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Letter

Carbonylation of Aromatic Nitro Compounds to Isocyanates using a Homogeneous *trans*-$Pd(Py)_2Cl_2$ Complex Catalyst: IR Spectroscopic Study and Reaction Mechanism

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It is well known that reductive carbonylation of aromatic nitro compounds to isocyanates is catalysed by homogeneous PdL_2X_2 (where L = heterocyclic ligand, X = halogen) complexes [1 - 5]. This reaction is commercially important, as it provides a novel route for the manufacture of isocyanates without the use of phosgene [6]. A detailed investigation on screening of catalysts, promoters and solvents, as well as kinetics of this reaction, has been recently reported [4, 5]. It is generally believed that the reductive carbonylation of nitro compounds proceeds through nitrene intermediates [7 - 9], however, our understanding of the activation of nitro compounds and CO by complexes of the type PdL_2X_2 is not very clear.

This note reports the preliminary results of an IR spectroscopic study of palladium complexes isolated from the reaction mixture and proposes a possible reaction mechanism.

Experimental

Solvents were dried and freshly distilled under N_2. Nitrobenzene, *m*-nitrochlorobenzene and nitrosobenzene were purchased from M/s. Fluka and were freshly distilled under vacuum before use. Carbon monoxide gas, generated, purified and compressed in our own laboratory, was used and its purity found to be >99.8%. Palladium chloride obtained from Arora Mathey Ltd., India, was used without further purification. The complex, *trans*-$Pd(Py)_2Cl_2$, was prepared by the procedure described elsewhere [10].

The carbonylation experiments were carried out in a high pressure stirred autoclave according to the procedure described in our earlier work [4]. In a typical experiment carried out with the aim of isolating the catalytic complex, $Pd(Py)_2Cl_2$ (6.6 mmol) and *m*-nitrochlorobenzene (12.7 mmol) were charged into the high pressure reactor and the solution made up

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to 100 cm^3 using monochlorobenzene as a solvent. Reaction was continued for 4 h at 150 °C and 80 atm. At the end of the reaction, liquid as well as gas samples were analyzed by GC and IR techniques respectively. To isolate the catalytic complex, the reaction mixture was discharged under CO atmosphere. The contents were then concentrated under CO in a dry box, and the catalytic complex was precipitated by addition of n-hexane to this solution. The yellow complex thus obtained was washed with n-hexane and dried under CO. Mulls of this complex were prepared in a dry box and IR spectra recorded using a Perkin-Elmer 283 B grating spectrophotometer in the range of 4000 - 200 cm^{-1}.

Results and discussion

In this work the carbonylation of *m*-nitrochlorobenzene (*m*-NCB), nitrobenzene (NB) and nitrosobenzene was studied using $Pd(Py)_2Cl_2$ complex catalyst. The results are summarized in Table 1. For these substrates, the corresponding isocyanate derivatives were formed along with CO_2. Initially several blank stoichiometric reactions were carried out using $Pd(Py)_2Cl_2$ complex catalyst in monochlorobenzene as a solvent. It was observed that when $PdCl_2$ alone was used there was no reaction, but with $PdCl_2$ in the presence of free pyridine, carbonylation was found to proceed at rates comparable to those with $Pd(Py)_2Cl_2$. This indicates the importance of pyridine as a ligand in the catalytic process. The stoichiometric reaction of $Pd(Py)_2Cl_2$ and NB as well as *m*-NCB under N_2 atmosphere and 200 °C resulted in no change in the form of $Pd(Py)_2Cl_2$. On the other hand, the reaction of CO and $Pd(Py)_2Cl_2$ in monochlorobenzene at 80 atm pressure and 30 °C resulted in the reduction of the complex to metallic Pd. Under conditions of carbonylation, however, there was no observation of metallic Pd and the conversion of nitro compound to isocyanate occurred progressively, with generation of CO_2. The above results indicate that activition of CO is a first step prior to activation of the nitro compound. The observation of a clear solution under reaction conditions suggests that the activated state of the complex is stabilized only in the presence of CO and nitro compound. This was also evident from the observation that for the sample withdrawn from the reactor, exposure to air immediately led to decomposition of the catalytic species to metallic Pd. The colour of the initial solution of $Pd(Py)_2Cl_2$ was yellow, but turned to pale green on treatment with nitro compound and CO under reaction conditions (100 atm CO pressure and 200 °C). Thic characteristic pale green colour of the solution was observed for both NB and *m*-NCB as substrates. Carbonylation of nitrosobenzene was also found to proceed smoothly with $Pd(Py)_2Cl_2$ complex catalyst (Table 1). In this case too, a clear solution of the catalyst was observed. This suggests that the reduction of nitro compound is likely to proceed via nitroso compound as an intermediate.

