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Application of Pd(II) Complexes with Pyridines as Catalysts for the Reduction of Aromatic Nitro Compounds by CO/H_2O

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S *Supporting Information*

ABSTRACT: Many efforts have been undertaken to minimize the cost of large-scale conversion of aromatic nitro compounds to amines. Toward this end, application of CO/H_2O as a reducing agent instead of molecular hydrogen seems to be a promising method, and the process can be catalyzed by Pd(II) complexes. In this work, the catalytic activity of square planar complexes of general structure $PdCl_2(X_nPy)_2$ (where X_nPy = pyridine derivative) was studied. Particular attention was paid to the effects of substituents both in the aromatic ring of X_nPy (ligand) and the nitro compound to be reduced ($YC_6H_4NO_2$). Incorporation of electron-withdrawing Y in the aromatic ring of $YC_6H_4NO_2$ increases the conversion, indicating that the kinetics of this process is similar to that for the carbonylation of nitrobeznene by CO in the absence of water (described in *J. Mol. Catal. A: Chem.* 2011, *337*, 9−16). Surprisingly, the incorporation of electron-withdrawing substituents into the aromatic ring of the X_nPy ligand also increases the conversion of $YC_6H_4NO_2$ (regardless of the structure of the $YC_6H_4NO_2$ substrate).

■ INTRODUCTION

Aromatic amines are important industrial intermediates and final products. They are typically produced by the reduction of nitro compounds.[1,2] Synthesis of amines by the direct hydrogenation of nitro compounds is expensive and non-selective;[3] thus, other methods of reduction are needed in industry. The most promising method for this employs the inexpensive and easily accessible mixture of CO/H_2O as the reducing agent.[4−20] Our previous studies on the carbonylation of nitrobenzene to ethyl *N*-phenylcarbamate (EPC) by carbon monoxide in the presence of $PdCl_2(X_nPy)_2$ complexes (where X = Cl or CH_3, and n = 0−2) showed that the activity of the catalyst increases as the basicity of the X_nPy ligand increases.[21,22] Thus, the activity of $PdCl_2(X_nPy)_2$ catalyst is strongly correlated with the electron density on the nitrogen atom of the X_nPy ligand. Recently, we proposed a mechanism for this carbonylation: the process starts from the reduction of NB to aniline, which is subsequently carbonylated to EPC.[21,23−26] The carbonylation can be stopped at this "initial aniline" step if the process is carried out in the presence of water, and this method can be convenient for the synthesis of aromatic amines.[21,27−29] The results of the carbonylation carried out in the presence of water allowed us to hypothesize that electron transfer from Pd(0) to the nitro compound is the rate-determining step (RDS), as was previously observed for the carbonylation of NB to EPC in the absence of water.[21,22] If electron transfer from palladium to NB is indeed the RDS, then an increase in the electron density on Pd by introducing electron-donating substituents in the X_nPy ligand would result in improved catalyst activity. In this work, we verify this hypothesis in a series of reduction processes of various nitro compounds ($YC_6H_4NO_2$) catalyzed by 12 $PdCl_2(X_nPy)_2$ complexes (**I**−**XII**), where X_nPy = pyridine, 2-methylpyridine, 3-methylpyridine, 4-methylpyridine, 2,6-dimethylpyridine, 2,4-dimethylpyridine, 3,5-dimethylpyridine, 2-chloropyridine, 3-chloropyridine, 2,6-dichloropyridine, 2,4-dichloropyridine, and 3,5-dichloropyridine. We also varied the structure of aromatic nitro compound $YC_6H_4NO_2$ (where Y = 3-Cl, 3-CH_3, 4-Cl, and 4-CH_3) to obtain deeper insight into the structure−activity relationship of this catalytic reduction.

■ RESULTS AND DISCUSSION

The mechanism of the reduction of NB by CO/H_2O in the presence of many catalytic systems has been investigated, but, to our knowledge, no report has been published on the kinetics and mechanism of the reduction of NB by CO/H_2O catalyzed by Pd(II) complexes with pyridine derivatives. Therefore, in this work, we describe the catalytic activity of Pd(II) complexes and the effect of the substrate's structure on the mechanism of the reduction of aromatic nitro compounds to amines.

