



Catalytic activity of PdCl₂ complexes with pyridines in nitrobenzene carbonylation

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ABSTRACT

Synthesis of square planar palladium(II) complexes of general structure PdCl₂(X_nPy)₂ (where: Py = pyridine; X_nPy = 2-MePy; 3-MePy; 4-MePy; 2,4-Me₂Py; 2,6-Me₂Py; 2-ClPy; 3-ClPy and 3,5-Cl₂Py) has been performed in order to study activity of these complexes as catalysts of nitrobenzene (NB) carbonylation – a process of industrial importance leading to production of ethyl N-phenylcarbamate (EPC). Electron withdrawing/electron donating properties of X_nPy ligands (described by experimentally determined acidity parameter pK_a) have been correlated with activities of PdCl₂(X_nPy)₂ complexes during NB carbonylation in presence of catalytic system PdCl₂(X_nPy)₂/Fe/I₂/X_nPy. We observed that conversions of substrates and yields of EPC increase within increasing basicity of X_nPy ligand (for not sterically hindered X_nPy's). On the basis of current work and our previous studies a detailed mechanism of catalytic carbonylation of NB is proposed.

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1. Introduction

Over the last few decades square planar palladium(II) complexes with nitrogen donor ligands have received much attention. These complexes can be applied as catalysts for the carbonylations [1–5], polymerizations [6–8], and other reactions in synthetic organic chemistry [9–12]. Moreover, the cytotoxic activity of palladium complexes leads to great interest in potential application of these compounds as anticancer agents [13–17].

The catalytic activity of metal complexes with nitrogen containing ligands depends on electron density of the palladium atom [18]. Taking into account the steric and electronic effects, the strategy to design (and to obtain) more active catalysts is based on incorporation of new, more electron donating ligands in the palladium complexes. Typical electron donating ligands contain nitrogen: pyridine, bipyridine, phenanthroline and their derivatives [18–25], other ligands containing phosphorus are very common P-donor phosphines [22,23,26]. Palladium(II) complexes with these ligands are used as active catalysts, particularly in the carbonylation of nitro-compounds [27–31] and amines [32–36] to form carbamates, isocyanates and ureas, etc. The application of Pd(II) complexes with pyridine ligands as catalysts in carbonylation of nitro-compounds and amines was a subject of a few reports only [37–39]. The studies were limited

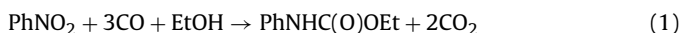
to complexes of other metals [40–43]: *cis*-[Rh(CO)₂(X_nPy)₂]PF₆, [Rh(COD)(X_nPy)₂]PF₆ and [Ir(COD)(X_nPy)₂]PF₆ where COD is 1,5-cyclooctadiene and X_nPy is pyridine itself or 2-methylpyridine; 3-methylpyridine; 4-methylpyridine; 2,6-dimethylpyridine; 3,5-dimethylpyridine and those complexes were tested as catalysts in reduction of nitrobenzene to aniline by CO/H₂O. There is a general agreement that catalytic activity of complexes depends on basicity of a pyridine ligand [18]. Another important factor is a localization of methyl group at pyridine ring – a strong connection of catalyst activity with ligand structure has been reported by Halligudi et al. [38] during their studies on Pd complexes as active catalysts of carbonylation of nitrobenzene and aliphatic amines to ureas in the presence of FeCl₃ or CuCl₂ as co-catalysts.

In our previous studies we applied and described PdCl₂/Fe/I₂/pyridine system as catalyst for carbonylation of nitro-compounds and aromatic amines [44–46]. Concentration of each component, the molar ratio, CO pressure and other parameters were examined in order to explain their influence on the rate, conversion, and selectivity of nitrobenzene (NB) carbonylation to ethyl N-phenylcarbamate (EPC) [44,45,47].

In several reports two mechanisms of NB carbonylation were considered: direct carbonylation or indirect carbonylation of NB via stage of aniline [29,38,48,49]. One of us previously reported a detailed study of mechanism via an intermediate stage of initially formed aniline. The aniline is carbonylated to urea that subsequently reacts with ethanol yielding EPC and, again, aniline [45]. The initial amount of aniline is formed as a product of nitrobenzene reduction in the presence of traces of water or ethanol [34,45,50–52].

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Overall process of NB carbonylation is described by general equation:



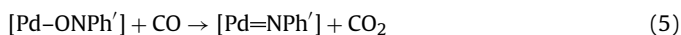
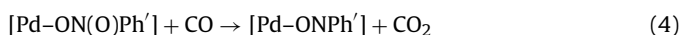
However, the presence of catalytic amount of aniline is essential for NB to be reduced:



Diphenylurea reacts with ethanol to yield aniline and ethyl N-phenylcarbamate:



Thus, aniline generated in reactions (2) and (3) is, in turn, consumed in reaction (2). Both reactions are complex, multistage processes. Reaction (2) represents a sequence of reactions (4)–(6).



Removal of the first oxygen atom from nitrobenzene can be assumed to be the rate determining step in the nitrobenzene carbonylation over $\text{PdCl}_2/\text{Fe}/\text{I}_2/\text{Py}$ catalyst [46], however, according to our knowledge, no evidence has been reported about electron transfer from palladium to nitrobenzene during the reaction catalyzed by palladium complexes with monodentate N-donor ligands like pyridine.

