preparation of **SILP-2**: A mixture of 1.66 mmol (400 µl) 3-chloropropyl-triethoxysilane 6 ml toluene and 1 g silica (Kieselgel 60 (0.040-0.063 mm), Merck, pre-treated by heating for 6 h at 250 ^oC) was heated under argon at 120 ^oC for 24 h. Then the solid material was filtered, washed with 2 ml toluene, 2 ml dichloromethane and 2 ml methanol and dried in vacuo. Then it was suspended in 5 ml toluene and, under stirring, 5 mmol (397 µl) 1-methylimidazole was added dropwise in an inert atmosphere. The mixture was heated at 80 ^oC for 24 h. Then the solid material was filtered, washed with 2 ml toluene, 2 ml dichloromethane and 2 ml methanol and dried in vacuo for 8 h (Anal. Found: C, 7.66; H, 1.18; N, 1.58.). Ionic liquid loading: 0.74 mmol/g silica (determined by measuring the weight increase after heating the material to constant weight at 150 ^oC in vacuo).

2.2. Preparation of the supported catalysts

2.2.1. Preparation of CAT-1

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 under inert conditions. Then 500 mg of **SILP-1** 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 ^oC in vacuo for 3 h.

2.2.2. Preparation of CAT-2** and **CAT-3

A solution of 17.9 mmol µmol $Pd(OAc)_2$ (for **CAT-2**) or $PdCl_2$ (for **CAT-3**) in 2 ml ethanol was stirred for 15 min under inert conditions. Then 500 mg of **SILP-1** was added and the resulting mixture was stirred for 24 h at room temperature. Then the solid material was filtered, washed with 2 ml ethanol and 2 ml diethylether and dried at 35 ^oC in vacuo for 3 h.

2.2.3. Preparation of CAT-4 — CAT-8

Under inert conditions, 3.12 mmol (350 mg) KO^tBu was added with stirring to a mixture containing 2g of **SILP-2** and 20 ml solvent (see Table 1). The resulting mixture was stirred for 10 min, and after the addition of 1.60 mmol Pd-salt (see Table 1), it was stirred at room temperature for 24 h (**CAT-4**, **CAT-5**) or 48 h (**CAT-6 — CAT-8**). Then the solid material was filtered, washed with 20 ml ethanol and 20 ml diethylether and dried in vacuo for 5 h.

2.3. Catalytic reactions

2.3.1. Catalytic reactions at high pressure

In a typical experiment the catalyst (containing 6 μmol Pd) was placed in a stainless steel autoclave. Iodobenzene (**1**) (0.2 mmol, 22.5 μl), aniline (0.5 mmol), 0.7 mmol (100 μl) triethylamine and DMF (1 ml) were transferred into it under an inert atmosphere. It was charged with carbon monoxide (30 bar) and heated with stirring in an oil bath at 100 ^{o}C. After cooling to room temperature, the liquid phase was removed with a syringe. The reaction mixture was analysed by gas chromatography.

2.3.2. Catalytic reactions at atmospheric pressure

In a typical experiment a solution containing the palladium catalyst (with 6 μmol Pd-content) was placed in a Schlenk-tube. Under argon, 0.2 mmol (22.5 μl) iodobenzene (**1**), 0.5 mmol amine reagent, 0.7 mmol (100 μl) triethylamine and 1 ml solvent was added and the atmosphere was changed to carbon monoxide. The reaction mixture was heated with stirring in an oil bath at 100 ^{o}C and was analysed by gas chromatography.

In recycling experiments, the catalyst was filtered and a fresh supply of reagents was added.

2.4. Analytical measurements

Solid state NMR experiments were performed on a Bruker Avance 400 spectrometer. IR spectra were made using a Thermo Nicolet Avatar 330 FT-IR instrument. Samples were prepared in KBr.

For the determination of Pd content on the surface, X-ray photoelectron spectroscopy were applied using a KRATOS XSAM 800 XPS machine equipped with an atmospheric reaction chamber. Al Kα characteristic X-ray line, 40 eV pass energy and FAT mode were applied for recording the XPS lines of Pd 3d, C 1s, O 1s and Si 2p. Si 2p binding energy at 103.3 eV was used as reference for charge compensation.

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

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 products **3**, **5a-j**, **7a-i**, **9a-c**, **10a-c** and **11a,b** were identified on the basis of their MS spectra.