Optimization of Reaction Conditions. Depending on the reaction conditions, in a water-free environment, nitrobenzene is carbonylated by CO to phenylcarbamate, whereas in the presence of a CO/H_2O mixture, the main product of the process is aniline. We varied the amount of water added in each experiment, and Figure 1 presents the relationship between the reaction parameters (conversion and yield) and the amount of water (see also Table S2, Supporting Information). Initially, the yield of aniline increases as the amount of water increases (at the same time, the yield of phenylcarbamate decreases). However, further increasing the H_2O content reduces the conversion, yield (of AN), and selectivity of the catalyst. The highest selectivity (with respect to AN) was observed for the 1:1 molar ratio of H_2O/NB (0.7 mL of water). The effects of temperature and time on the conversion and yield were also studied. Reduction of nitrobenzene by CO/H_2O in the presence of $PdCl_2(Py)_2$ as catalyst (where Py = pyridine) was carried out over the temperature range 100−180 °C for 60−120 min. For a reaction time of 60 min at 180 °C, the

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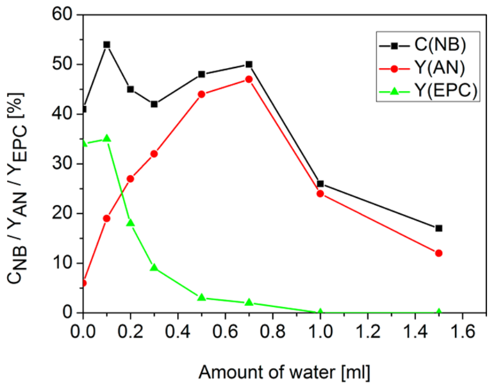
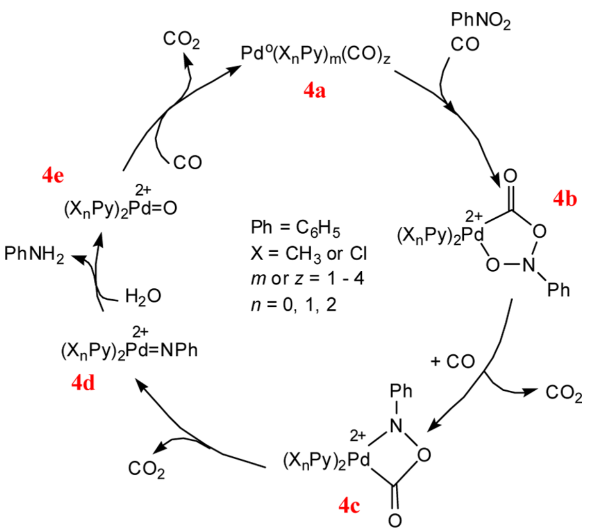


Figure 1. Conversion (C) and yield (Y) for the reduction of nitrobenzene by CO/H_2O as a function of the amount of water. Reaction conditions: $PdCl_2(Py)_2$/Fe/I_2/X_nPy = 0.056/2.68/0.12/6.2 mmol, NB = 40 mmol, ethanol = 20 mL, H_2O = 0−1.5 mL, 180 °C, 4 MPa CO, 60 min. Py = pyridine, NB = nitrobenzene, AN = aniline, and EPC = ethyl *N*-phenylcarbamate.

$PdCl_2(Py)_2$ complex exhibits the highest catalytic activity (see Table S3, Supporting Information). High values for NB conversion, yield of aniline, and TOF were also obtained for this catalyst at 160 °C, whereas at 140, 120, and 100 °C, these parameters were dereased. Thus, it can be stated that the conversion and yield increase with increasing temperature and time (see Table S3, Supporting Information), with the highest selectivity of the catalyst observed at 180 °C for 60 min.

Scheme 1. Proposed Mechanism for the Reduction of Nitrobenzene by CO/H_2O



Mechanism of the Reduction of Nitro Compounds to Amines by CO/H_2O in the Presence of Pd(II) Complexes. On the basis of our previous studies of the catalytic carbonylation[21,23] and reduction[27,29] of NB, we propose the following mechanism. Before the cyclic mechanism shown in Scheme 1 starts, a trace amount of the central atom in $PdCl_2(X_nPy)_2$ is reduced to palladium(0) by CO/H_2O: $Pd^{2+} \rightarrow Pd^0$. Reduction of palladium gives (yet unidentified) complexes with a likely composition of $Pd^0(X_nPy)_m(CO)_z$ (**4a** in Scheme 1), with *m* and *z* depending on the coordinating ability of Pd(0), the amount of X_nPy, and the pressure of CO. Inactive Pd_{black} is recovered to Pd^{2+} by the action of iron complexes and I_2.[24] A molecule of the nitro compound forms with $Pd^0(X_nPy)_m(CO)_z$ (**4a**), producing cyclic intermediate (**4b**); in this step, Pd^0 is oxidized to Pd^{2+}, and the nitro group is reduced. [Cyclic intermediate **4b** can also be formed as a result of nucelophilic attack by the nitro compound on a carbonylpalladium(II) species.] Complex **4c** is formed after abstraction of an oxygen atom from the nitro group by a molecule of CO. Although intermediates **4b** and **4c** have never been isolated or characterized, we postulate their formation because many metallacycles similar to intermediates **4b**[30−33] and **4c**[33−35] have been proposed in the literature for other metals (Pd, Ru, Rh, Ir) and ligands (especially bidentate N-donor ligands or P-donor ligands). Leconte et al.[36] isolated and characterized a metallacyclic complex (Figure 2), and they suggested that it is directly involved in the catalytic process of nitrobenzene carbonylation. Other metallacycles similar to **4b** and **4c** have also been proposed.[30,36]

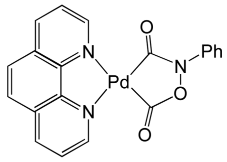


Figure 2. Structure of metallacyclic complex isolated and characterized by Leconte et al.[36]

On the basis of the literature data, we suggest that **4b** and **4c** are possible, nonstable intermediates, although the transformation of **4b** into **4c** still remains unexplored. Osborn et al. proposed the formation of a trimembered ring (after the release of carbon dioxide) followed by attack of CO to form **4c**.[33] Similar trimembered structures were also characterized by Pizzotti et al. for Pt-based catalysts.[37] At present, another possibility cannot be excluded, namely, that addition of CO_2 to **4b** gives unstable intermediates such as **4b**′ and **4b**″ (shown in Figure 3), which decompose to the more stable structure **4c** with the release of CO_2.

Figure 3. Proposed structures of unstable intermediates formed during the reduction of nitrobenzene by CO/H_2O.

The abstraction of a second oxygen atom from the nitro group (in complex **4c**) forms a nitrene complex (**4d**), which subsequently reacts with a molecule of water, and this step gives aniline and intermediate compound **4e**, both of which are intermediates (with phosphane ligands) proposed by Bouwman.[38] Compound **4e** reacts with CO to regenerate the starting active species, Pd^0 (**4a**). We have excluded the participation of the water−gas shift reaction because a separate experiment gave a negative result: water and CO do not react with the catalytic system − no CO_2 detected, (conditions: 2 mL of water, 20 mL of ethanol, 0.056 mmol of $PdCl_2$, 0.12 mmol I_2, 2.68 mmol of Fe were heated in the autoclave at 180 °C for 120 min under 4

MPa CO). Recently, we carried out a series of reductions of aromatic nitro compounds, $YC_6H_4NO_2$, by CO/H_2O in the presence of $PdCl_2$ as the catalyst.[26] Electron-withdrawing substituents Y make the process faster, and these results point toward the electron transfer from Pd(0) to the nitro compound being the RDS.[26] A similar situation was observed previously for the carbonylation of NB in the absence of water, i.e., a decrease in the electron density of the aromatic ring of $YC_6H_4NO_2$ increases the rate of the process; thus, electron transfer from palladium to $YC_6H_4NO_2$ was determined to be the RDS, and this step was accelerated as the electron density on the Pd atom increased (for the carbonylation of NB in the absence of water).[21]