Our studies have long been concerned with the substituent effects in the nitrobenzene and aniline ring on the yield of EPC in the carbonylation of either NB or mixture NB/AN (where AN is aniline), respectively [46,53]. A presence of an electron-withdrawing substituent in nitrobenzene ring causes an increase of the nitrobenzene conversion [46], however, we did not observe any significant effect of the substituent in the aniline ring on the yield of the substituted carbamates formed [53]. Our previous studies were limited to PdCl_2 and PdCl_2Py_2 complexes without detailed research on the nature of a ligand and the structure of a catalyst, therefore, in this work we try to get knowledge on the role of ligand structure in the catalyst activity in the mechanism of carbonylation of NB. We decided to investigate the complexes of general structure $\text{PdCl}_2(\text{X}_n\text{Py})_2$, where X_nPy = pyridine, 2-methylpyridine; 3-methylpyridine; 4-methylpyridine; 2,4-dimethylpyridine; 2,6-dimethylpyridine; 2-chloropyridine; 3-chloropyridine; 3,5-dichloropyridine to get knowledge on the role of X_nPy ligand during the catalysis of NB carbonylation. In this report we are trying to investigate substituent effects of X_nPy in $\text{PdCl}_2(\text{X}_n\text{Py})_2$ catalyst for both kinds of substrates: for NB as well as for mixture of NB/AN. The second system has been chosen in order to eliminate the initial step of aniline formation.

2. Experimental

2.1. Materials

All operations were carried out using standard Schlenk techniques under oxygen-free and water-free argon. Carbon monoxide (99.9%), PdCl_2 , iodine and iron powder were used as received. Pyridine (Py), substituted pyridines (2-MePy; 3-MePy; 4-MePy; 2,4-Me₂Py; 2,6-Me₂Py; 2-ClPy; 3-ClPy; 3,5-Cl₂Py), nitrobenzene, aniline and ethanol were distilled (or fractionally distilled) over CaH_2 and stored under argon.

2.2. pK_a measurements

Spectrophotometric titrations were performed as described by Albert and Sergeant [54,55]. Briefly, small volumes of titrant (1 M

KOH in water) were subsequently added to 200 ml of substituted pyridine or pyridine solution at a concentration of 10^{-4} M in methanol:water (1:1). A precision pH meter was used with a combined pH glass electrode calibrated on standards for methanol:water solution. After each addition of titrant and when pH value was stable, small 0.5 ml samples of titrated solution were transferred to quartz cuvettes (optical path 10 mm), and UV-vis spectra in the range 200–400 nm were recorded. Each time the samples were returned to the main titrated solution. The pK_a 's were calculated by means of DATAN 3.1 (MultiD Analyses). The software analyzes complete spectra (instead of single analytical wavelength) and calculates protolytic equilibria as a function of pH and protolytic constants on the basis of principal component analysis.

2.3. Synthesis of $\text{PdCl}_2(\text{X}_n\text{Py})_2$ (compounds I–IX)

Palladium chloride complexes with pyridines were prepared under argon. A known amount (1.128 mmol) of PdCl_2 was placed in 10 ml flask equipped with magnetic stirrer and 2.26 mmol of Py or substituted X_nPy in 10 ml acetonitrile were added. Reaction was carried out at room temperature for 24 h. After the reaction was completed, yellow precipitate was crystallized from acetone.

Elemental analysis of the $\text{PdCl}_2(\text{X}_n\text{Py})_2$ complexes was carried out by a conventional method (see Table S1 in Supporting Material). Single yellow crystals of $\text{PdCl}_2(2,4\text{-Me}_2\text{Py})$ (II), $\text{PdCl}_2(4\text{-MePy})$ (III), $\text{PdCl}_2(3\text{-MePy})$ (V) and $\text{PdCl}_2(2\text{-ClPy})$ (VIII), obtained by slow evaporation of their acetone solution, were characterized by X-ray diffraction measurements [56].

2.4. Synthesis of $\text{PdCl}_2(\text{PhNH}_2)_2$

PdCl_2Py_2 complex (0.56 mmol), aniline (10.8 mmol), pyridine (1.24 mmol) and ethanol (4 ml) were heated at 180 °C for 60 min. On completion of the reaction golden-yellow flakes of $\text{PdCl}_2(\text{PhNH}_2)_2$ complex were obtained. The precipitate was crystallized from acetone, mp = 240–245 °C. Anal. Calcd. for $\text{PdCl}_2(\text{PhNH}_2)_2$ (%): C, 39.66; H, 3.86; N, 7.71; Cl, 19.56. Found: C, 39.98; H, 3.97; N, 7.74; Cl, 19.04. IR (KBr): 3287, 3202, 3117, 1594, 1573, 1111, 756 cm^{-1} .

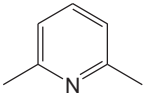
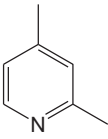
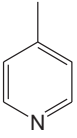
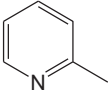
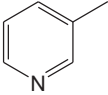

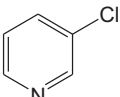
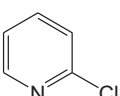
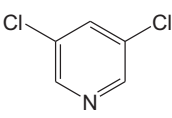
2.5. The reaction of $\text{PdCl}_2(\text{PhNH}_2)_2$ complex with carbon monoxide

$\text{PdCl}_2(\text{PhNH}_2)_2$ complex (0.7 mmol), in chlorobenzene (10 ml) was heated at 150 °C under CO pressure of 4 MPa for 60 min. On reaction completion a white product and palladium black precipitated. On dissolution and crystallization from ethanol, white needles were identified as diphenylurea using HPLC. mp = 235–237 °C, IR (KBr): 3328, 3198, 1649 cm^{-1} .

