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Tuning of the catalytic properties of $PdCl_2(X_nPy)_2$ complexes by variation of the basicity of aromatic ligands

Agnieszka Krogul*, Jadwiga Skupińska, Grzegorz Litwinienko

Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland

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ABSTRACT

The position and number of substituents in pyridine ligands (X_nPy) were correlated with structural, physical, and chemical properties of $PdCl_2(X_nPy)_2$ complexes applied as catalysts for the carbonylation of aromatic nitrocompounds (phosgene-free method of carbamates production). Thermal stability and catalytic activity of $PdCl_2(X_nPy)_2$ complexes without steric hindrance increases with increasing X_nPy's basicity whereas a decrease of thermal stability and catalytic activity of the complexes is observed for sterically crowded complexes (with the *ortho*-substituted X_nPy). The complexes with X = Cl in *meta*- position of X_nPy decompose to a mixture of $PdCl_2$ and metallic Pd (similarly to complexes with Me_nPy) whereas complexes with *ortho*-chlorine (in X_nPy) decompose to the organopalladium products. Therefore, two different mechanisms of thermal decomposition are proposed for $PdCl_2(Cl_nPy)_2$ and $PdCl_2(Me_nPy)_2$. The results of complex thermal and structural analysis of a series of $PdCl_2(X_nPy)_2$ complexes allow us to get insight into the mechanism of nitrobenzene (NB) carbonylation catalyzed by $PdCl_2(X_nPy)_2$ at 150–180 °C. We conclude that ~~the~~ electron transfer from Pd(0) to nitrobenzene is the rate determining step of catalytic cycle of NB carbonylation.

1. Introduction

Polyurethanes belong to the most common polymers and their global production is still increasing, from 13.65 mln tonnes in 2010 to 17.95 mln tonnes expected by 2016 (with market value $55,480 mln) [1]. The polyurethanes are produced from methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI). Currently, the main method of industrial synthesis of isocyanates is a process employing phosgene – a toxic and relatively expensive gas produced from carbon monoxide and chlorine. The phosgene employing method is a potential source of species depleting the ozone layer and, therefore, needs to be eliminated [2]. The efforts to develop environmental friendly methods have been directed toward phosgene-free processes and one of the most promising method is the carbonylation of aromatic nitrocompounds catalyzed by transition metal complexes, leading to production of isocyanates and their precursors–carbamates (Scheme 1).

Although the yield and costs of catalytic carbonylation still cannot compete with the phosgene method, the carbonylation of nitro-compounds has additional advantage because it directly involves CO (without the step of phosgene synthesis from CO and Cl_2) giving an additional reduction of the costs [3–6].

There is a great interest in studies of more effective catalysts and Pd complexes receive much attention because of their relatively low cost (comparing to Rh and Ru compounds) and high effectiveness [7–15]. Recently, our research group have reported the system based on $PdCl_2(X_nPy)_2$ complexes (where: Py = pyridine, X = Me or Cl, n = 0–2) as the effective catalyst for carbonylation of nitrobenzene (NB) to ethyl *N*-phenylcarbamate (EPC) [16]. The current work aims to connect physical/chemical properties of $PdCl_2(X_nPy)_2$ with their catalytic activity and this is an extention of the research on Pd(II) complexes with substituted pyridines and their toxicity [17,18]. We also proposed the mechanism of carbonylation of NB with electron transfer from the palladium atom to nitrobenzene as the rate determining step as well as we determined spectral properties of $PdCl_2(X_nPy)_2$ in solution to confirm their square planar coordination geometry [16,17].

Carbonylation of NB to ethyl *N*-phenylcarbamate is carried out at relatively high-temperatures (150°–180 °C) and thermal stability of a catalyst is of crucial importance for its activity. Therefore, from the engineering point of view it is necessary to correlate the physical properties (particularly thermal stability) of Pd(II) complexes applied as catalysts with their catalytic activity in carbonylation. Thermal analysis (DSC and TG) seem to be the most appropriate for such studies of $PdCl_2(X_nPy)_2$.

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* Corresponding author. Tel.: +48 22 8220211x378; fax: +48 22 8225996.
E-mail address: akrogul@chem.uw.edu.pl (A. Krogul).

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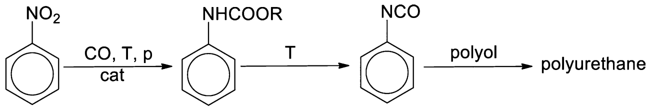

Scheme 1. Products of carbonylation of nitrobenzene in the presence of CO.