3: MS(m/z/rel.int.): 197(M^+)/42; 105/100; 77/52; 51/14

5a: MS(m/z/rel.int.): 211(M^+)/47; 105/100; 77/45; 51/8

5b: MS(m/z/rel.int.): 211(M^+)/39; 105/100; 77/47; 51/9

5c: MS(m/z/rel.int.): 253(M^+)/57; 210/32; 105/100; 77/46; 51/5

5d: MS(m/z/rel.int.): 225(M^+)/25; 120/8; 105/100; 91/4; 77/40; 51/6; 40/17

5e: MS(m/z/rel.int.): 242(M^+)/9; 198/23; 105/100; 77/47; 51/9

5f: MS(m/z/rel.int.): 242(M^+)/7; 105/100; 77/51; 51/8

5g: MS(m/z/rel.int.): 242(M^+)/6; 105/100, 77/42; 51/6

5h: MS(m/z/rel.int.): 227(M^+)/51; 122/5; 105/100; 95/4; 77/38; 51/6

5i: MS(m/z/rel.int.): 239(M^+)/25; 105/100; 77/39; 51/6; 43/3

5j: MS(m/z/rel.int.): 247(M^+)/46; 105/100; 77/42; 51/6

7a: MS(m/z/rel.int.): 277(M^+)/33; 275(M^+)/33; 185/100; 183/100; 157/39; 155/39;104/6; 76/26; 65/14; 50/8

7b: MS(m/z/rel.int.): 233(M^+)/9; 231(M^+)/28; 141/31; 139/100; 113/13; 111/42; 75/13; 65/6

7c: MS(m/z/rel.int.): 215(M^+)/32, 123/100; 95/48; 75/10; 65/5

7d: MS(m/z/rel.int.): 242(M^+)/32; 150/100; 104/38; 92/8; 76/27; 65/8; 50/8

7e: MS(m/z/rel.int.): 242(M^+)/38; 150/100; 120/16; 104/39; 92/19; 76/25; 65/8; 50/8; 39/4

7f: MS(m/z/rel.int.): 269(M^+)/3; 267(M^+)/18; 265(M^+)/26; 177/10 175/64; 173/100; 149/3; 147/17; 145/26; 109/12; 75/6; 65/8

7g: MS(m/z/rel.int.): 227(M^+)/12; 135/100; 107/6; 92/12; 77/14; 65/5

7h: MS(m/z/rel.int.): 225(M^+)/25; 133/100; 105/27; 77/15; 65/6; 51/4

7i: MS(m/z/rel.int.): 247(M^+)/18; 155/100; 127/72; 101/5; 77/6; 65/5; 51/3

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

9b: MS(m/z/rel.int.): 175(M^+)/44; 174/28; 146/28; 105/100; 77/57; 51/16

9c: MS(m/z/rel.int.): 177(M^+)/13; 176/42; 148/3; 134/3; 105/100; 77/49; 51/10

10a: MS(m/z/rel.int.): 219(M^+)/6; 114/11; 105/100; 86/4; 77/54; 70/26; 51/22

10b: MS(m/z/rel.int.): 203(M^+)/1; 202/4; 105/70; 98/100; 77/51; 70/30; 56/26; 55/54; 51/21; 50/70

10c: MS(m/z/rel.int.): 205/(M^+)/4; 106/58; 100/100; 77/43; 72/71; 51/17

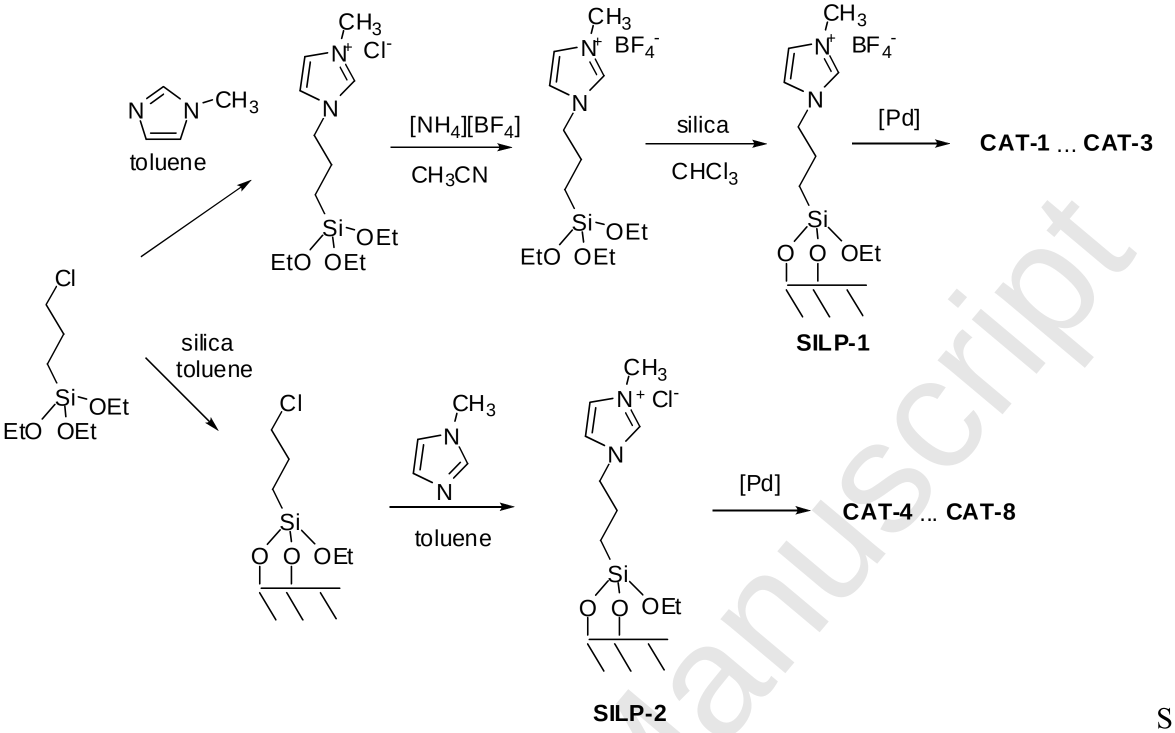
11a: MS(m/z/rel.int.): 115(M^+)/87; 100/62; 86/49; 72/20; 56/100

