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# Palladium-catalyzed reductive carbonylation of nitrobenzene for producing phenyl isocyanate

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ABSTRACT

Direct reductive carbonylation of nitrobenzene to phenyl isocyanate with carbon monoxide was performed using various types of palladium catalysts together with many types of *N*-donor ligands. The effect of reaction time, pressure, temperature, ligand amount, and molar ratio to establish the optimized conditions was also investigated. With this, we were able to achieve up to 100% conversion and 63.5% yield with $PdCl_2$ and alkylimidazole system (1:3) within 2 h at 220 ºC and 1400 psi of CO in toluene.

## 1. Introduction

Nowadays, organic isocyanates (R–NCO) have become more and more industrially and commercially important as chemical intermediates in the manufacture of thermoplastic foams, elastomers, adhesives, and agrochemicals [1]. They can be converted to carbamates and ureas through the addition of alcohol and amine, respectively; and those carbamates and ureas can also be transformed back to isocyanates via thermal decomposition (Scheme 1a and 1b). Because of this conversion, mono- and diisocyanates have established their importance in the synthesis of a variety of polyurethane (flame-retarding) foams [2-6], (bio-degradable) plastics [7-10], pesticides [11, 12], adhesives [13-15], and coatings [16-19].

The conventional route to make methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI), as well as a variety of other isocyanates is often referred to as the 'phosgene route' (Scheme 1c) [20]. Despite the high yield and good selectivity obtained with the phosgene route, there are major drawbacks including toxicity of phosgene, formation of corrosive hydrochloric acid, and limited concentration of reactant.

Carbonylation with carbon monoxide is an attractive alternative, because it can provide a one-step conversion of nitro aromatics to the isocyanate without the use of environmentally unfriendly phosgene [21-24]. In the direct method (Scheme 1d), a catalyst activates the nitro group and carbon monoxide to form the isocyanate with liberation of carbon dioxide. Initially, a variety of elements were investigated as catalyst for the conversion of nitroaromatic compounds to isocyanates [24-26], such as sulfur [27-29], copper [30, 31], and especially selenium [25], which was reported to be very efficient. However, these derivatives seem to be far too toxic to be applied in industry [27-29] and it appears difficult to separate the catalyst from the final product [32]. Alternatively, group 8–10 metal compounds can be applied, and in 1967, Hardy and Bennett were the first to report the direct conversion of nitro compounds to isocyanates using rhodium, palladium or other noble metal salts as catalyst with a Lewis acid promoter at high temperature and high pressure of carbon monoxide [21, 33]. Regarding the direct carbonylation of mono- or dinitroaromatic compounds, it has been reported that heterogeneous catalyst such as Pd/C or Rh/C [31] as well as inorganic polymeric precursors like $PdCl_2$ and $RhCl_3$ give poor results [34]. *N*-containing ligands are also often used in Pd-catalyzed carbonylation reactions for enhancing activity and stability of Pd catalyst since they can have coordination with the palladium atom and prevent aggregation of Pd black. Such soluble palladium complexes consisting of *N*-heterocyclic ligands such as $Pd(Py)_2Cl_2$ has been employed to generate phenyl isocyanate from nitrobenzene at pressures up to 1600 psi in the temperature range of 170-230 °C, though the turnover rates of isocyanates is not very high [35]. Also the addition of a Lewis acid promoter (such as $MoCl_5$, $VCl_4$, $FeCl_3$, etc.) may strongly increase both the rate and selectivity of the reaction towards isocyanates [36-40], but the catalyst is quite rapidly deactivated.

In this research we present the direct reductive carbonylation of nitrobenzene to phenyl isocyanate using the catalytic system consisting of $PdCl_2$ together with *N*-donor ligands (monodentate and bidentate, phosphine and amine) and promoters. The optimized reaction conditions using the $PdCl_2$ and 1-butylimidazole system, which showed best activity, is also ac

pressure. Moreover, the complex of $PdCl_2$ and 1-butylimidazole, which is believed to be the active species, was also prepared and tested as catalyst for the reductive carbonylation reaction.