2.6. Carbonylation procedure

The procedure has been described elsewhere [46]. Briefly, the reaction was carried out in a 200-ml stainless-steel autoclave equipped with magnetic stirrer. Before experiment, the autoclave was heated at 120 °C for 3 h and cooled down to room temperature. Subsequently, 0.056 mmol of catalyst $\text{PdCl}_2(\text{X}_n\text{Py})_2$ and 2.68 mmol of Fe powder were placed in the autoclave, the air was evacuated and the system was filled with purified argon. Then, under an argon stream, other reagents and solvents were added: 0.12 mmol of I_2 , 6.2 mmol of Py or X_nPy , 81 mmol of nitrobenzene or 27 mmol of nitrobenzene and 54 mmol of aniline; 20 ml ethanol (solvent). The amounts of nitrobenzene and aniline (27 and 54 mmol) are related to carbonylation of mixture of NB/AN in stoichiometric molar ratio 1:2 (see Eq. (2)). The cover was closed and autoclave was directly filled with carbon monoxide (4 MPa), fixed, placed in a hot oil bath and kept at 180 °C for 1 or 2 h, depending on the reaction rate (see

Table 1
Structures, abbreviations and acidity parameters (pK_a 's) of nine pyridine ligands $X_n\text{Py}$, the symbols of the $\text{PdCl}_2(X_n\text{Py})_2$ complexes.

$X_n\text{Py}$ Structure (abbreviation)	pK_a				$\text{PdCl}_2(X_n\text{Py})_2$ Symbol ^a
	b	c	d	e	
 (2,6-Me ₂ Py)	6.81–7.06	6.63	14.4	6.2 ^f	I
 (2,4-Me ₂ Py)	5.07–6.98	6.80	15.4	6.05 ^f	II
 (4-MePy)	6.04	6.05	14.0	5.43	III
 (2-MePy)	5.76	5.97	13.5	5.38	IV
 (3-MePy)	5.67	5.69	13.4	5.17	V
 (Py)	5.21	5.23	12.5	4.09	VI
 (3-ClPy)	2.74	2.83	10.8	2.6 ^f	VII
 (2-ClPy)	0.49	0.61	7.1	2.0 ^f	VIII
 (3,5-Cl ₂ Py)	–	–	–	1.22 ^f	IX

^a Symbol of complex formed by ligand with PdCl_2 .^b From Ref. [58].^c From Ref. [59].^d From Ref. [60].^e This work. pK_a values (with error ± 0.05 unit) for ligands measured in methanol/water (50/50), see Section 2.^f For these ligands pK_a values are determined with error ± 0.10 .

footnotes for Tables 2 and 3). After the reaction was completed, the autoclave was cooled in a water bath then vented and a liquid sample of the reaction mixture was analyzed. The yield of the reaction was calculated on the basis of GC–FID and GC–MS analyses.

3. Results

3.1. Ligand acidity

The presence of substituents in pyridine ring influences the electron density on nitrogen atom and, thus, the basicity of the pyridine. The basicity of pyridine ligands is linearly related to their nucleophilicity [57] and directly affects the electron density on

the central Pd atom. In order to describe electron donor properties of ligands we determined experimentally acidity parameter, pK_a . Results compared with other accessible in the literature [58–60] are collected in Table 1. The basicity of pyridine derivatives decreases in the following order: 2,6-Me₂Py > 2,4-Me₂Py > 4-MePy > 2-MePy > 3-MePy > Py > 3-ClPy > 2-ClPy > 3,5-Cl₂Py (as it is shown in Table 1).

3.2. Carbonylation reactions catalyzed by $\text{PdCl}_2(X_n\text{Py})_2$

Palladium chloride complexes with $X_n\text{Py}$ ligands (where: Py = pyridine, X = –CH₃, –Cl; n = 0–2) were used as catalysts for reductive carbonylation of NB to form ethyl

Table 2
Conversion and selectivity of the carbonylation of nitrobenzene in presence of complex PdCl₂(X_nPy)₂ as catalyst (X = -CH₃, -Cl; n = 0–2)^a.

No.	Catalyst PdCl ₂ (X _n Py) ₂	Conversion NB (mmol)	Yield EPC (mmol)	Yield AN (mmol)	Selectivity ^b EPC (%)	TOF ^c (mmol mmol ⁻¹ h ⁻¹)
I	PdCl ₂ (2,6-Me ₂ Py) ₂	24	15	1	63	134
II	PdCl ₂ (2,4-Me ₂ Py) ₂	41	36	5	88	321
III	PdCl ₂ (4-MePy) ₂	54	48	6	89	429
IV	PdCl ₂ (2-MePy) ₂	39	32	5	82	286
V	PdCl ₂ (3-MePy) ₂	45	39	6	87	348
VI	PdCl ₂ Py ₂	40	34	6	85	304
VII	PdCl ₂ (3-ClPy) ₂	33	26	5	79	232
VIII	PdCl ₂ (2-ClPy) ₂	28	19	5	68	170
IX	PdCl ₂ (3,5-Cl ₂ Py) ₂	30	23	4	77	205

^a Reaction conditions: PdCl₂(X_nPy)₂/Fe/I₂/X_nPy = 0.056/2.68/0.12/6.2 mmol; NB = 81 mmol; ethanol = 20 ml; T = 180 °C; p(CO) = 4 MPa; time = 120 min. Py = pyridine; (X = -CH₃, -Cl; n = 0–2); AN = aniline; NB = nitrobenzene; EPC = ethyl N-phenylcarbamate.