11b: MS(m/z/rel.int.): 99(M^+)/100; 98/15; 71/63; 70/25; 56/7

3. Results and Discussion

3.1. Preparation of the supported catalysts

Solid supports **SILP-1** and **SILP-2** were obtained by grafting 1-methyl-3-(3-triethoxysilylpropyl)imidazolium tetrafluoroborate and 1-methyl-3-(3-triethoxysilylpropyl)imidazolium chloride, respectively, on silica (Scheme 1).



S

cheme 1. Preparation of the supported catalysts

The heterogeneous catalysts were prepared by the addition of the palladium precursors (Table 1), $Pd_2(dba)_3.CHCl_3$, $Pd(OAc)_2$, $PdCl_2$, $PdBr_2$ or $PdSO_4$, to the imidazolium modified support. In case of **CAT-2**, **CAT-3** and **CAT-5** — **CAT-8** EtOH was used as solvent to reduce Pd(II) to Pd(0) [21]. During the preparation of **CAT-4** — **CAT-8** KOtBu was also added to facilitate deprotonation of the C2-H of the imidazolium ring and formation of Pd-NHC complexes [22] that can act as catalysts themselves or serve as reservoir for palladium nanoparticles [23].

Palladium content of the catalysts was determined by ICP (Table 1).

Table 1. Supported palladium catalysts used during the carbonylation reactions

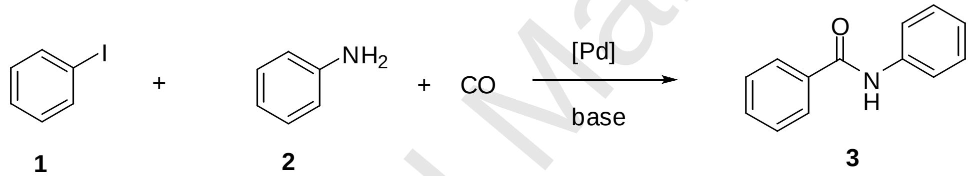
catalyst	Pd-precursor	solvent	additive	Pd-content [m/m%][a]
CAT-1	$Pd_2(dba)_3.CHCl_3$	CH_3CN+ THF	-	0.29
CAT-2	$Pd(OAc)_2$	EtOH	-	0.77
CAT-3	$PdCl_2$	EtOH	-	0.26
CAT-4	$Pd(OAc)_2$	THF	KOtBu	0.26
CAT-5	$Pd(OAc)_2$	EtOH	KOtBu	0.60
CAT-6	$PdCl_2$	EtOH	KOtBu	0.49
CAT-7	$PdBr_2$	EtOH	KOtBu	0.55
CAT-8	$PdSO_4$	EtOH	KOtBu	0.37

[a]: determined by ICP.

*3.2. Aminocarbonylation of iodobenzene (**1**) with aniline (**2**)*

The activities of the supported catalysts were compared in aminocarbonylation of iodobenzene with aniline as the nucleophile (Scheme 2, Table 2). Selective monocarbonylation took place in all cases leading to amide **3**.

The catalysts obtained by immobilisation of palladium on **SILP-1** (**CAT-1** — **CAT-3**) gave good results under 30 bar CO pressure, but a significant decrease of activity was observed upon reuse in each case (Table 2, entries 1, 3, 5). As it could be expected after our previous results obtained in aminocarbonylation with **CAT-1** using morpholine as nucleophile [20], **CAT-1** and **CAT-2** showed poor performance at atmospheric pressure. In contrast, catalysts obtained starting from **SILP-2** were considerably more active under atmospheric conditions (entries 6-8). Both activity and recyclability of these catalysts were affected by the immobilisation method, the choice of palladium precursor and solvent. Total conversion of iodobenzene to amide **3** was observed in the first run with **CAT-4**, **CAT-5** and **CAT-8**. With producing 100% conversion in the first run and exhibiting little loss of activity upon recycling, the catalyst obtained by immobilisation of $Pd(OAc)_2$ in ethanol (**CAT-5**) was chosen for further investigations.