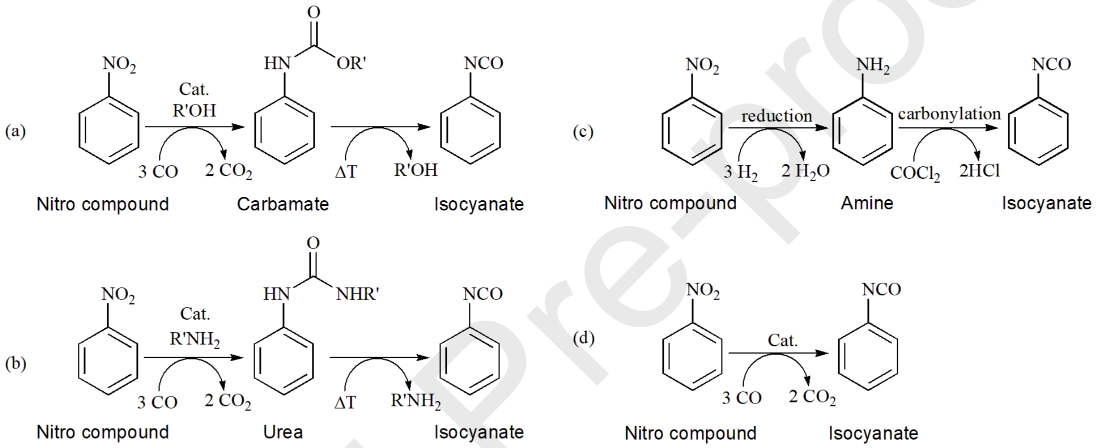
## 2. Results and Discussion

### *2.1. Reductive carbonylation of nitrobenzene to phenyl isocyanate using $PdCl_2$*

To begin with, the reductive carbonylation of nitrobenzene to phenyl isocyanate was carried out using palladium chloride as main catalyst and various types of *N*-donor ligands (Fig. 1) in toluene at 220 °C and 1400 psi of carbon monoxide for 4 h, and the results are summarized in Table 1. The result shows that pyrazole (**L1**), 4-dimethylaminopyride (DMAP) (**L2**), pyridine (**L3**), and benzimidazole (**L4**) had some catalytic activity while 1,2,4-triazole (**L5**), pyrazine (**L6**), and 1,3,5-triazine (**L7**) almost had no activity (entries 1-7). It also shows that among the imidazoles chosen for this reaction, only the ones with the electron–donating groups (such as alkyls; **L9-L11**) exhibited fairly good catalytic activity (Table 1, entries 4 and 8-16).

the amount of ligand was investigated, and the results are summarized in Table 2. The results show that the best catalyst/ligand ratio is 1/3. More or less amount of ligand resulted in the decrease in phenyl isocyanate yield. Less amount of ligand might not be enough to both create the active species and provide the necessary basicity for the reaction, while more amount of ligand might react with nitrobenzene to form the undesirable but stable intermediate (Fig. S1) which will use up the substrate and hinder the carbonylation process.

It is known that addition of metal oxides of V, Mo, W, Nb, and other groups of V and VI transition metals promote the catalytic activity of $PdCl_2$ in the carbonylation of nitrobenzene [23]. The promoting effect can be explained in various ways. Firstly, the compounds mentioned above are Lewis acids, so they could be used to reoxidize Pd(0) to Pd(II), thus preventing the formation of inactive Pd black. They could also activate the nitro group by coordination, favoring the following deoxygenation.



**Scheme 1.** (a, b) The indirect, (c) the conventional, and (d) the direct method for the reductive carbonylation of nitro compounds.

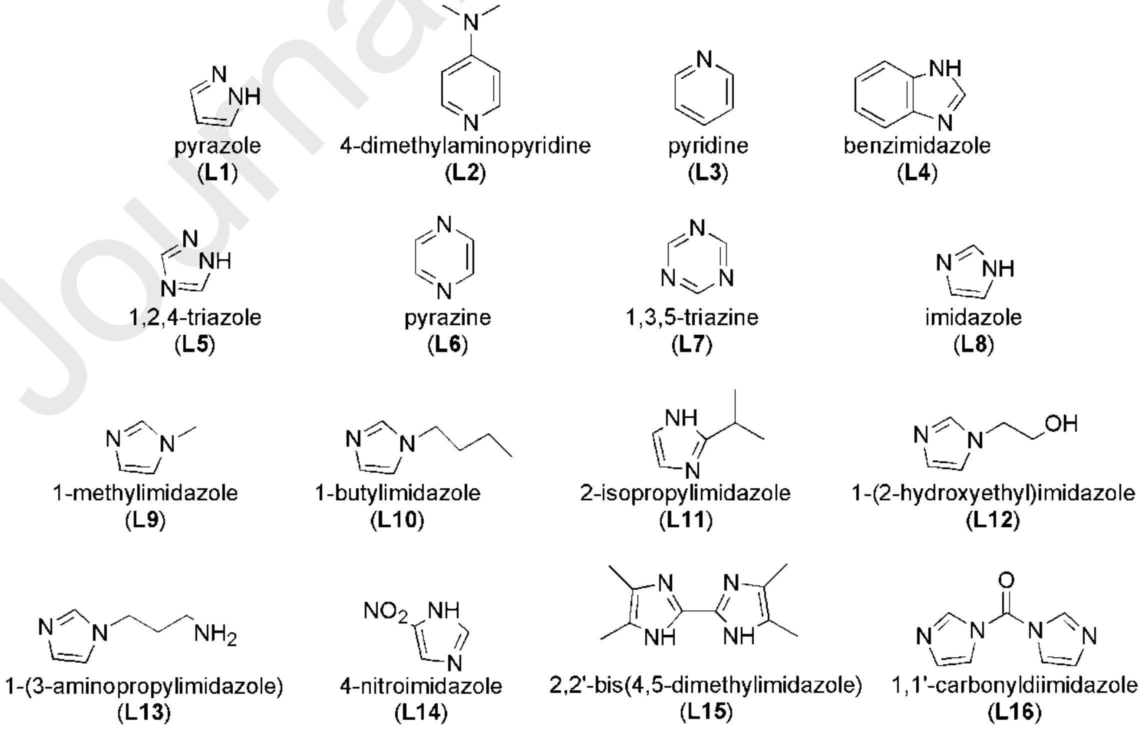
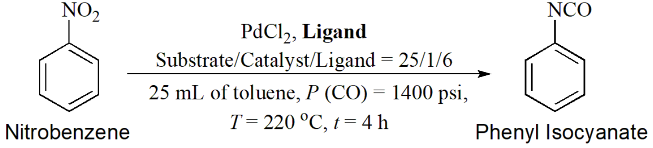


