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The aminocarbonylation of 1,2-diiodoarenes with primary and secondary amines catalyzed by palladium complexes with imidazole ligands

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ABSTRACT

The efficient carbonylative cyclization of 1,2-diiodobenzene with different primary and secondary amines was performed using a palladium complex with an imidazole ligand, $PdCl_2(BIM)_2$, as a catalyst. In reactions performed at 1 atm of CO with primary amines, phthalimides were obtained as the only products with yields of up to 100% in 4 h. An even shorter time, 1 h, was sufficient to obtain the same products employing methyl-2-iodobenzoate as a substrate instead of 1,2-diiodobenzene. In an analogous reaction with secondary amines, 1,2-diiodobenzene was converted to three products, formed in amounts dependent on the reaction conditions. The presence of Pd NPs and soluble palladium intermediates indicated their participation in the catalytic reaction.

1. Introduction

Isoindole-1,3-diones, commonly known as phthalimides, have widespread pharmaceutical applications. Their structural motif occurs in anti-inflammatory drugs (Apremilast) [1], in medicines used in the treatment of cancer (Pomalidomide) [2] and AIDS (Thalidomide) [3], in other pharmaceuticals [4], and in pesticides (Phosmet, Amphotalide, Dialifor) [5]. Derivatives of phthalimides show potential activity as androgen antagonists [6] and a TNF-α inhibitor (PP-33 [2-[2,6-di(propan-2-yl)phenyl]-1*H*-isoindole-1,3(2*H*)-dione] [7]. Moreover, pyromellitic diimide has been used as a high-performance polymeric material for aircraft or spacecraft (Kapton) [8,9].

The most popular method of phthalimide synthesis involves the condensation of a phthalic anhydride and a primary amine [10–16]. A good alternative for such synthesis is the palladium-catalyzed aminocarbonylation of *o*-dihaloarenes with a primary amine. The first example of such a reaction was published in 1991. Perry and Turner reported the double carbonylative cyclization of o-dihaloarenes with aryl amines using $PdCl_2(PPh_3)_2$ as a catalyst [18], based on the earlier work of Ban and co-workers [17]. Only two decades later, several articles about the aminocarbonylation of 1,2-dihalobenzenes with primary amines have been published [19–27]. Thus, the *N*-substituted isoindole-1,3-diones have been synthesized by the carbonylative cyclization of primary amines with *o*-halobenzoates [19,20,28,29] or with o-halobenzoic acids [19,20,29]. Furthermore, N-substituted phthalimides have been obtained by the ruthenium-catalyzed carbonylation at ortho C—H bonds in aromatic amides [30] and by the rhodium(III)-catalyzed oxidative carbonylation of benzamides with CO [31].

Palladium-catalyzed aminocarbonylation became powerful tool for the amide synthesis. Especially last years showed great potential this reaction for synthesis of various products, like advanced amides [32–34] and quinazolinones [35].

To the best of our knowledge, palladium complexes with nitrogen ligands have not been applied yet as catalysts in the aminocarbonylation of *o*-dihaloarenes with primary amines [18–29]. Therefore, we decided to test Pd-imidazole complexes as catalysts for the carbonylative cyclization of 1,2-diiodobenzene with a range of primary and secondary amines to get phthalimides. The same complexes were also employed in analogous reactions with methyl-2-iodobenzoate used as a substrate instead of 1,2-diiodobenzene. We selected Pd complexes with non-toxic imidazole ligands, which showed an excellent activity in the Suzuki [36] and carbonylative Suzuki cross-coupling reactions [37]. Advantageously, Pd–imidazole complexes can be easily prepared, and they are also easy to handle and stable in the presence of water and air.

2. Experimental section

2.1. Reagents

All reagents were purchased from Sigma-Aldrich or Alfa Aesar and used without purification. Solvents were dried by standard methods [38]. The $PdCl_2(cod)$ precursor was synthesized as previously reported [39]. The palladium complexes, $Pd(1\text{-}BI)_2Cl_2$ and $Pd(1\text{-}MI)_2Cl_2$, were obtained according to the literature method [36].

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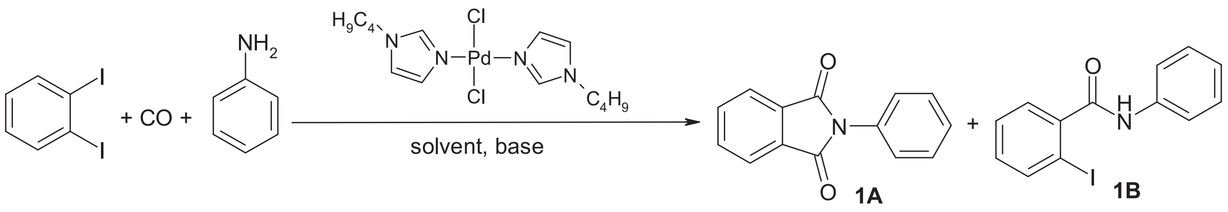

Scheme 1. The aminocarbonylation of 1,2-diiodobenzene with aniline.

2.2. Instrumental methods

^{1}H NMR and ^{13}C NMR were recorded on a Bruker Avance 500 MHz spectrometer (^{1}H NMR 500 MHz, ^{13}C NMR 125 MHz) using TMS as the internal reference. IR and FIR measurements were performed in KBr or Nujol with a Bruker 113 V FTIR. Elemental analyses were performed on a 2400 CHNS Vario EL III apparatus. TEM measurements were carried out using a FEI Tecnai G^{2} 20 X-TWIN electron microscope operating at 200 kV. XRD measurements were carried out with a Bruker D8 Advance diffractometer operating with a Cu-Kα radiation line and equipped with a Vantec detector.

GC and GC–MS analyses of organic products were performed using a Hewlett Packard 5890 Series II gas chromatograph connected to a HP 5971 A mass selective detector. Separation was achieved on a capillary HP-5 column coated with a diphenyl (5%) dimethylsiloxane (95%) copolymer film. Helium was used as the carrier gas. Organic products were separated by flash chromatography (CombiFlash Rf 200) on silica gel.

2.3. General procedure for aminocarbonylation

A 50 cm^{3} Schlenk flask was charged with an ortho-substituted iodoarene (1×10^{-3} mol), an amine ($1.1–5 \times 10^{-3}$ mol), K_2CO_3 (2×10^{-3} mol), a catalyst (5×10^{-6} mol), and a stirring bar. Next, 5 cm^{3} of DMF was added. Under balloon pressure of CO, the reaction mixture was stirred at 100 °C for 1–6 h. After the reaction, the Schlenk flask was cooled down, and the organic products were extracted with 3 × 7 cm^{3} of diethyl ether (3 × 15 min with stirring) and then GC analyzed with dodecane as the internal standard (0.076 cm^{3}, 5.46×10^{-4} mol). Each reaction was repeated minimum twice and the average value from two experiments was reported. The difference between two results was below 5%.

After the solvents were evaporated, the crude product was purified by flash chromatography on silica gel using hexane/ethyl acetate (10:4) as the eluent, and the corresponding N-substituted phthalimides were obtained.

2.4. Catalytic experiments in an autoclave

In a typical experiment, an *ortho*-substituted iodoarene (1×10^{-3} mol), a catalyst (5×10^{-6} mol), an amine (2×10^{-3} mol), K_2CO_3 (2×10^{-3} mol), and DMF (5 ml) were transferred under an inert atmosphere into a stainless steel autoclave. It was charged with carbon monoxide (10 atm) and heated with stirring at 100 °C for 1–4 h. The reaction mixtures were analyzed by gas chromatography (Hewlett Packard 5890). Conversions and the selectivities of the reactions were determined by GC using dodecane as the internal standard. After the solvents were evaporated, the crude products were purified by flash chromatography on silica gel using hexane/ethyl acetate (1 : 2) as the eluent, and the corresponding ketocarboxamide-carboxamide derivatives were obtained.

2.5. Procedure for catalyst recycling

After the first catalytic cycle, the organic products were separated by extraction (with diethyl ether). The liquid phase with the reagents was moved to another glass flask using a stainless steel tube (catheter tubing), and only the palladium residue was left in the Schlenk flask. Then, the palladium residue was washed with diethyl ether and dried in vacuum. After that, the Schlenk flask was charged again with reagents: 1,2-diiodobenzene (1 mmol), aniline (2 mmol), K2CO3 (3 mmol), DMF (5 ml), and dodecane (0.076 ml). The yellow mixture was frozen in liquid nitrogen, the air was evacuated from the Schenk flask. Next, the Schlenk tube was filled again with carbon monoxide from a balloon (three times). The balloon was disconnected. The mixture was heated to 100 °C and stirred for 4 h. After that, the reaction mixture was cooled, and the organic products were separated by extraction with diethyl ether (3 times with 7 ml) and analyzed by GC with dodecane as the internal standard.

3. Results and discussion

3.1. Catalytic activity of Pd(1-BI)$_2$Cl$_2$ in aminocarbonylation of 1,2-diiodobenzene with aniline

The coupling of 1,2-diiodobenzene with aniline under a CO atmosphere was selected as a model reaction to study (Scheme 1).

A lot of experiments were carried out to optimize the reaction conditions, such as the solvent, the base, the temperature, the time, the amount of amine, and the catalyst. The obtained results are presented in Table 1.

First, the effects of the solvent and the base were studied (Table 1, entries 1–9). The highest yield of N-phenylphthalamide (**1A**) was obtained in DMF with K_2CO_3 as the base (Table 1, entry 8). Moreover, the application of an organic base (Et_3N) instead K_2CO_3 provided a lower yield of the desired product (Table 1, entry 9).

Further studies focused on the examination of the effect of the temperature and the amount of amine on the reaction course (Table 1, entries 10–12). Both lowering the temperature and the use of almost equimolar amounts of the substrates led to the decrease of **1A** yield (Table 1, entries 10 and 12). Furthermore, a reduction of the temperature from 100 °C to 70 °C resulted in the formation of 2-iodo-*N*-phenylbenzamide (12%) as a byproduct (Table 1, entry 12). As regards the amount of the catalyst (Table 1, entries 13–15), 100% of **1A** was formed in the presence of 0.5 mol% of the catalyst. With a smaller amount of the catalyst (0.25 mol%), a longer reaction time is required to receive a reasonable conversion (Table 1, entry 15).

After the optimization of the reaction conditions, we tested another palladium complex with imidazole ligands Pd(1-BI)$_2$Cl$_2$ (Scheme 2) and other palladium precursors in order to estimate the effect of the imidazole ligand on the reaction course (Table 2).

The obtained results showed that the complex Pd(1-BI)$_2$Cl$_2$ was the most catalytically active, forming 100% of **1A** after 4 h (Table 2, entry 1). The complex Pd(1-MI)$_2$Cl$_2$ was slightly less active (Table 2, entry 2). When precursors without an imidazole ligand, Pd(cod)Cl$_2$ and PdCl$_2$, were applied, the yield of the desired product was not higher than 71% (Table 2, entries 3 and 5). However, upon the addition of the imidazole ligand to Pd(cod)Cl$_2$ or to PdCl$_2$, the yield of N-phenylphthalimide increased from 71% to 82% for Pd(cod)Cl$_2$ and from 54% to 70% for PdCl$_2$ (Table 2, entries 4 and 6). The same effect was also observed after a shorter reaction time (2 h), where the addition of the imidazole ligand increased the yield of the product from 38% to 51% (Table 2, entries 7

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