Scheme 2. Aminocarbonylation of iodobenzene (**1**) with aniline (**2**)

Table 2. Aminocarbonylation of iodobenzene (**1**) with aniline (**2**) with different catalysts [a]

entry	catalyst	CO pressure [bar]	yield of **3** [%][b]		
			run 1	run 2	run3
1	**CAT-1**	30	80	62	61
2	**CAT-1**	1	37	25	10
3	**CAT-2**	30	81	72	70
4	**CAT-2**	1	26	18	16
5	**CAT-3**	30	87	86	57
6	**CAT-4**	1	>99	88	76
7	**CAT-5**	1	>99	97	95
8	**CAT-6**	1	83	45	33
9	**CAT-7**	1	66	53	49
10	**CAT-8**	1	>99	63	53

[a]: reaction conditions: 0.2 mmol **1**, 0.5 mmol **2**, 0.7 mmol Et_3N, catalyst (with 6 μmol Pd-content), 1 ml DMF, 4h, 100 ^{o}C; [b]: determined by GC.

In order to optimise the reaction conditions, carbonylation was carried out in different solvents and, as an increase in the reaction time had been shown to lead to a more efficient recycling [20], with a longer reaction time (8 or 16h). No conversion was obtained in dioxane, and toluene or acetonitrile were found to be only a bit more effective (Table 3, entries 1-3). Both DMF and DMSO turned out to be suitable solvents and **1** was fully converted to **3** even in the third runs. The amount of palladium leached into the reaction mixtures was determined by ICP. As it was expected, an increase in the reaction time led to lower leaching of palladium but the difference was found to be not significant (compare entries 4-6 and 7-9). At the same time, a considerably greater loss of palladium was observed in DMSO (entries 10-12).

To obtain information about the homogeneous or heterogeneous nature of the catalytic reaction, hot filtration and mercury poising tests were carried out (Table 4).

Catalytic mixtures obtained in DMF and DMSO was filtered after an hour and half an hour, respectively. One half of the mixtures was heated further in CO atmosphere, the other was treated similarly but in the presence of mercury.

Table 3. Effect of solvent on the aminocarbonylation of iodobenzene (**1**) with aniline (**2**) with **CAT-5**[a]

entry	solvent	reaction time [h]	run	yield of **3** [%][b]	Pd-leaching [%][c]
1	1,4 dioxane	8	1	-	n.d.
2	toluene	8	1	17	n.d.
3[d]	CH_3CN	8	1	19	n.d.
4	DMF	8	1	100	2.2
5	DMF	8	2	100	3.6
6	DMF	8	3	100	3.5
7	DMF	16	1	100	1.2
8	DMF	16	2	100	3.2
9	DMF	16	3	100	3.4
10	DMSO	8	1	100	14.9
11	DMSO	8	2	100	12.3
12	DMSO	8	3	100	6.7

[a]: reaction conditions: 0.2 mmol **1**, 0.5 mmol **2**, 0.7 mmol Et_3N, **CAT-5** (with 6 μmol Pd-content) and 1 ml solvent, 1 bar CO, 100 °C; [b]: determined by GC; [c]: determined by ICP ((mmol Pd in the reaction mixture/ mmol Pd on the fresh catalyst)x100); [d]: the reaction was carried out at 80 °C

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

entry	solvent	first step		second step		
		reaction time [h]	yield of **3** [%][b]	Hg	reaction time [h]	yield of **3** [%][b]
1	DMF	1	46	-	4	51
2				+	4	46
3	DMSO	0.5	64	-	4	85
4				+	4	75

[a]: reaction conditions: 0.2 mmol **1**, 0.5 mmol **2**, 0.7 mmol Et_3N, **CAT-5** (with 6 μmol Pd-content) and 1 ml solvent, 1 bar CO, 100 °C; [b]: determined by GC;

According to the results, in DMF only a slow conversion of iodobenzene occurred after the removal of the heterogeneous catalyst and the reaction could be completely stopped by the addition of mercury (Table 4, entries 1,2). This shows that a small amount of catalytically active palladium nanoparticles may have leached to the reaction mixture. In contrast, in DMSO a noticeable carbonylation took place in the absence of the heterogeneous catalyst and, at a lower rate, even in the presence of mercury (Table 4, entries 3,4). As DMSO is a good ligand for palladium [24], it can be assumed that in this case soluble palladium complexes are among the active catalytic species. This can explain the higher amount of leached palladium in reactions carried out in DMSO (Table 3, entries 10-12).