**Fig. 1.** The structure of the *N*-donor ligands.

With this information, some types of metal oxides were tested as p [illegible] 1-6). The results show that among the oxides chosen for this reaction, the best promoter for this reaction was $TiO_2$, still it was not as good as when not using the promoter. Complex of moblydenum and 1-methylimidazole, i.e. $[l\text{-}Hmim]_4[Mo_8O_{26}(1\text{-}mim)_2]\cdot 2H_2O$, could be made using $MoO_3$ and 1-methylimidazole (1 to 1 ratio) under reflux condition in 12 h [41]. Similarly to molybdenum, 1-methylimidazole could also be able to form complexes with zinc [42], titanium, $Ti_2S_6O(MeIm)_2$ [43], vanadium, and $[VOL(1\text{-}methimz)_2]$ [44] while tungsten can form bidentate complex with 2-(1*H*-Imidazol-2-yl)pyridine [45]. So it is believed that all of the promoter used in this experiment can form complex with 1-butylimidazole, creating a competition between main catalyst ($PdCl_2$) and promoter in making complex with 1-butylimidazole, thus reduces the amount of ligand needed for the reaction, and decreases the phenyl isocyanate yield.

**Table 1**
Screening of the N-donor ligands for the reductive carbonylation of nitrobenzene to phenyl isocyanate.[a]



| Entry | N-donor ligand | Conversion (%) | Yield (%) |
|---|---|---|---|
| 1 | **L1** | 100 | 28.8 |
| 2 | **L2** | 100 | 25.4 |
| 3 | **L3** | 96.6 | 14.8 |
| 4 | **L4** | 62.3 | 24.2 |
| 5 | **L5** | 34.6 | 1.9 |
| 5 | **L6** | 14.2 | 0.6 |
| 6 | **L7** | 25.9 | 0.7 |
| 8 | **L8** | 17.8 | 1.2 |
| 9 | **L9** | 100 | 38.4 |
| 10 | **L10** | 100 | 38.2 |
| 11 | **L11** | 97 | 34.9 |
| 12 | **L12** | 37.5 | 8.6 |
| 13 | **L13** | 80.8 | 0 |
| 14 | **L14** | 20.1 | 0 |
| 15 | **L15** | 86.3 | 8.6 |
| 16 | **L16** | 20.6 | 0 |

[a] The reaction was carried out with nitrobenzene (7.5 mmol), $PdCl_2$ (0.3 mmol), and ligand (1.8 mmol) in 25 mL of toluene at 220 °C.

After surveying the *N*-donor ligands and promoter effects, we turned our attention to other reaction conditions such as time, temperature, pressure, and substrate/catalyst molar ratio; and the results are summarized in Table 4.

When the reductive carbonylation was conducted by varying the reaction time from 1 to 8 hours, the maximum yield of 63.5% was achieved at 2-hour reaction time (Table 4, entries 1-6). This can be attributed to the formation of phenyl isocyanate during the 2-hour reaction then converted to the undesired by-product of $C_6H_5\text{-}N{=}C{=}N\text{-}C_6H_5$ when prolonging the reaction time. Although it is stated that *N,N'*-diphenylcarbodiimide, or $C_6H_5\text{-}N{=}C{=}N\text{-}C_6H_5$, could be formed at 250 °C with or without catalyst [46-49] or higher temperature [50], it still has a chance to be formed in our reaction with prolonged reaction time.

**Table 2**
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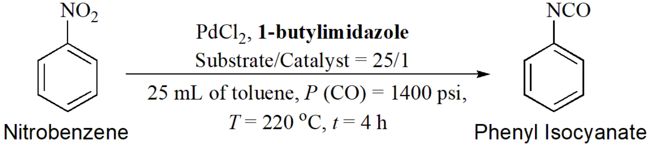
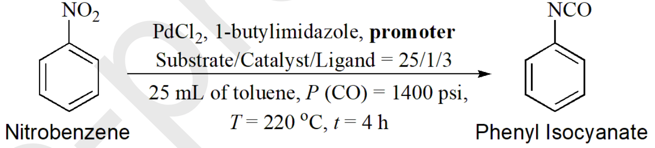


| Entry | Substrate/Catalyst/Ligand | Conversion (%) | Yield (%) |
|---|---|---|---|
| 1 | 25/1/1 | 95.1 | 40.5 |
| 2 | 25/1/2 | 92.6 | 37.7 |
| 3 | 25/1/3 | 100 | 52 |
| 4 | 25/1/4 | 99.4 | 50.8 |
| 5 | 25/1/5 | 100 | 48.3 |
| 6 | 25/1/6 | 100 | 38.2 |
| 7 | 25/1/10 | 96.7 | 15 |

[a] The reaction was carried out with nitrobenzene (7.5 mmol), $PdCl_2$ (0.3 mmol), and 1-butylimidazole in 25 mL of toluene at 220 °C.