Carbonylation of *m*-nitrochlorobenzene under experimental conditions allowed us to isolate the catalytic intermediate. This yellow-coloured complex was stable only under CO atmosphere, and decomposed slowly in air to metallic Pd. The IR spectrum of this complex was obtained by careful

TABLE 1

Carbonylation of aromatic nitroso and nitro compounds to isocyanate

Run No.	Catalyst precursor[a]	Substrate[b]	Conversion (wt.%)	Selectivity for isocyanate (%)
1	$PdCl_2$	nitrobenzene	nil	nil
2	$PdCl_2$ + pyridine[c]	nitrobenzene	18	68
3	$Pd(Py)_2Cl_2$	nitrobenzene	20	72
4	$Pd(Py)_2Cl_2$	*m*-nitrochlorobenzene	33	48
5	$Pd(Py)_2Cl_2$	nitrosobenzene	62	41

[a] Catalyst precursor 3.0 mmol.

[b] Substrate 40 mmol.

[c] Pyridine 6.6 mmol, solvent (monochlorobenzene) 90 cm^3, P_{CO} 100 atm, T 200 °C, reaction time 2 h.

handling under CO, and the IR results were compared with those of the original $Pd(Py)_2Cl_2$ complex.

An interesting feature observed in the spectrum of the active complex isolated from the reaction mixture, with *m*-NCB as substrate and using $Pd(Py)_2Cl_2$ catalyst, was a strong band at 1920 cm^{-1} (Fig. 1a), which can be assigned to the ν(C–O) stretching frequency [11]. The ν(C–O) wave number is lower in this case than normally observed for palladium carbonyls (2150 - 2000 cm^{-1}). The low value of ν(C–O) indicates a highly activated C–O bond and a high degree of π back-bonding from Pd to the π^* orbital of CO [11, 12]. The absorption band at 640 cm^{-1} (Fig. 1c) is consistent with the ν(Pd–C) stretching frequency reported in the literature [11]. The above data confirms the existence of coordinated CO in the active complex.

The spectra of isolated complex and $Pd(Py)_2Cl_2$ in the metal–halogen stretching vibration region (370 - 250 cm^{-1}) are shown in Fig. 1d. The Pd–Cl stretching frequency can be easily distinguished from other metal–ligand stretching frequencies in this region by their characteristic intense absorption bands. It can be noted that the ν(Pd–Cl) stretching frequency at 357 cm^{-1} [13] in *trans*-$Pd(Py)_2Cl_2$ is shifted to 262 cm^{-1} in the isolated complex. The fine splitting of the Pd–Cl band at 262 cm^{-1} is likely to be due to the presence of other ligands such as CO, pyridine and *m*-nitrosochlorobenzene. The appearance of single absorption band at 262 cm^{-1} is suggestive of a *trans* arrangement of Cl atoms in the isolated complex. However, the present evidence does not allow a definitive conclusion on the nature of the Pd–Cl bonding in the active complex. The IR spectra in Fig. 1b show new bands at 1568, 1545 and 1480 cm^{-1} due to the coordinated nitroso group of *m*-nitrosochlorobenzene [14 - 17], while the band due to coordinated pyridine in the original $Pd(Py)_2Cl_2$ complex at 1603 cm^{-1} [10] has been shifted to 1580 cm^{-1}. Figures 1c and d show frequencies of coordinated pyridine at