There are many examples of studies that deal with substituent effect in aromatic ring on properties of transtion metal (i.e. Fe, Cu) complexes with pyridine ligands [19]. Knowledge on the relationship between thermal stability of palladium(II) complexes and their catalytic activity will be also helpful in elucidation of mechanism of NB carbonylation in more details. Catalytic carbonylation can be described as a cyclic sequence of steps initiated by reaction of $PdCl_2(X_nPy)_2$ catalyst with aniline replacing the X_nPy ligands to form $PdCl_2(PhNH_2)_2$ that reacts with CO and X_nPy to give diphenylurea and $Pd^0(X_nPy)_2$ [16]. Subsequently, $Pd^0(X_nPy)_2$ complex reacts with nitrobenzene molecule and with CO. Rearrangements in cyclic intermediates lead to the formation of palladium–nitrene complex consecutively reacting with aniline. It is difficult to clearly distinguish whether the carbonylation occurs by a direct attack of aniline on the already coordinated molecule of CO or by a coordination of aniline to the metal, followed by attack of aniline on the adjacent coordinated CO. According to the literature both mechanisms are possible [4,20,21]. On the basis of calculation made by Hong et al. and on the basis of our own studies we suggest that both molecules, aniline and CO, are coordinated to Pd and then react [21]. After addition of another molecule of carbon monoxide, the complex decomposes with diphenylurea reacting immediately with ethanol to produce aniline and ethyl *N*-phenylcarbamate and the complex $Pd^0(X_nPy)_2$ is recovered and able to start next catalytic cycle [16]. All these processes form a catalytic cycle but at first, a replacement of X_nPy in $PdCl_2(X_nPy)_2$ complex by aniline initiates a series of carbonylations.

In this report we present thermal data for a series of $PdCl_2(X_nPy)_2$ complexes in order to correlate them with their catalytic activity. We hope the obtained data will be helpful during elucidation of detailed mechanism of the carbonylation process and during design and development of new Pd(II)-based catalysts.

2. Experimental

2.1. Materials

$PdCl_2$ was used as received. Pyridine (Py), substituted pyridines (2-MePy; 3-MePy; 4-MePy; 2,6-Me_2Py; 2,4-Me_2Py; 3,5-Me_2Py; 2-ClPy, 3-ClPy; 2,4-Cl_2Py), acetonitrile and acetone were distilled (or fractionally distilled) over the drying agent and stored under argon. Substituted pyridines: 2,6-Cl_2Py and 3,5-Cl_2Py were used as received.

2.2. Synthesis of $PdCl_2(X_nPy)_2$ (compounds **I–XII**)

The procedure has been described elsewhere [16]. Palladium chloride complexes with pyridines were prepared under argon. $PdCl_2$ (1.128 mmol) 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. The elemental analyses of complexes **I**, **II**, **V**, **IX**, **XI** and **XII** were performed by a conventional method [16]. Single yellow crystals of **III**, **IV** and **VIII** obtained by a slow evaporation of their acetone solutions, were characterized by X-ray diffraction [17] and crystals of **VI**, **VII** and **X** are described in this work.

2.3. X-ray structure determinations

All measurements of crystal structure were performed on a KM4CCD κ-axis diffractometer with graphite-monochromated MoKα radiation. The crystals were positioned at 62 mm from the CCD camera. 1600 frames were measured at 0.5° intervals with a counting time of 11 s. The data were corrected for Lorentz and polarization effects. Empirical correction for absorption was applied [22]. Data reduction and analysis were carried out with the Oxford Diffraction programs [23]. The structures were solved by direct methods [24] and refined using SHELXL [25]. The refinement was based on F^2 for all reflections except those with very negative F^2. Weighted *R* factors *wR* and all goodness-of-fit *S* values are based on F^2. Conventional *R* factors are based on *F* with *F* set to zero for negative F^2. The $F_0^2 > 2\sigma(F_0^2)$ criterion was used only for calculating *R* factors and is not relevant to the choice of reflections for the refinement. The *R* factors based on F^2 are about twice as large as those based on *F*. All hydrogen atoms were located geometrically and their positions were refined. Temperature factors for some hydrogen atoms were fixed. Scattering factors were taken from Tables 6.1.1.4 and 4.2.4.2 [26]. The crystallographic data for the complexes are summarized in Table S1 (in Supplementary Material).

2.4. Thermal analysis, XRD and SEM measurements

Thermal stability of $PdCl_2(X_nPy)_2$ complexes was measured by Differential Scanning Calorimeter DSC 910 Du Pont Instruments (USA) connected to the thermal analyzer 9900 Computer/Thermal Analyzer and GBIP interface. The termogravimetric (TG) measurements were performed by means of termogravimeter Du Pont TGA 951 also connected to a thermal analyzer 9900 Computer/Thermal Analyzer and GBIP interface. All DSC and TG curves were recorded under nitrogen flow (6 dm^3/h), heating rate = 10 K/min. Thermal stability of the complexes was determined in temperature range 80–400 °C and mass of each sample was about 4 mg. Weight loss during thermal decomposition of $PdCl_2(X_nPy)_2$ was determined in temperature range 80–600 °C. TG measurements were performed in platinum cells and the average weight of sample was about 5–8 mg. Each result presented in this paper is the arithmetic mean of 3 repetitions and the difference of results in a series of determinations of the sample is up to 2%. Analysis of the products of thermal decomposition of $PdCl_2(X_nPy)_2$ complexes was carried out using powder diffractometer, working with copper lamp (radiation length 1.54) with a snap allowing to measure in the temperature range from 180 to 350 °C. The camera was equipped with a table for reflectometric measurements. Scanning electron microscope (SEM, model LEO 435 VP, Zeiss) equipped with an energy dispersive spectroscopy (EDS, Roentec) was used to examine the composition of the residue obtained after thermal decomposition of $PdCl_2(X_nPy)_2$ complexes.

2.5. Carbonylation procedure

The procedure has been described elsewhere [16]. 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 $PdCl_2(X_nPy)_2$ 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