**Table 3**
Effect of promoter on the reductive carbonylation of nitrobenzene to phenyl isocyanate.[a]



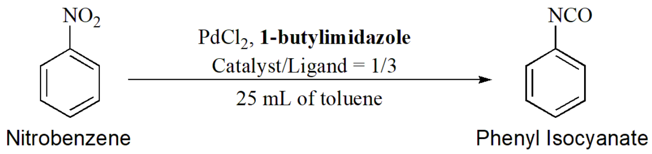
| Entry | Promoter | Catalyst/Promoter | Conversion (%) | Yield (%) |
|---|---|---|---|---|
| 1 | - | - | 100 | 52 |
| 2 | $TiO_2$ | 1/1 | 100 | 48.8 |
| 3 | $V_2O_5$ | 1/1 | 100 | 35.9 |
| 4 | $MoO_3$ | 1/1 | 100 | 43.5 |
| 5 | $WO_3$ | 1/1 | 100 | 44.3 |
| 6 | ZnO | 1/1 | 100 | 47.1 |

[a] The reaction was carried out with nitrobenzene (7.5 mmol), $PdCl_2$ (0.3 mmol), 1-butylimidazole (0.9 mmol), and promoter in 25 mL of toluene at 220 °C.

Effect of temperature on the reductive carbonylation was carried out by varying the reaction temperature from 160 to 240 °C. Table 4 (entries 2 and 7-10) shows that when increasing the reaction temperature, the nitrobenzene conversion and the phenyl isocyanate yield increased and achieved maximum value at T = 220 °C (100% conversion and 63.5% yield). However, when increasing the temperature to higher than 220 °C, the phenyl isocyanate yield decreased because of the thermolysis–decarboxylation that led to the formation of *N,N'*-diphenylcarbodiimide as explained above [46-50].

As the CO pressure increases from 1000 to 1400 psi, the nitrobenzene conversion and the phenyl isocyanate yield increased and achieved maximum value at P = 1400 psi (Table 4, entry 2 and 11-12). But when continuing to increase the pressure to higher than 1400 psi, more byproducts were formed, and the phenyl isocyanate yield decreased (entries 13-14). This may be due to the deactivation of catalyst caused by the formation of the inactive $PdCl_2(CO)$ or $Pd_2Cl_4(CO)_2$ complexes at high CO pressure [51].

Effect of reaction conditions on the reductive carbonylation of nitrobenzene to phenyl isocyanate.[a]



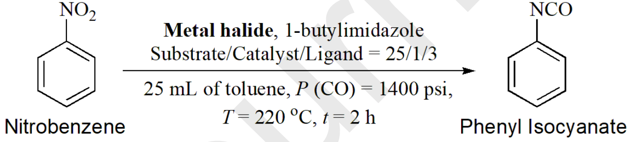
| Entry | Substrate/Catalyst | Time (h) | Pressure (psi) | Temperature (°C) | Conversion (%) | Yield (%) |
|---|---|---|---|---|---|---|
| 1 | 25/1 | 1 | 1400 | 220 | 58.4 | 29.9 |
| 2 | 25/1 | 2 | 1400 | 220 | 100 | 63.5 |
| 3 | 25/1 | 3 | 1400 | 220 | 100 | 50.1 |
| 4 | 25/1 | 4 | 1400 | 220 | 100 | 52 |
| 5 | 25/1 | 5 | 1400 | 220 | 100 | 39 |
| 6 | 25/1 | 8 | 1400 | 220 | 100 | 29 |
| 7 | 25/1 | 2 | 1400 | 160 | 34.5 | 7.9 |
| 8 | 25/1 | 2 | 1400 | 180 | 84.5 | 34.8 |
| 9 | 25/1 | 2 | 1400 | 200 | 94.5 | 40.8 |
| 10 | 25/1 | 2 | 1400 | 240 | 95.9 | 14.8 |
| 11 | 25/1 | 2 | 1000 | 220 | 59.7 | 25.1 |
| 12 | 25/1 | 2 | 1200 | 220 | 81.7 | 38.4 |
| 13 | 25/1 | 2 | 1600 | 220 | 94.5 | 40.8 |
| 14 | 25/1 | 2 | 1800 | 220 | 97.4 | 47.5 |
| 15 | 100/1 | 2 | 1400 | 220 | 41 | 11.2 |
| 16 | 50/1 | 2 | 1400 | 220 | 80.6 | 19.4 |
| 17 | 20/1 | 2 | 1400 | 220 | 97.4 | 63.6 |

[a] The reaction was carried out with nitrobenzene (7.5 mmol)

We also attempt to optimize reaction condition by decreasing the substrate/catalyst ratio from 100 to 25. The nitrobenzene conversion and the phenyl isocyanate yield reached maximum value at the ratio of 25, then it did not show any increase when further increasing the amount of catalyst (Table 4, entries 2 and 15-17).