3.3. Aminocarbonylation of other substrates

With the optimal reaction conditions in hand, aminocarbonylation of iodobenzene (**1**) was carried out using substituted aniline derivatives (**4a-j**) as nucleophiles (Figure 1) and various aryl iodides as substrates (Figure 2). As it could be expected, the presence of electron withdrawing groups in the nucleophiles (Figure 1, **4e-g, 4i**), as well as a sterically crowded nitrogen (**4d**) led to lower yields of the products (**5e-g, 5i 5d**) but the catalyst could efficiently be recycled even in these cases. Excellent results were obtained with different aryl iodides (Figure 2) with the exception of derivatives with electron donating groups (**7g, 7h**). It should be mentioned that selective substitution of iodine was observed in case of chloro- (**6b, 6f**) or bromo substituted compounds (**6a**). Carbonylation of 4-iodophenol or 4-iodoaniline led to some unidentified polymeric material.

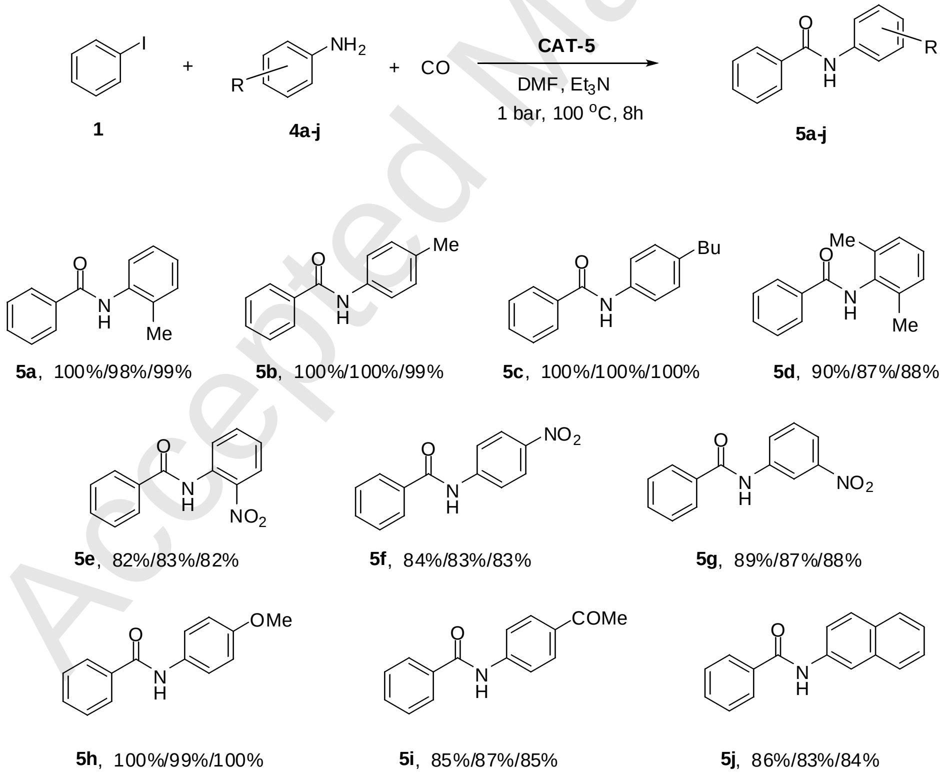


Figure 1. Aminocarbonylation of iodobenzene (**1**) with various aromatic amines (**4a-j**) in the presence of **CAT-5** (Reaction conditions: 0.2 mmol **1**, 0.5 mmol nucleophile, 10 mg catalyst, 1 ml DMF, 1 bar CO, 100 ^{o}C, 8h. Yields of three successive runs, determined by GC.)