Effects of Substituents in X_nPy on the Reduction of NB. Electron density on the Pd atom was modified by introducing electron-donating and -withdrawing substituents into the aromatic ring of the X_nPy ligand in $PdCl_2(X_nPy)_2$ complexes (where Py = pyridine, X = CH_3 or Cl, and $n = 0-2$). The results collected in Table 1 demonstrate that NB conversion increases when progressing from methylpyridines to unsubstituted pyridine and chloropyridines; the observed tendency is in agreement with the decreasing basicities of the X_nPy ligands (expressed as the pK_a of the protonated form of ligand).

Table 1. Conversion (C_{NB}), Yield (Y_{AN}, Y_{EPC}), Selectivity (S_{AN}), and Turnover Frequency (TOF) of Nitrobenzene Reduction by a CO/H_2O Mixture in the Presence of $PdCl_2(X_nPy)_2$ Complexes[a,b]

complex	symbol	C_{NB} (%)	Y_{AN} (%)	S_{AN}[c] (%)	TOF[d]
$PdCl_2(2,6\text{-}Me_2Py)_2$	**V**	11	9	82	66
$PdCl_2(2,4\text{-}Me_2Py)_2$	**VI**	16	14	88	103
$PdCl_2(3,5\text{-}Me_2Py)_2$	**VII**	25	24	96	176
$PdCl_2(4\text{-}MePy)_2$	**IV**	36	34	94	249
$PdCl_2(2\text{-}MePy)_2$	**II**	23	21	91	154
$PdCl_2(3\text{-}MePy)_2$	**III**	44	41	93	300
$PdCl_2Py_2$	**I**	50	47	94	344
$PdCl_2(3\text{-}ClPy)_2$	**IX**	65	62	94	454
$PdCl_2(2\text{-}ClPy)_2$	**VIII**	83	73	88	535
$PdCl_2(3,5\text{-}Cl_2Py)_2$	**XII**	87	81	93	593

[a] Reaction conditions: $PdCl_2(X_nPy)_2/Fe/I_2/X_nPy$ = 0.056/2.68/0.12/6.2 mmol, NB = 40 mmol, ethanol = 20 mL, H_2O = 0.7 mL, 180 °C, 4 MPa CO, 60 min. Py = pyridine (X = CH_3 or Cl, and $n = 0-2$), NB = nitrobenzene, and AN = aniline. [b] Presented results are calculated as mean values from at least three experiments. [c] Selectivity of AN was calculated as (mmol AN) × (mmol converted NB)$^{-1}$ × 100%. [d] Turnover frequency is expressed in mmol AN × (mmol Pd)$^{-1}$ × h^{-1}.

Among all investigated complexes, compound **XII** (with 3,5-dichloropyridine; see Table 1 for numbering) was the most active catalyst, with TOF = 593 mmol AN × (mmol Pd)$^{-1}$ × h^{-1}; for this complex, the conversion of NB reached 87 mmol, the yield of AN was 81 mmol, and the selectivity was 93%. High conversion, yield, and selectivity were also observed for $PdCl_2(2\text{-}ClPy)_2$ (**VIII**) and $PdCl_2(3\text{-}ClPy)_2$ (**IX**).

For other complexes having electron-donating X_nPy ligands, conversions and yields were almost one-half of that for **XII** (see Table 1). Steric hindrance is also important: we noticed a decrease in the selectivity when complexes with ortho-substituted pyridines were used: $PdCl_2(2\text{-}MePy)_2$ (**II**), $PdCl_2(2,6\text{-}Me_2Py)_2$ (**V**), $PdCl_2(2,4\text{-}Me_2Py)_2$ (**VI**), and $PdCl_2(2\text{-}ClPy)_2$ (**VIII**).

The process is accelerated for electron-deficient nitro compounds $YC_6H_4NO_2$ (i.e., having electron-withdrawing substituents Y), and if electron transfer from Pd to the nitro compound is the RDS, then the process should be facilitated by increasing the nucleophilicity of the metal center. Thus, electron-donating or -withdrawing groups in the pyridine ring of the catalyst should accelerate or retard the electron transfer, respectively.