Other metal halide compounds were employed as main catalyst to find alternative for expensive $PdCl_2$, and the results are listed in Table 5. Although $PtCl_2$ and $RuCl_3$ showed some catalytic activity but not as good as $PdCl_2$, $NbCl_5$, $FeCl_2$, and $CuCl_2$ showed some little activity while other metal halides showed no activity.

**Table 5**
Effect of metal halides on the reductive carbonylation of nitrobenzene to phenyl isocyanate.[a]



| Entry | Metal Halides | Conversion (%) | Yield (%) |
|---|---|---|---|
| 1 | $PdCl_2$ | 100 | 63.5 |
| 2 | $FeCl_2$ | 49.7 | 15 |
| 3 | $CoCl_2$ | 17.3 | 0 |
| 4 | $NiCl_2$ | 25.7 | 0 |
| 5 | $CuCl_2$ | 61.7 | 15 |
| 6 | $ZnCl_2$ | 16.9 | 0 |
| 7 | $NbCl_5$ | 94.8 | 12.2 |
| 8 | $RuCl_3$ | 87 | 39.7 |
| 9 | $InCl_3$ | 26.7 | 0 |
| 10 | $SnCl_2$ | 30.4 | 0 |
| 11 | $PtCl_2$ | 97.1 | 44.1 |

[a] The reaction was carried out with nitrobenzene (7.5 mmol), metal halide (0.3 mmol), and 1-butylimidazole (0.9 mmol) in 25 mL of toluene at 220 °C.

### *2.2. Effect of the two-component system of $PdCl_2$ and 1-butylimidazole*

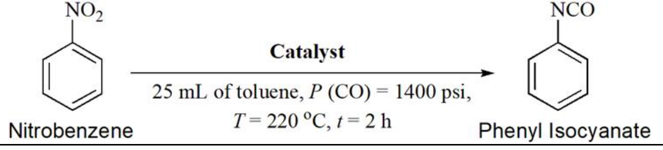
Under the optimized reaction conditions, we tried to find the active species of our catalytic system. Table 6 (entries 1-3) shows that the reaction only happened when using the two-component system, which means that first palladium chloride and 1-butylimidazole might have reacted with each other to create some active species, then that active species would act as catalyst for the reaction. For this reason, we would try to make that catalyst in acetone and the synthesized Pd(1-butylimidazole)$_2$Cl$_2$ [Pd(1-C$_4$Im)$_2$Cl$_2$] was analyzed using $^1$H NMR (Fig. S3), FTIR (Fig. S4), and EA (Table S1).

In $^1$H NMR spectra of 1-butylimidazole and Pd(1-butylimidazole)$_2$Cl$_2$, the protons of the 1-butyl group are similar, while the protons of the imidazole ring experienced a downfield shift (8.10 ppm compared to 7.60 ppm, 7.25 ppm compared to 7.15, and 7.12 compared to 6.93), suggesting that there was a coordination between palladium and 1-butylimidazole. Also, there are very few impurity peaks in the NMR diagram of Pd(1-C$_4$Im)$_2$Cl$_2$ complex, suggesting that the complex was well-made.

FTIR spectra of $PdCl_2$, 1-butylimidazole and Pd(1-C$_4$Im)$_2$Cl$_2$ are shown in Fig. S4. The peaks in the 3200 – 2800 cm$^{-1}$ region belong to C–H stretching region of 1-butylimidazole [52], and the peaks in the 1700–1000 cm$^{-1}$ region belong to C=C, C–C, C=N, C–N stretching region in the imidazole ring of 1-butylimidazole. All of these peaks appeared in both Fig. S4b and S4c but didn’t appear in Fig. S4a, suggesting that the complex of $PdCl_2$ and 1-butylimidazole was successfully made.

As indicated in Table S1, although being synthesized in acetone, EA results of the synthesized Pd(1-C$_4$Im)$_2$Cl$_2$ complex does not correspond to the EA of acetone solvate [Pd(1-butylimidazole)$_2$Cl$_2$(acetone)$_x$], but matches with that of Pd(1-C$_4$Im)$_2$Cl$_2$ (calculated and published research) [53], also indicating that the desired complex was successfully made.