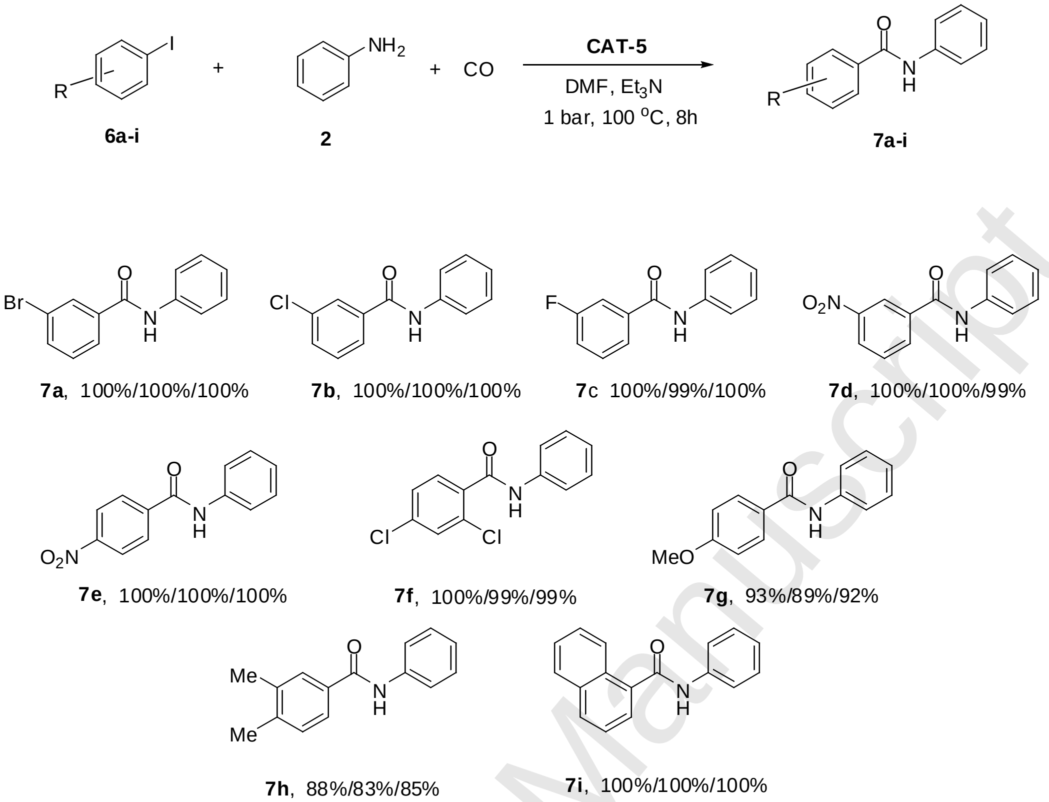
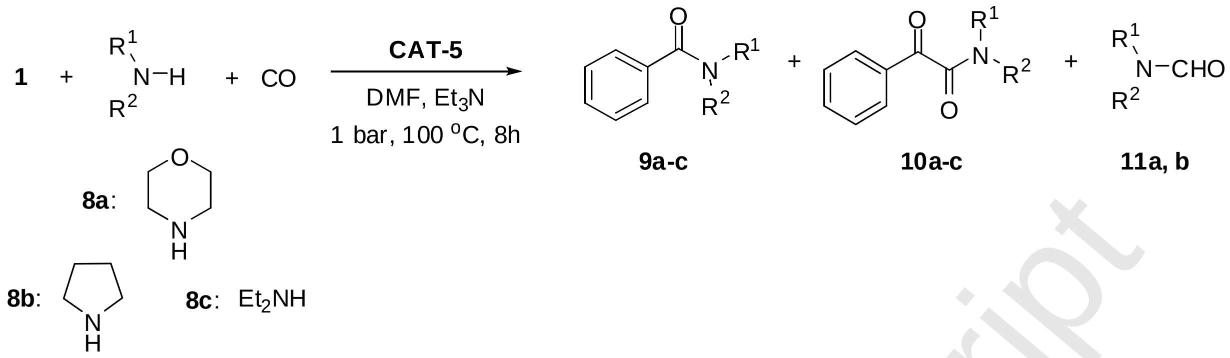


Figure 2. Aminocarbonylation of aryl iodides (**6a-i**) with aniline (**2**) in the presence of **CAT-5** (Reaction conditions: 0.2 mmol aryl iodide, 0.5 mmol **1**, 10 mg catalyst, 1 ml DMF, 1 bar CO, 100 °C, 8h. Yields of three successive runs, determined by GC.)

Aminocarbonylation of iodobenzene (**1**) with aliphatic amines (Scheme 3, **8a-c**) was also attempted. Lower conversion of iodobenzene, compared to that in the reaction of aniline, and poor selectivities were observed in each case (Table 5). Beside the amide products **9a-c**, the presence of the corresponding α-ketoamides (**10a-c**), obtained by double carbonylation, was also detected. Moreover, in case of cyclic amines (**8a,b**) formylation of the amino group led to products **11a,b**, which lowered the concentration of the nucleophilic reagent available for carbonylation.



Scheme 3. Aminocarbonylation of iodobenzene (**4**) with morpholine (**5a**) as the nucleophile

Table 5. Aminocarbonylation with aliphatic amines[a]

amine	conversion of **1** [%][b]	product distribution [%][b,c]		product distribution [%][b,d]		
		9	**10**	**9**	**10**	**11**
morpholine (**8a**)	67	70	30	47	20	33
pyrrolidine (**8b**)	80	80	20	61	16	23
diethylamine (**8c**)	77	83	17	83	17	-

[a]: reaction conditions: 0.2 mmol **1**, 0.5 mmol amine (**8a-c**), 0.7 mmol Et_3N, **CAT-5** (with 6 µmol Pd-content) and 1 ml solvent, 1 bar CO, 100 °C; [b]: determined by GC; [c]: for products obtained from iodobenzene (**1**): [mmol **9** (or **10**)/ (mmol **9** + mmol **10**)]x100; [c]: for products obtained from the amine (**8a-c**): [mmol **9** (or **10** or **11**)/ (mmol **9** + mmol **10**+ mmol **11**)]x100;

*3.4. Characterisation of catalyst **CAT-5***

Immobilisation of the ionic liquid on the surface of silica was proved by solid state ^{13}C CP MAS measurements (Figure 3). The peaks at chemical shifts of 123.7 ppm and 136.8 ppm correspond to the three imidazole ring carbon atoms. The four signals in the region of 9.0 ppm — 53.0 ppm can be assigned to the carbons of the alkyl side chains. The lack of peaks of ethoxy groups proves the successful grafting of the ionic liquid on the surface. The spectrum of the spent catalyst is essentially the same, with signals corresponding to residual DMF (164.4 ppm, 31.8 ppm) and aromatic product (164.4 ppm and around 131 ppm).

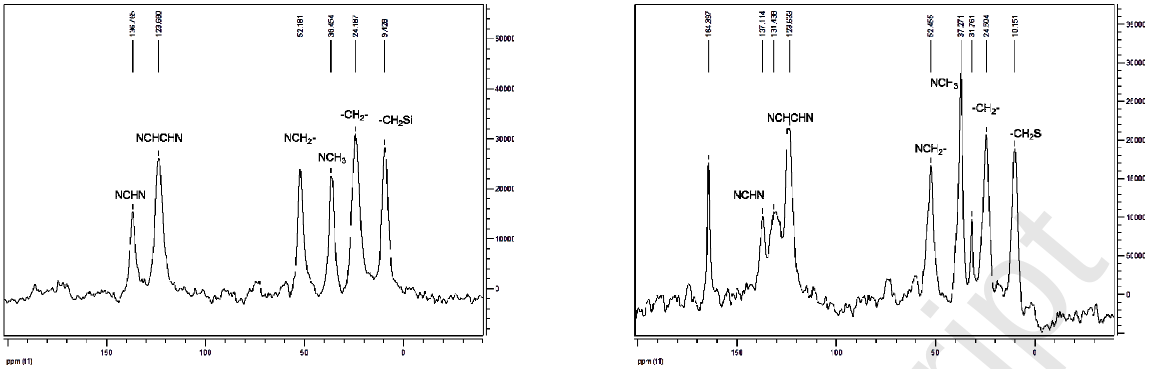


Figure 3. ^{13}C CP MAS spectra of **CAT-5** (as synthesized (left), spent (right))

Comparison of the IR spectra of silica and **CAT-5** (Figure 4) shows the appearance of peaks corresponding to CH stretching and a decrease in the intensity of the OH stretching band in the latter spectrum. The spectrum of the spent catalyst is similar, the appearance of a band around 1660 cm^{-1} can be attributed to the amide group of residual DMF and product.

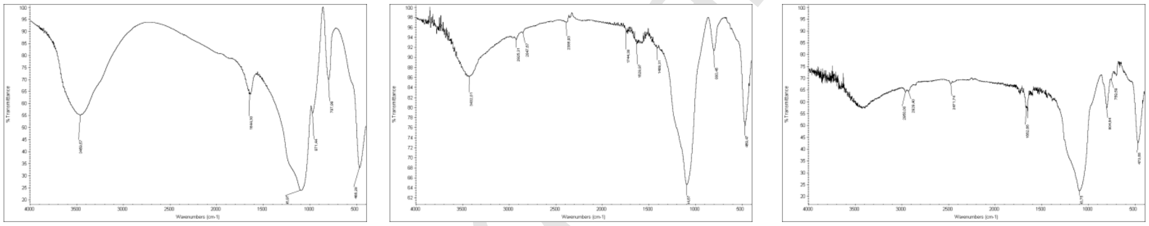


Figure 4. IR spectra of silica (left) and **CAT-5** (as synthesized (middle), spent (right))

X-ray photoelectron spectroscopy (XPS) analysis was performed on the as-synthesized as well as on the spent catalyst **CAT-5** (after 2 cycles) (Table 6, Figure 5). The Pd *3d* regions of the catalysts are shown in Figure 6. The two bands at around 335.1 eV and 340.4 eV were assigned to Pd^o (3d$_{5/2}$ and 3d$_{3/2}$ respectively), while the bands at around 337.3 eV and 342.6 eV were attributed to Pd(II) (3d$_{5/2}$ and 3d$_{3/2}$ respectively). These results are strengthened by several previous ones reported elsewhere [25-27].