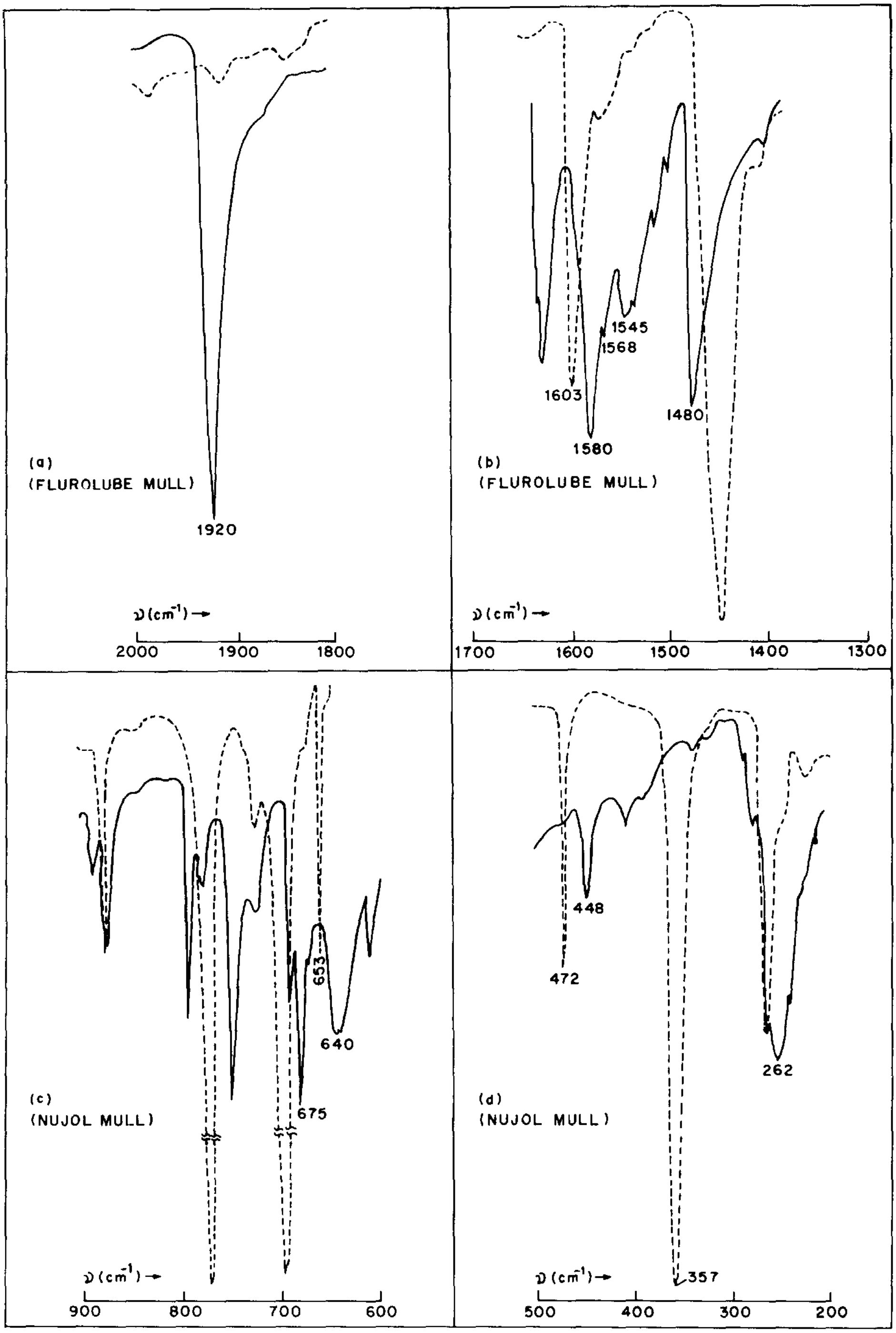
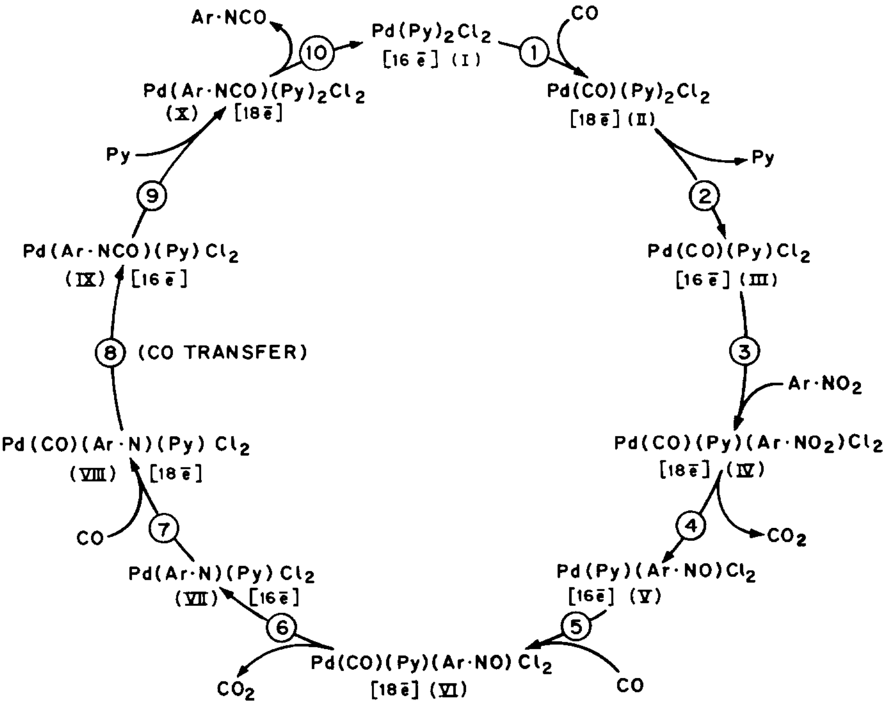


Fig. 1. IR spectra of *trans*-Pd(Py)$_2$Cl$_2$ (- - - -) and yellow complex isolated from reaction mixture (———).

653 and 472 cm^{-1} in $Pd(Py)_2Cl_2$ [10, 18]. These frequencies are shifted to 675 and 448 cm^{-1} respectively in the isolated complex. These data indicate the possibility of coordinated *m*-nitrosochlorobenzene and pyridine in the isolated complex.

Based on these preliminary results of IR spectroscopy, a speculative mechanism of carbonylation of nitro compounds by $Pd(Py)_2Cl_2$ complex catalyst is proposed, as shown in Scheme 1. This scheme is based on the assumption that the reaction proceeds via a nitrene intermediate. Since it is observed that nitrosobenzene can be reduced by CO to phenylisocyanate and CO_2 using $Pd(Py)_2Cl_2$ complex catalyst (Table 1), the reaction pathway through nitrosobenzene and nitrene appears to be most likely. The key step in this catalytic reaction is the oxygen transfer from the nitro group to coordinated CO. It is already known that carbonylation of $Ni(NO_2)_2(PEt_3)_2$ proceeds via oxygen atom transfer to form CO_2 and $Ni(NO_2)(NO)(PEt_3)_2$ [19]. A similar mechanism is likely in the present case, and forms the basis for steps 4 to 6 in Scheme 1. Based on the spectroscopic evidence, compound (VI) in Scheme 1 is a likely intermediate isolated from the carbonylation reaction.



Scheme 1. Proposed catalytic mechanism.

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