^b Selectivity of EPC expressed as mmol EPC × (mmol converted NB)⁻¹.

^c Turnover frequency expressed in (mmol EPC × (mmol Pd)⁻¹ × h⁻¹).

N-phenylcarbamate, Eq. (1). Conversion of NB, yield of EPC and selectivity of catalysts presented in Table 2 indicates that for PdCl₂(X_nPy)₂ catalysts the conversion of NB increases in the range: chloropyridines < unsubstituted pyridine ≈ 2-methylpyridine < methylpyridines and the observed tendency is in agreement with increasing basicities of X_nPy ligands (the lower pK_a of protonated ligand the lower conversion) with one exception, for 2,6-Me₂Py ligand, assigned to steric crowding caused by two ortho-methyl groups (see below). Despite EPC, aniline was detected as a by-product of the reaction (see Table 2). Also found among the reaction products were 2-methylquinoline (up to 3%), diphenylurea, diphenyldiazene, diphenyldiazene oxide below 1% and diethyl carbonate in trace amounts.

Among all investigated complexes, compound **III** (with 4-methylpyridine) was the most active catalyst (TOF = 429), and for this complex the conversion of NB reached 54 mmol, the yield of ethyl N-phenylcarbamate was 48 mmol and selectivity 89%. Also high conversion, yield, and selectivity were observed for PdCl₂(3-MePy)₂ catalyst (see Table 2). The results obtained for other complexes with electron withdrawing X_nPy ligands are much lower – for chloropyridines, the conversions and yields are almost half of the values obtained for **III** (see Table 2). The decrease of the catalyst activity is accompanied by its declining selectivity. When complexes with ortho-substituted pyridines: PdCl₂(2,6-Me₂Py)₂, PdCl₂(2,4-Me₂Py)₂, PdCl₂(2-MePy)₂, were used, the lower conversions of nitrobenzene and lower yields of EPC were obtained than it would be expected according to basicities of X_nPy ligands (Table 2, compounds **I**, **II**, **IV**). The lowest conversion (24 mmol), EPC yield (15 mmol) and selectivity (63%) were observed for the complex with 2,6-dimethylpyridine.

Results shown in Table 3 refer to carbonylation of NB with initially added AN. For not sterically hindered catalysts the con-

version of AN decreases within decreasing X_nPy ligand basicity (the lower pK_a of protonated ligand the lower conversion), in similar way as it was observed for carbonylation of NB without initially added AN. We also monitored the conversion of NB in the systems containing a mixture NB/AN as starting material. The data collected in Table 3 shows similar correlation between basicity of used X_nPy ligand and conversion of NB, as for conversion of aniline. As it was observed for carbonylation of NB, 2-methylquinoline, diphenylurea, diphenyldiazene, diphenyldiazene oxide and diethyl carbonate were identified as by-products of the NB/AN carbonylation. Additionally, N-ethylaniline and N-phenylformamide were found among the products of the reaction.

4. Discussion

Our former research concerned the role of each component of the PdCl₂/Fe/I₂/Py catalytic system as well as activity and selectivity in carbonylation of NB to ethyl N-phenylcarbamate [44,47]. We investigated the substituent effect in NB and AN rings on the reductive carbonylation of NB [46] and oxidative carbonylation of AN [53], respectively. In order to understand the mechanism a detailed explanation of each step of catalytic process of carbonylation is necessary and the purpose of this work was to study the effects of structural and electronic changes in the pyridine ligand on the activity of PdCl₂(X_nPy)₂ complexes as catalyst of NB carbonylation. The pyridine derivatives were modified by incorporation of electron-withdrawing or electron-donating substituents. Due to some limitations (X should not undergo the carbonylation reaction), we excluded NH₂ and NO₂ groups from our considerations, and X is chlorine atom or methyl group.

Table 3
Conversion and selectivity of the carbonylation of nitrobenzene and aniline in presence of PdCl₂(X_nPy)₂ as catalyst (X = -CH₃, -Cl; n = 0–2)^a.

No	Catalyst PdCl ₂ (X _n Py) ₂	Conversion AN ^b (mmol)	Conversion NB (mmol)	Yield EPC (mmol)	TOF ^c (mmol mmol ⁻¹ h ⁻¹)
I	PdCl ₂ (2,6-Me ₂ Py) ₂	19	8	18	321
II	PdCl ₂ (2,4-Me ₂ Py) ₂	25	15	23	411
III	PdCl ₂ (4-MePy) ₂	35	23	27	482
IV	PdCl ₂ (2-MePy) ₂	24	13	23	411
V	PdCl ₂ (3-MePy) ₂	27	20	26	464
VI	PdCl ₂ Py ₂	25	18	24	429
VII	PdCl ₂ (3-ClPy) ₂	23	16	22	392
VIII	PdCl ₂ (2-ClPy) ₂	19	9	18	321
IX	PdCl ₂ (3,5-Cl ₂ Py) ₂	20	12	19	339

^a Reaction conditions: PdCl₂(X_nPy)₂/Fe/I₂/X_nPy = 0.056/2.68/0.12/6.2 mmol; NB = 27 mmol; AN = 54 mmol; ethanol = 20 ml; T = 180 °C; p(CO) = 4 MPa; time = 60 min. Py = pyridine; (X = -CH₃, -Cl; n = 0–2); AN = aniline; NB = nitrobenzene; EPC = Ethyl N-phenylcarbamate.