The atomic ratios on the surface were calculated using sensitivity factors given by the manufacturer. These ratios for the Pd, Si and C are presented in Table 6. The Pd^o content were similar for both of the samples, although after the catalytic cycle the Pd(II)/Pd^o ratio decreased. It can be described as the effect of the Pd^o enrichment on the surface upon the catalytic reaction. The effect of the catalytic reaction can be observed in the changes of the Pd/Si and Pd/C ratios as well. The smaller Pd/Si and Pd/C ratios were typical for the sample after catalytic cycle. These changes of the surface structure coupled with the different Pd(II)/Pd^o can be described as the effect of the catalytic reaction.

Table 6. XPS Pd $3d_{5/2}$ binding energies (eV), Pd(II)/Pd^o, Pd/Si and Pd/C surface atomic ratios of as prepared and spent Pd catalysts

Sample	Position of the peak Pd $3d_{5/2}$		Ratio of the atomic concentrations		
	Pd^o (eV)	Pd(II) (eV)	Pd(II)/Pd^o	Pd/Si	Pd/C
CAT-5	335.1	337.3	2.45×10^{-1}	2.75×10^{-1}	4.66×10^{-1}
CAT-5 (spent)	335.1	337.0	2.05×10^{-1}	1.46×10^{-1}	1.59×10^{-1}

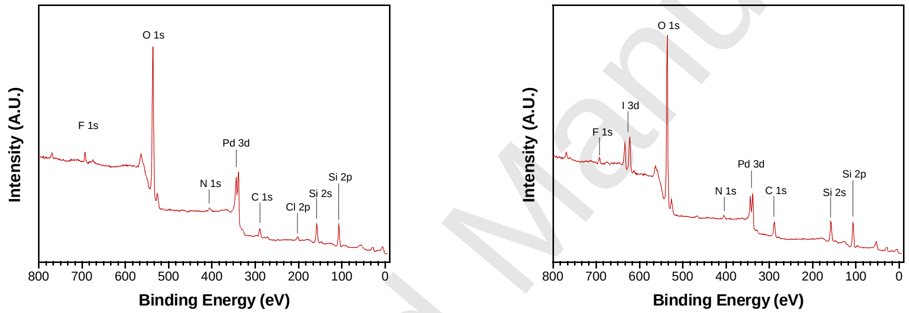


Figure 5. Wide scan XPS spectra of Pd catalyst **CAT-5** (as synthesized (left), spent (right))

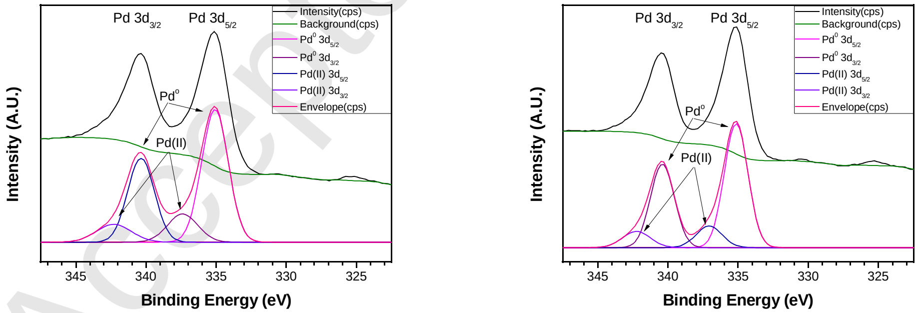


Figure 6. Pd 3d XPS spectra of Pd catalyst **CAT-3** (as synthesized (left), spent (right))

4. Conclusions

Various phosphine-free silica supported palladium catalysts were prepared and tested in atmospheric aminocarbonylation of iodobenzene in the presence of aromatic amines. Activity of the catalysts were found to be affected both by the choice of the palladium precursor and conditions of immobilisation. The catalyst obtained from $Pd(OAc)_2$ in ethanol and using KOtBu as an additive was found to be the most suitable one for carbonylations carried out in DMF. It performed high activity and good recyclability for the reaction of iodobenzene with a number of aromatic amines, as well as for the carbonylation of substituted iodobenzenes with aniline. It was shown that the greater drop of catalytic activity, as well as a higher amount of leached palladium in reactions in DMSO solvent are due to the formation of soluble palladium complexes.

In carbonylations with aliphatic amines, side reactions leading to α-ketoamides and N-formyl amines could be detected.

Acknowledgments

The authors thank for the support of the Hungarian National Science Foundation (OTKA K105632) and project TÁMOP-4.2.2.A-11/1/KONV-2012-0071, realised with the support of the Hungarian Government and the European Union, with the co-funding of the European Social Fund. Mr. A. Tóth is acknowledged for his assistance in GC-MS measurements.

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***Graphical Abstract (for review)**