The obtained results (Figure 4) indicate that a lower electron density on the palladium center in $PdCl_2(X_nPy)_2$ accelerates the reduction of nitrobenzene, and this is not in agreement with the hypothesis that electron transfer from Pd to nitrobenzene is the RDS of the catalytic reduction. In order to provide a better understanding of the mechanism and, particularly, to optimize the reaction conditions of the reduction, we carried out two series of experiments. In the first series, we varied the Y substituent in $YC_6H_4NO_2$ (during reduction performed in the presence of different catalysts), and in the second series of experiments, we varied X in the X_nPy ligand during the reduction of $YC_6H_4NO_2$.

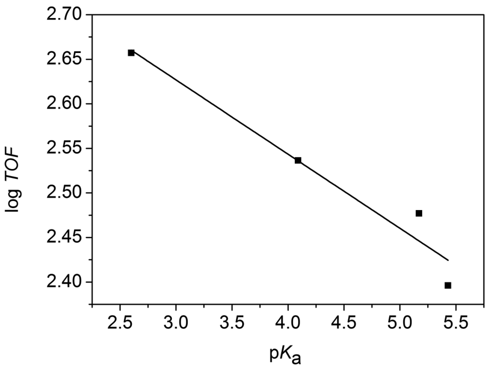


Figure 4. Log TOF versus pK_a values of X_nPy ligands for the reduction of nitrobenzene by CO/H_2O in the presence of $PdCl_2(X_nPy)_2$. For reaction conditions, see footnote *a* in Table 1.

Effects of Substituents in X_nPy and $YC_6H_4NO_2$ on the Rate of Reduction of Various $YC_6H_4NO_2$. We measured the effects of substituent Y in $YC_6H_4NO_2$ for two other catalytic systems, namely, for the most and least active catalysts, i.e., $PdCl_2(3,5\text{-}Cl_2Py)_2$ (**XII**) and $PdCl_2(3,5\text{-}Me_2Py)_2$ (**VII**), respectively, applied to a series of $YC_6H_4NO_2$. On the basis of the results collected in Tables S4–S9 in the Supporting Information, it can be stated that the conversion and yield increase as the electron-withdrawing ability of Y increasess, $4\text{-}Me\text{-}C_6H_4NO_2 < 3\text{-}Me\text{-}C_6H_4NO_2 < C_6H_5NO_2 < 3\text{-}Cl\text{-}C_6H_4NO_2 < 4\text{-}Cl\text{-}C_6H_4NO_2$, regardless of the structure and activity of the catalyst. Acceleration of the process is observed for decreasing electron density in the aromatic ring of $YC_6H_4NO_2$, and such results indicate that electron transfer from the Pd center to $YC_6H_4NO_2$ is the RDS. During the next step, we measured the effects of substituent X in X_nPy for the reduction of various derivatives of nitrobenzene. For the reduction of $3\text{-}Cl\text{-}C_6H_4NO_2$ (as an example of a $YC_6H_4NO_2$ substrate), the conversion and yield increased in the following order of $PdCl_2(X_nPy)_2$ ligands: 4-MePy < Py < $3,5\text{-}Me_2Py$ < 3-MePy < 3-ClPy < $3,5\text{-}Cl_2Py$ (see Table S4, Supporting Information), in reasonable agreement with the decreasing basicity of X_nPy. The same tendency is observed for the whole series of $YC_6H_4NO_2$ nitro compounds, and it can be stated that electron-withdrawing X in X_nPy accelerates the reaction rate, regardless of the structure of

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$YC_6H_4NO_2$ (see Table S5–S7 and Figures S1–S3, Supporting Information). These contradictory results obtained for ligands X_nPy suggest that pyridine affects other steps. We propose that X_nPy plays a crucial role during the formation of Pd(0) active species (involving their shape, size, and catalytic activity). This hypothesis is based on the results of our studies (to be published) on the thermal decomposition of $PdCl_2(X_nPy)_2$.[22] We observed different shapes and sizes of the obtained Pd(0) depending on the X_nPy applied, namely, smaller particles were obtained in the presence of chloropyridines. It is possible that the same phenomena might be responsible for different activity of Pd(0) generated in the presence of Cl_nPy and Me_nPy.

CONCLUSIONS

The effects of the structures of the catalyst and substrate (aromatic nitro compound) on the reaction rate were investigated. The catalytic activity of Pd(II) complexes always increased with decreasing basicity of X_nPy. The best results during the reduction of aromatic nitro compounds ($YC_6H_4NO_2$) with CO/H_2O as a reducing agent were obtained for three catalysts with chloropyridine ligands, $PdCl_2(2\text{-}ClPy)_2$, $PdCl_2(3\text{-}ClPy)_2$, and $PdCl_2(3,5\text{-}Cl_2Py)_2$, regardless the structure of the $YC_6H_4NO_2$ substrate. On the basis of these results, it is impossible to clearly identify the RDS. Nevertheless, our experiments provide new insights into the structure–activity relationship for the reduction of aromatic nitro compounds by CO/H_2O, which might contribute to understanding its mechanism better. Strategies to develop catalysts for the reduction process should be based on the introduction of electron-withdrawing substituents to the 3- or 4- position of the pyridine ring.

EXPERIMENTAL SECTION

Materials. Carbon monoxide (99.9%), $PdCl_2$, iodine, and iron powder were used as received. Pyridine (Py), liquid-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), nitrobenzene (NB) and its liquid derivatives (3-MeNB), and ethanol were distilled (or fractionally distilled) over a drying agent and stored under argon. Solid-substituted pyridines (2,6-Cl_2Py and 3,5-Cl_2Py) and solid-substituted nitrobenzenes (3-ClNB, 4-MeNB, 4-ClNB) were used as received.

Synthesis of $PdCl_2(X_nPy)_2$ (Compounds I–XII). The procedure has been described elsewhere.[21] Palladium chloride complexes with pyridines were prepared under argon. $PdCl_2$ (1.128 mmol) was placed in a 10 mL flask equipped with a magnetic stirrer, and 2.26 mmol of Py or substituted X_nPy in 10 mL of acetonitrile was added. The reaction was carried out at room temperature for 24 h. Elemental analyses of complexes **I**, **II**, **V**, **IX**, **XI**, and **XII** were performed by a conventional method[21] (see Table S1, Supporting Information). Single yellow crystals of **III**, **IV**, **VI**, **VII**, **VIII**, and **X**, obtained by slow evaporation of their acetone solutions, were characterized by X-ray diffraction.[22,39]

Reduction Procedure. The reaction was carried out in a 200 mL stainless steel autoclave equipped with a magnetic stirrer. Before starting the experiment, the autoclave was heated at 120 °C for 3 h and then cooled to room temperature. Subsequently, $PdCl_2(X_nPy)_2$ catalyst (0.056 mmol), Fe powder (2.68 mmol), and a solid derivative of nitrobenzene (40 mmol) 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: I_2 (0.12 mmol), Py or X_nPy (6.2 mmol), nitrobenzene or its liquid derivative (40 mmol), water (0–1.5 mL), and ethanol (20 mL). The cover was closed, and the autoclave was directly filled with carbon monoxide (4 MPa), fixed, placed in a hot oil bath, and maintained at 100–180 °C for 30–120 min, depending on the reaction. After the reaction was completed, the autoclave was cooled in a water bath and vented, and a liquid sample of the reaction mixture was analyzed. The yield of the reaction was calculated on the basis of GC-FID analysis using *n*-decyl alcohol as standard.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.oprd.5b00273.

> Elemental analysis of Pd(II) complexes; conversion, yield, and selectivity for the reduction of nitrobenzene by CO/H_2O in the presence of $PdCl_2Py_2$ complexes as a function of the amount of water; conversion, yield, and selectivity for the reduction of nitrobenzene and various nitro compounds in the presence of Pd(II) catalysts; Hammett type plots for the reduction of nitro compounds (PDF)

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Notes

The authors declare no competing financial interest.

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