**Table 6**
Effect of the two component systems of $PdCl_2$ and 1-butylimidazole on the reductive carbonylation of nitrobenzene.[a]



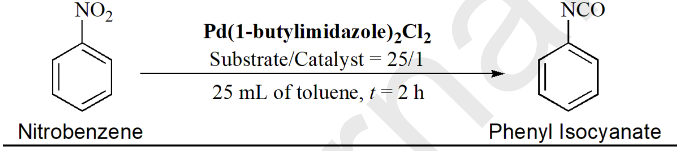
| Entry | Catalysts | Ligands (Catalyst/Ligand) | Conversion (%) | Yield (%) |
|---|---|---|---|---|
| 1 | $PdCl_2$ | - | 24.6 | 0 |
| 2 | - | 1-butylimidazole | 26.4 | 0 |
| 3 | $PdCl_2$ | 1-butylimidazole (1/3) | 100 | 63.5 |
| 4 | $Pd(OAc)_2$ | 1-butylimidazole (1/3) | 7.5 | 0.9 |
| 5 | $Pd(1\text{-butylimidazole})_2Cl_2$ | - | 82.5 | 57.1 |
| 6 | $Pd(1\text{-butylimidazole})_2Cl_2$ | 1-butylimidazole (1/1) | 79.5 | 53.2 |

[a] The reaction was carried out with nitrobenzene (7.5 mmol), catalyst (0.3 mmol), and 1-butylimidazole in 25 mL of toluene at 220 °C.

Table 6 shows that when applied as catalysts, $Pd(1\text{-}C_4Im)_2Cl_2$ prepared in acetone gave as nearly good result as our best catalytic system consisting of $PdCl_2$ and 1-butylimidazole (1/3) (entries 3 and 5), but the activity decreased when adding more 1-butylimidazole (entry 6), suggesting that when more 1-butylimidazole is added the active species is affected and its catalytic activity decreased.

Contrary to $PdCl_2$, $Pd(OAc)_2$ didn't show any catalytic activity when using together with 1-butylimidazole, which may attributed to inappropriate formation of active site (entry 4). It is also noteworthy that the type of Pd precursor greatly influence the catalytic activity.

**Table 7**
Activities of $Pd(1\text{-butylimidazole})_2Cl_2$ in the reductive carbonylation of nitrobenzene to phenyl isocyanate.[a]



| Entry | Temperature (°C) | Pressure (psi) | Conversion (%) | Yield (%) |
|---|---|---|---|---|
| 1 | 220 | 1400 | 82.5 | 57.1 |
| 2 | 220 | 1000 | 39.3 | 18.6 |
| 3 | 220 | 1200 | 98.1 | 26.9 |
| 4 | 220 | 1725 | 85.8 | 37.7 |
| 5 | 180 | 1400 | 36.8 | 21.5 |
| 6 | 200 | 1400 | 69.7 | 39.3 |
| 7 | 240 | 1400 | 99.1 | 27.1 |

[a] The reaction was carried out with nitrobenzene (7.5 mmol) and $Pd(1\text{-}C_4Im)_2Cl_2$ (0.3 mmol) in 25 mL of toluene.

Once again, to determine the optimized conditions for the reaction, $Pd(1\text{-}C_4Im)_2Cl_2$ was also tested as catalyst in different variations of pressure and temperature, which is shown in Table 7. Similar to the $PdCl_2$/1-butylimidazole (1/3) system, 220 °C and 1400 psi seem to be the best reaction condition, where any changes in pressure (entries 2-4) and temperature (entries 5-7) hich can be explained similarly to the above sections.

## *2.3. Interaction between substrates (nitrobenzene and CO) and $Pd(1\text{-butylimidazole})_2Cl_2$*

For further understanding the interaction between nitrobenzene and $Pd(1\text{-}C_4Im)_2Cl_2$, more characterizations were done via cyclic voltammetry (CV).

To measure the oxidation–reduction potential of nitrobenzene with and without $Pd(1\text{-}C_4Im)_2Cl_2$ as catalyst, CV analysis of nitrobenzene together with the complex was performed and the diagrams are described in Fig. 2. It is indicated that there is one oxidation peak at around -1.04 V and one reduction peak at around -1.22 V (Fig. 2a), which corresponds to the one-electron participating oxidation–reduction between nitrobenzene and radical (Scheme S1) [54].

From Fig. 2, it can be clearly seen that upon adding $Pd(1\text{-}C_4Im)_2Cl_2$ the reduction peak of nitrobenzene started at a more positive position than when not using any catalyst or when using $Pd(OAc)_2$ (-0.95 V compared to -1.02 V and -1.05 V, respectively). It suggests that the presence of $Pd(1\text{-}C_4Im)_2Cl_2$ as catalyst would take less energy for nitrobenzene to undergo reduction, thus the reductive carbonylation of nitrobenzene would take place more easily than $Pd(OAc)_2$ catalyst (Table 6, entries 3-5). Moreover, the increased current for nitrobenzene reduction after addition of $Pd(1\text{-}C_4Im)_2Cl_2$ can be related to the increased turnover frequency which corresponds to higher phenyl isocyanate yield at constant reaction time (Tables 5-7).