^b Amount of aniline is a result of calculation made according to the following equation: amount of AN in the reaction mixture = unreacted aniline in reaction (2) + amount of AN formed in the NB reduction – AN consumed in the EPC formation.

^c Term and units explained in footnote “c” in Table 2.

4.1. pK_a values

Basicity of ligands directly affects the electron density on the central Pd atom, therefore, we decided to study how electron-withdrawing (EW) and electron-donating (ED) substituents X in $X_n\text{Py}$ ligands are connected with catalytic activity of $\text{PdCl}_2(X_n\text{Py})_2$ complexes. We considered acidity (pK_a defined for deprotonation equilibria of a pyridinium salt: $[X_n\text{PyH}]^+ \rightleftharpoons X_n\text{Py} + \text{H}^+$) as reasonable and convenient parameter to get knowledge on EW/ED properties of $X_n\text{Py}$. Basicity of a pyridine nitrogen (or acidity of protonated pyridines) was studied by several authors, however, the literature data are not consistent because of a number of methods and conditions employed. According to our literature search, it was not possible to find pK_a values measured by one method for the whole series of $X_n\text{Py}$ compounds used in our work (where $X = -\text{Cl}$ and $-\text{CH}_3$). Thus, it was necessary to re-measure acidities for all the compounds. Since the pK_a values measured in non-aqueous solutions are sometimes questionable, we decided to range the acidities of $X_n\text{Py}$ ligands in 1:1 water/methanol (v/v) solution by spectrophotometric titration method [54,55], which can be successfully used for compounds of low solubility and having extremely low or extremely high pK_a 's. The measured values for nine $X_n\text{Py}$ ligands are collected in Table 1, listed together with literature data. The presented parameters are in rather good agreement with the previously published ones, however, for 2-chloro- and 3,5-dichloropyridine the less satisfying agreement was obtained, perhaps because of their very weak basicity. Strong acidity of their conjugated acids (the extremely low pK_a) might be a reason for significant differences observed in literature data. Our experimental pK_a 's for 2-chloro- and 3,5-dichloropyridine are also obtained with larger errors, however, values for both pyridines (as well as pK_a 's for other $X_n\text{Py}$ ligands) perfectly correlate with thermodynamic pK_{HB} scale for hydrogen bond formation in $X_n\text{Py} \cdots \text{HO}-\text{CH}_3$ systems based on IR measurements of OH stretching published by Berthelot et al. [61]. Taking into account that both scales (pK_a and pK_{HB}) are based on EW/ED properties of $X_n\text{Py}$ ligand, we believe that our series of pK_a values reasonably represent acidities of all nine compounds and can be applied for assessment of EW/ED properties of $X_n\text{Py}$ ligand.

4.2. Substituent effect on the rate determining step

Previous studies, described in the Introduction, have demonstrated that carbonylation reaction of NB to EPC is a multistep reaction, with aniline as essential intermediate. Initial small amount of AN is formed as a product of hydrogen atom transfer from ethanol to NB and once aniline is generated, it reacts with nitrobenzene and carbon monoxide to form ethyl N-phenylcarbamate with AN being recycled (general reactions (2) and (3)). We showed that in the $\text{PdCl}_2/\text{Fe}/\text{I}_2/\text{Py}$ system invented in our laboratory [45] a palladium complex PdCl_2Py_2 is an active center of carbonylation and we concluded that the abstraction of the first oxygen atom from nitrobenzene (reaction (4)) is a rate determining step [46]. Literature survey indicates that only two catalytic systems (both based on phenanthroline) have been investigated in depth [62] and according to our knowledge, no conclusive evidence of electron transfer from Pd to nitrobenzene during the carbonylation catalyzed by Pd complexes with monodentate N-donor ligands has been reported. Therefore, we decided to explore the mechanism of that reaction. If electron transfer from palladium to NB is a rate determining step – any change in $X_n\text{Py}$ ligand nucleophilicity would be manifested by increase or decrease of catalyst activity. There are some limitations in X selection (vide supra) and X is limited to chlorine atom and methyl group. During his research on catalysts containing phenanthroline derivatives, Ferretti et al. [63] suggested that halogen atoms are not suitable substituents in phenanthro-

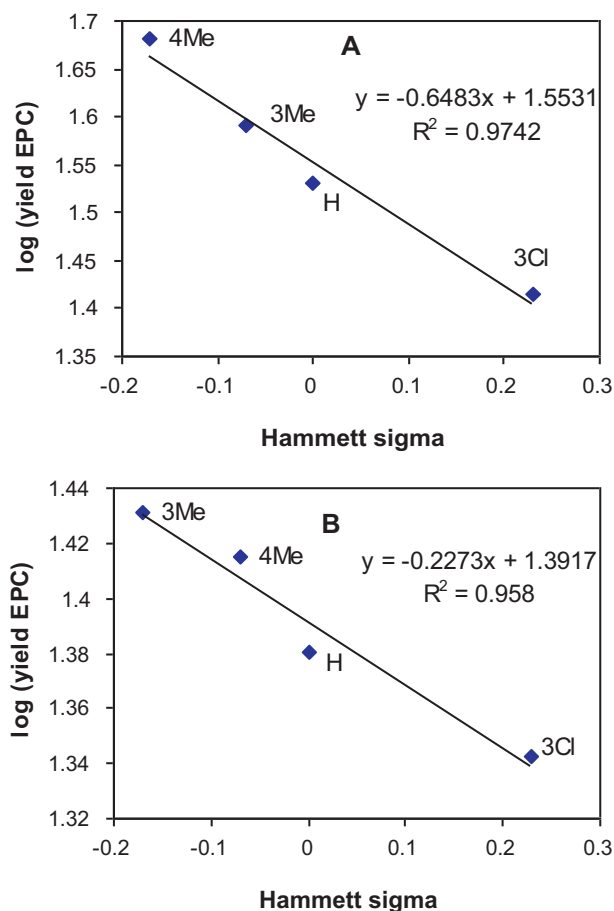


Fig. 1. Hammett type plots for carbonylation of nitrobenzene (A), and mixture of nitrobenzene/aniline (B) to carbamates. For reaction conditions see footnotes "a" in Tables 2 and 3.

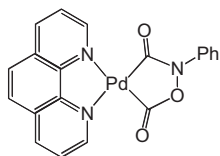
line ligands used under carbonylation conditions in presence of $\text{Pd}(\text{phenanthroline})_2[\text{BF}_4]_2$ catalysts because of oxidative addition of halogenated ligand to palladium. We did not observe that reaction in our $\text{PdCl}_2(X_n\text{Py})_2$ complexes. It was expected that increased nucleophilicity of the metal center would increase the catalytic activity of the catalyst: the presence of ED groups on the pyridine ring was supposed to facilitate electron transfer by increasing the nucleophilicity of Pd, and, contrary, the EW groups should retard carbonylation. To examine the impact of ED and EW groups we used a modified Hammett equation [64] connecting the yield of the carbonylation process with the Hammett σ constants of X in $X_n\text{Py}$ ligands:

$$\log(\text{yield}) = \rho\sigma + \text{const} \quad (7)$$

A linear dependence with a good correlation $R^2 = 0.97$ and $\rho = -0.65$ have been obtained for our $\text{PdCl}_2(X_n\text{Py})_2/\text{Fe}/\text{I}_2/X_n\text{Py}$ system with pyridine and substituted pyridines in carbonylation of nitrobenzene. Additionally, $R^2 = 0.96$ and $\rho = -0.23$ have been obtained for NB/AN carbonylation. (Fig. 1).

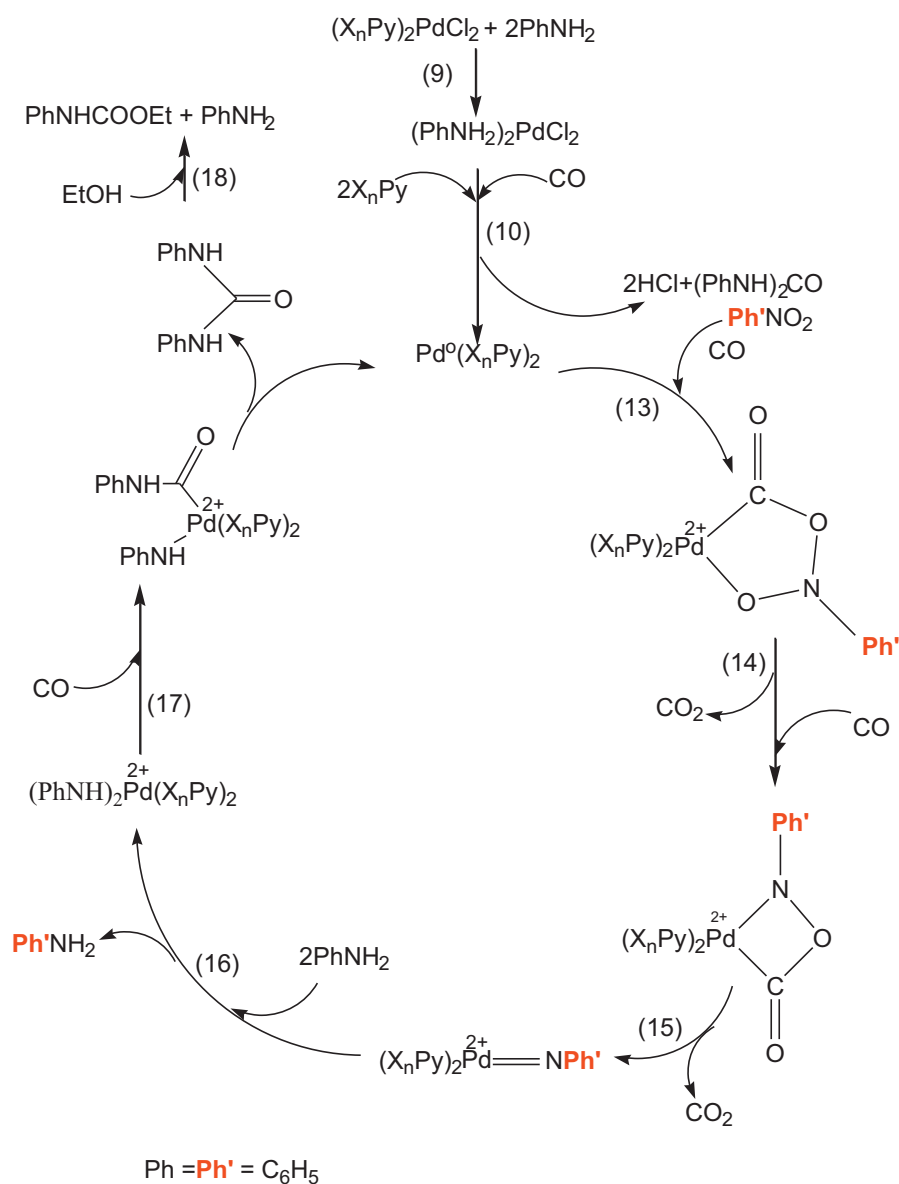
The steric effects of substituents in position 2- are strong enough in comparison to inductive effects and for these substituents the Hammett equation fails. The negative ρ -value indicates that higher electron density on the palladium center in $\text{PdCl}_2(X_n\text{Py})_2$ accelerates the carbonylation. The results confirm our previous hypothesis that electron transfer is the rate determining step [46] and are also in agreement with mechanisms of carbonylation proposed for other catalysts based on Pd and Ru complexes containing phenanthroline or phosphine as a ligand [48,65–70]. Some of these mechanisms have been confirmed by isolation

