



# 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.

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## 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, 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. Alkoxy carbonylation [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  $\alpha$ -ketoamides. A silica-supported polytitazane–palladium (Ti–N–Pd) complex [11], Pd/C used together with PPh<sub>3</sub> 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

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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<sub>2</sub> 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  $\alpha$ -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 °C in vacuo).

Preparation of SILP-2: A mixture of 1.66 mmol (400  $\mu$ l) 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 °C) was heated under argon at 120 °C 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  $\mu$ l) 1-methylimidazole was added dropwise in an inert atmosphere. The mixture was heated at 80 °C 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 °C in vacuo).

### 2.2. Preparation of the supported catalysts

#### 2.2.1. Preparation of CAT-1

A solution of 8.95  $\mu$ mol (9.3 mg) Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub>— 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 °C in vacuo for 3 h.

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

A solution of 17.9 mmol  $\mu$ mol Pd(OAc)<sub>2</sub> (for CAT-2) or PdCl<sub>2</sub> (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 °C in vacuo for 3 h.

#### 2.2.3. Preparation of CAT-4–CAT-8

Under inert conditions, 3.12 mmol (350 mg) KOtBu was added with stirring to a mixture containing 2 g of SILP-2 and 20 ml solvent

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

Catalyst	Pd-precursor	Solvent	Additive	Pd-content (m/m%) <sup>a</sup>
CAT-1	Pd <sub>2</sub> (dba) <sub>3</sub> ·CHCl <sub>3</sub>	CH <sub>3</sub> CN + THF	–	0.29
CAT-2	Pd(OAc) <sub>2</sub>	EtOH	–	0.77
CAT-3	PdCl <sub>2</sub>	EtOH	–	0.26
CAT-4	Pd(OAc) <sub>2</sub>	THF	KOtBu	0.26
CAT-5	Pd(OAc) <sub>2</sub>	EtOH	KOtBu	0.60
CAT-6	PdCl <sub>2</sub>	EtOH	KOtBu	0.49
CAT-7	PdBr <sub>2</sub>	EtOH	KOtBu	0.55
CAT-8	PdSO <sub>4</sub>	EtOH	KOtBu	0.37

<sup>a</sup> Determined by ICP.

(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  $\mu$ mol Pd) was placed in a stainless steel autoclave. Iodobenzene (**1**) (0.2 mmol, 22.5  $\mu$ l), aniline (0.5 mmol), 0.7 mmol (100  $\mu$ l) 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 °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  $\mu$ mol Pd-content) was placed in a Schlenk-tube. Under argon, 0.2 mmol (22.5  $\mu$ l) iodobenzene (**1**), 0.5 mmol amine reagent, 0.7 mmol (100  $\mu$ l) 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 °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 K $\alpha$  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<sup>+</sup>)/42; 105/100; 77/52; 51/14

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

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

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