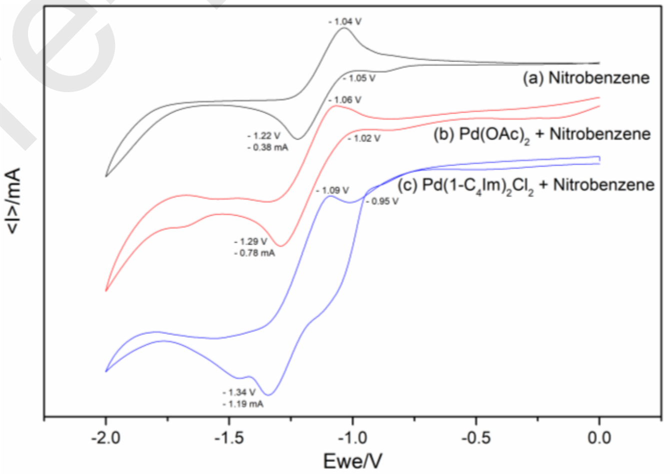


**Fig. 2.** Cyclic voltammetry (CV) profiles of (a) nitrobenzene, and its mixture with (b) $Pd(OAc)_2$ and (c) $Pd(1\text{-}C_4Im)_2Cl_2$ in acetonitrile.

Finally, the proposed mechanism of palladium-catalyzed reductive carbonylation of nitrobenzene into phenyl isocyanate (as shown in Scheme S2) could be explained similarly to the previously proposed mechanism [54], where a series of stepwise deoxygenation/carbonylation processes involving metallacyclic intermediates take place. These intermediates containing the metallacyclic carbonyl group could be detected by FTIR. To prove this proposition, $Pd(1\text{-}C_4Im)_2Cl_2$ complex was also introduced with CO during 24 h at room temperature and its FTIR spectrum was measured (Fig. 3). It exhibits two characteristic ν(CO) bands appeared at 2167 and 2123 $cm^{-1}$ in the solid state probably due to solid-state splitting [55] in the metal carbonyl complexes. This strongly proves that there are some interactions between palladium and CO but, it was limited by detection of intermediates during the reaction.

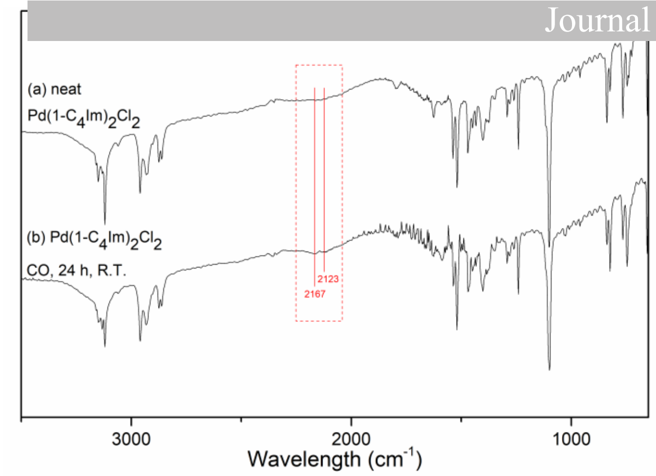


**Fig. 3.** FTIR spectra of (a) neat $Pd(1-C_4Im)_2Cl_2$ and (b) 24 h after exposed to CO at room temperature.

## 3. Conclusions

In this research, after optimizing the reaction conditions by testing various catalytic systems consisting of different types of ligands, promoters with different reaction time, temperature, and pressure, we developed a catalyst system comprising $PdCl_2$ and alkylimidazole (1:3) for producing phenyl isocyanate from reductive carbonylation of nitrobenzene. Best result was 100% conversion and 63.5% yield (63.5% selectivity) using 1-butylimidazole as ligand within 2 h at 220 °C and 1400 psi of CO in toluene with substrate/catalyst molar ratio of 25. We were also successful in synthesizing the $Pd(1-C_4Im)_2Cl_2$ complex, which is believed to be the most probable catalyst of the reaction and achieved comparable result of 82.5% conversion and 57.1% yield (69.2% selectivity).

Further research on this matter will try to find more effective ligands and more customized reaction conditions throughout the studying the mechanism of the reaction, as well as the recovery of phenyl isocyanate from the reaction mixture.

## 4. Experimental

### 4.1. Materials

All chemicals and reagents (salts, ligands, and oxides) were purchased from Sigma-Aldrich Chemical Co., U.S.A., and used immediately without any further purification. Toluene was of analytic grades and was distilled with appropriate drying agents under a nitrogen atmosphere prior to use. An over 99% purity carbon monoxide cylinder was purchased from Gong-Dan Industrial Gas Co, Korea.