and identification of intermediates. Skoog et al. [67] investigated carbonylation of nitroarenes catalyzed by $\text{Ru}(\text{dppe})(\text{CO})_3$, where dppe = bis(diphenylphosphino)ethane and they provided kinetic evidence that the initial deoxygenation proceeds via rate determining inner-sphere electron transfer. Leconte et al. [65] isolated and characterized a metallacyclic complex, which appears to be directly involved in the catalytic process of nitrobenzene carbonylation:



Low ρ -value indicates that the carbonylation of nitrobenzene is probably a multistep reaction [64]. In order to find what reaction (initial formation of AN or electron transfer from Pd to NB) is a rate determining step we decided to carry out experiments with

added aniline to omit the first step (i.e. initial formation of aniline). We observed similar correlation of the carbonylation yield (or conversion, see Table 3) with ligand basicity in $\text{PdCl}_2(\text{X}_n\text{Py})_2$ catalyst as it was observed for carbonylation of NB without added aniline. Therefore, in both experiments (with and without initial addition of AN) the same process is a rate determining step and carbonylation of NB can be considered as carbonylation of AN with nitrobenzene being an oxidant, as suggested previously by one of us [46]. However, for carbonylation of NB/AN mixture (Table 3) the quantities of EPC are higher than the conversions of NB (see Introduction, reactions (1) and (2)). Thus, there must be another agent responsible for the oxidation of AN. As we showed earlier [53], molecular iodine (a catalyst component) can react with aniline in the presence of the palladium catalyst (Eq. (8)) and that reaction explains why carbamate is formed in amount exceeding the NB conversion (reactions (1) and (2)).

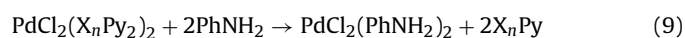


Scheme 1. Summaric scheme of the carbonylation reaction of nitrobenzene with carbon monoxide. The numbers in parentheses refer to the reactions described in the text. Symbols Ph' and Ph (both mean C_6H_5) were introduced to distinguish phenyl group from nitrobenzene (designed as $\text{Ph}'\text{NO}_2$) and from aniline (PhNH_2). However, there is no chemical difference between Ph' and Ph and first molecules of aniline are formed from nitrobenzene. Previous experiment [45] with 3-chloroaniline allowed us to distinguish Ph and Ph' for low conversions, because 3,3'-dichloro-N,N'-diphenylurea was detected.

Results obtained for carbonylation of NB (Table 2) and for carbonylation of NB/AN mixtures (collected in Table 3) show that for catalysts containing ligands with ortho-methyl group, i.e. **I**, **II** and **IV**, the conversion of NB is significantly smaller. These observations support the hypothesis, that during catalysis a molecule of NB is coordinated to Pd and this oxidative addition process is rate determining step.

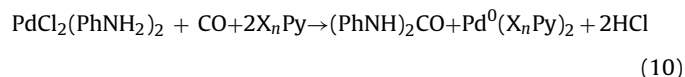
4.3. Mechanism of the process

Our previous studies on carbonylation [44,45] taken together with the results of this work allow to propose a detailed mechanism of the catalytic cycle of NB carbonylation and the proposed mechanism includes the changes in the oxidation state of central Pd atom. Catalytic amount of aniline generated by reaction of ethanol with NB (in the presence of $\text{PdCl}_2(\text{X}_n\text{Py})_2/\text{Fe}/\text{I}_2/\text{X}_n\text{Py}$ system) [34,50], initiates a series of carbonylations. Two molecules of AN react with $\text{PdCl}_2(\text{X}_n\text{Py})_2$ to form $\text{PdCl}_2(\text{PhNH}_2)_2$, reaction (9).

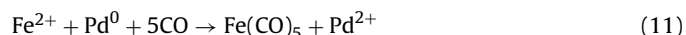


The presence of $\text{PdCl}_2(\text{PhNH}_2)_2$ complex has been detected and characterized by us during the reaction carried out with no carbon monoxide at 180 °C (see Section 2.4).

The aniline ligands react with CO to form urea (reaction (10)) and in this step a central atom is reduced $\text{Pd}^{2+} \rightarrow \text{Pd}^0$.

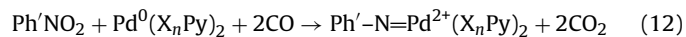


One of the proofs of the Pd^0 presence in the system is partial precipitation of inactive Pd_{black} as reported by Ragaini and Cenini [5] (see also Section 2.5). The transformation of oxidation state of Pd taken together with a change of chemical nature of a new ligand (aniline \rightarrow urea) generates weak complex and urea is immediately replaced by X_nPy ligands forming $\text{Pd}^0(\text{X}_n\text{Py})_2$ complex. The role of X_nPy is to prevent the precipitation of Pd_{black} and methyl pyridine derivatives (stronger bases) are better complexing agents than chloro- and dichloropyridines (weaker bases). Inactive Pd_{black} is recovered to Pd^{2+} form in the process:



where cations Fe^{2+} are generated from co-catalysts containing Fe (powder) and I_2 [47].

Complex $\text{Pd}^0(\text{X}_n\text{Py})_2$ formed in reaction (10) reacts with nitrobenzene and carbon monoxide, thus, central atom Pd^0 is oxidized to Pd^{2+} , according to Eq. (12).



The formation of nitrene intermediate state in the carbonylation of NB using palladium complex with 1,10-phenanthroline was also proposed by Halligudi et al. [48]. In fact, Eq. (12) can be considered as a sequence of three reactions including cyclic five and four membered rings (Scheme 1, reaction (13)–(15)).

The reduction of nitrobenzene to nitrene state requires six electrons: two electrons come from Pd^0 and four electrons from CO. Our results (significantly lower conversion degrees of NB for catalysts with pyridine derivatives substituted in 2- position, see Tables 2 and 3) lead us to conclusion that NB does not replace the X_nPy ligand from the complex but rather coordinates to $\text{Pd}^0(\text{X}_n\text{Py})_2$ as additional ligand (reaction (12)). When $\text{Pd}^0(\text{X}_n\text{Py})_2$ complex contains ortho-methylated pyridines, the steric crowd around the central Pd^0 atom is too big to make an access for a nitrobenzene molecule.

The palladium–nitrene complex, $(\text{X}_n\text{Py})_2\text{Pd}^{2+}=\text{N-Ph}$ immediately reacts with two molecules of AN.

At the same time the nitrene accepts two hydrogen atoms, one H atom from each aniline and new aniline molecule is formed (Scheme 1, reaction (16)).

Two molecules of AN coordinated to Pd^{2+} react with carbon monoxide forming diphenylurea as leaving molecule (Scheme 1, reaction (17)) and the complex $\text{Pd}^0(\text{X}_n\text{Py})_2$ is recovered being able to another cycle of NB reduction, whereas diphenylurea reacts with ethanol to form ethyl N-phenylcarbamate (Scheme 1, reaction (18)).

5. Conclusions

We synthesized a series of palladium chloride complexes with X_nPy_2 ligands (where: Py = pyridine, X = $-\text{CH}_3$, $-\text{Cl}$; $n=0-2$). EW and ED properties of these X_nPy ligands have been characterized on the basis of their experimental pK_a values measured by spectrophotometric titration. The synthesized $\text{PdCl}_2(\text{X}_n\text{Py})_2$ complexes have been used in catalytic system $\text{PdCl}_2(\text{X}_n\text{Py})_2/\text{Fe}/\text{I}_2/\text{X}_n\text{Py}$ for carbonylation of nitrobenzene and nitrobenzene/aniline mixture. In both reactions the conversion of nitrobenzene and aniline and yield of ethyl N-phenylcarbamate were monitored in order to investigate the impact of substituent effects in X_nPy ligands on the catalytic activity of $\text{PdCl}_2(\text{X}_n\text{Py})_2$ catalyst. We found that activity of $\text{PdCl}_2(\text{X}_n\text{Py})_2$ is correlated with the basicity of X_nPy derivatives: in both carbonylations (NB alone or NB/AN mixtures) for more basic X_nPy ligands the higher conversion of NB and yield of ethyl N-phenylcarbamate was observed. Catalytic carbonylation can be described as a cyclic sequence of reactions represented in Scheme 1. The process is initiated by reaction of $\text{PdCl}_2(\text{X}_n\text{Py})_2$ catalyst with aniline replacing X_nPy ligands to form $\text{PdCl}_2(\text{PhNH}_2)_2$ that reacts with CO and X_nPy to give diphenyl urea and $\text{Pd}^0(\text{X}_n\text{Py})_2$. The $\text{Pd}^0(\text{X}_n\text{Py})_2$ complex starts the catalytic cycle by reacting with nitrobenzene molecule and CO. Rearrangements in cyclic intermediates (Scheme 1, steps 14–15) lead to formation of palladium–nitrene complexes consecutively reacting with two molecules of aniline (steps 16). After addition of a molecule of carbon monoxide (Scheme 1, step 17), the complex decomposes with diphenyl urea reacting immediately with ethanol to produce aniline and ethyl N-phenylcarbamate. At this step the complex $\text{Pd}^0(\text{X}_n\text{Py})_2$ is recovered and able to start next catalytic cycle.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2011.01.007.

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