The proton nuclear magnetic resonance ($^1H$ NMR) spectra were recorded on a Bruker Spectrospin 300 MHz spectrometer at 25 °C with tetramethylsilane (TMS) as an internal standard. The Fourier-transform infrared spectroscopy (FTIR) spectra were recorded using Nicolet FTIR spectrometer (Nicolet 6700, Thermoelectron Co., MA, USA). The electrochemical properties were studied using an electrochemical workstation (VSP Potentiostat, Bio-Logic Science Instruments SAS, France). Cyclic voltammetry (CV) analysis was conducted using 32 mM nitrobenzene with 32 mM of Pd catalysts in acetonitrile at 25 °C and 0.1 M tetrabutylammonium perchlorate was used as electrolyte. Glassy carbon, Pt wire, and Ag/AgCl were used as a working, counter, and reference electrode, respectively. The scan

r a potential from 0 to -2 V, using a chronoamperometric method. The reduction peak current value for nitrobenzene inserted in Fig. 2 is acquired when the starting current is zero. Elemental analysis (EA) was conducted on a FlashSmart CHNS/O Elemental Analyzer (Thermo Scientific, MA, USA).

### 4.2. Preparation of $PdCl_2$ and 1-butylimidazole complexes

Pd(1-butylimidazole)$_2$Cl$_2$ [$Pd(1-C_4Im)_2Cl_2$] was synthesized by the following method: $PdCl_2$ (0.5 mmol) and 1-butylimidazole (1 mmol) in 50 mL of acetone were stirred at reflux condition for 24 h. After the solvent was evaporated, the complex was precipitated in acetone/hexane, filtered, and washed with hexane, then dried under vacuum overnight. Light yellow powder, 94.18% yield. $^1H$ NMR (DMSO-d$^6$, 300 MHz): δ 8.10 (s, 1H), 7.26 (t, J = 1.5 Hz, 1H), 7.19–7.09 (m, 1H), 4.01 (t, J = 7.1 Hz, 2H), 1.78–1.53 (m, 2H), 1.19 (dq, J = 14.5, 7.3 Hz, 2H), 0.86 (t, J = 7.3 Hz, 3H). FTIR (acetone, $cm^{-1}$): $\nu_{max}$ 3160, 3151, 3120 (–CH stretching, imidazole); 2960, 2933, 2923, 2875, 2860 (–CH stretching, $-CH_3$ and $-CH_2$); 1625, 1536, 1517 (–C=N stretching, imidazole), 1469, 1461 (–C=C–); 1373, 1346 (C–C); 1261, 1240 (C–N stretching, imidazole); 1114, 1097 (–C–H bending, imidazole). Elemental Analysis: Calculated for $Pd(C_7H_{12}N_2)_2Cl_2$ = $PdC_{14}H_{24}N_4Cl_2$, C, 39.50%; H, 5.68%; N 13.16%. Found C, 39.50%; H, 5.84%; N, 13.11%.

### 4.3. Catalytic testing

All the palladium-catalyzed reductive carbonylation reactions were conducted in a 100 mL stainless steel autoclave equipped with a magnetic stirrer and electrical heater. Nitrobenzene (7.5 mmol), different type of palladium catalyst (0.25 mmol, substrate/catalyst = 25), ligand and promoter (if necessary), and toluene (15 mmol) were added to the autoclave, respectively. The reactor was sealed and flushed three times with carbon monoxide. Then carbon monoxide was introduced into the autoclave (1400 psi), and the reactor was heated up to required temperature with stirring. Upon completion, the reactor was cooled to room temperature, and the residual gas was released. The reaction mixture was analyzed by gas chromatography (GC). Quantitative analyses were made on an Agilent 6890N gas chromatograph equipped with a flame ionization detector (FID) equipped with an DB-5MS column (30 m x 0.25 mm x 0.25 μm) and qualitative analyses were achieved on an Agilent 6890N-5975 mass spectrometer-gas chromatograph (MSD-GC) equipped with an HP-5 column (30 m × 0.32 mm × 0.25 μm).

The conversion of nitrobenzene and the yield and selectivity for phenyl isocyanate were calculated based on the calibration curves of pure samples of substrates and products using the following equations:

Conversion of nitrobenzene (%)

$$= \frac{Nitrobenzene\ remained\ (by\ GC-FID)\ (mmol)}{Nitrobenzene\ charged\ (mmol)} \times 100\%$$

Yield of phenyl isocyanate (%)

$$= \frac{Phenyl\ isocyanate\ produced\ (by\ GC-FID)\ (mmol)}{Nitrobenzene\ charged\ (mmol)}$$

$$\times\ 100\%$$

Selectivity of phenyl isocyanate (%)

$$= \frac{Yield\ of\ phenyl\ isocyanate\ (by\ GC-FID)\ (\%)}{Conversion\ of\ nitrobenzene\ (by\ GC-FID)\ (\%)} \times 100\%$$

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## Supplementary Material

Supplementary material that may be helpful in the review process should be prepared and provided as a separate electronic file. That file can then be transformed into PDF format and submitted along with the manuscript and graphic files to the appropriate editorial office.

# Highlights

- $PdCl_2$ with 1-butylimidazole (1:3) is active for direct reductive carbonylation
- Active species $Pd(1\text{-}C_4Im)_2Cl_2$ was successfully synthesized for the carbonylation
- Interaction between substrates and $Pd(1\text{-}C_4Im)_2Cl_2$ was detected
- Mechanism involving metallacyclic carbonyl compounds of palladium is proposed

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☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☒The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: