

Reusable polymer-anchored catalyst for carbonylation reaction: kinetics and mechanism for diphenylurea formation

D.K. Mukherjee^{a,*}, C.R. Saha^b

^a Department of Chemistry, Ramsaday College, Amta, Howrah 711401, India

^b Department of Chemistry, Indian Institute of Technology, Kharagpur 721302, India

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Abstract

The investigation of the catalytic activity of $[\text{RhA}(\text{CO})_2]$ (HA; anthranilic acid) and its polymer analogue $[\text{Rh}(\text{OOC}_6\text{H}_4\text{NHCH}_2\text{-P})(\text{CO})_2]$; P = polystyrene moiety, towards the reductive carbonylation of nitrobenzene in DMF medium has been reported. The maximum yield and selectivity of diphenylurea was achieved using methanol as cosolvent under optimum reaction conditions. Spectroscopic and kinetic studies showed that the reaction proceeds through a species $[\text{RhA}(\text{C}(\text{O})\text{OCH}_3)_2]$ and the isocyanate formed at an intermediate stage is immediately scavenged by excess amine to form *N,N'*-diphenylurea. A tentative reaction mechanism based on the identification of reactive intermediates has been proposed for the carbonylation process.

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1. Introduction

The last lap of the 20th century has been marked by a rapid development of petrochemicals. Many industrially important compounds such as ureas, carbamates, azo and azoxyarenes, oximes and several heterocyclic compounds can be selectively obtained by either reductive carbonylation of nitroaromatics [1–6] or oxidative carbonylation of anilines [7–12]. *N,N'*-Diphenylurea (DPU) and methyl-*N*-phenyl carbamate (MPC) are seeing growing interest in the field of chemical technology as evident from numerous patents and papers in the literature [13–21]. Most of the conversions have been found to be catalyzed by metal compounds—organometallics and complexes

either in the same phase as the reactants or in different phases. In homogeneous reactions catalyzed by organometallic compounds, the catalyst gets intimately involved with the reactants to form various distinct intermediates during the course of the reaction. Such reactions are often very selective in nature, allowing firm control on the nature of the product obtained and operate under milder reaction conditions. However, such processes present the difficulty of separating the product from excess of reactants and the catalyst. Here, the heterogeneous catalysts offer the advantage of easy separation though they often lack the delicate selectivity of homogeneously catalyzed reactions. The intermediates in such processes are less distinctly characterized, but may be rationalized in terms of the same principles as applicable for the soluble catalysts. The present paper reports the catalytic behavior of soluble and polymer-supported rhodium catalysts in mild coordinating solvents containing

* Corresponding author.

E-mail address: debkumarmukherjee@rediffmail.com (D.K. Mukherjee).

methanol to useful *N,N'*-diphenylureas and the relationship this has to the mechanism of the catalytic carbonylation process.

2. Experimental

2.1. Instrument and chemicals

Analytical grade reagents and freshly distilled solvents were used throughout the investigation. DMF was purified by drying over CaH_2 under N_2 for 24 h followed by distillation under reduced pressure. PhNH_2 was purified by vacuum distillation in an inert atmosphere prior to use. CO (99.5%) purchased from IOL, Mumbai and $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ from Arora Matthey Ltd., India, were used as received. Macroporous polystyrene beads cross linked with 5% DVB were supplied as hard insoluble 20–50 mesh spheres of average pore diameter 800 Å by Aldrich, USA.

The polymer-supported complex $[\text{Rh}(\text{OOC}_6\text{H}_4\text{NHCH}_2\text{-P})(\text{CO})_2]$, where P = polystyrene moiety having the same coordination environment as soluble rhodium complex $[\text{Rh}(\text{A})(\text{CO})_2]$ has been prepared and characterized as described below. Vibrational, electronic and PMR spectra were taken with Perkin-Elmer 883, Shimadzu MPC-3700 and Bruker 200 MHz instruments, respectively. XPS study and thermal analyses were made with VG—scientific ESCA lab mark (E) and Shimadzu DT-400 instruments, respectively. Gas chromatographic analysis was performed with chrompack CP-9000 with 15% FFAP stainless steel column and flame ionization detector with temperature programming from 110 to 240 °C at the rate of 10 °C min^{-1} . The progress of the reaction was monitored by periodic analysis of the reaction mixture by GC technique. Diphenylurea was identified and estimated by HPLC using a Bandopack column with mobile phase as 62% methanol in aqueous sodium acetate solution.

2.2. Carbonylation procedure

In a typical experiment, DMF solution (10 ml) of the catalyst (10^{-4} M) and the substrate (1.0 M) was taken in a 50 ml glass lined stainless steel autoclave provided with inlet and outlet and equipped with a magnetic element. The reactor was first evacuated and flushed

with nitrogen. After pumping out nitrogen, it was immersed in a thermostated silicone oil bath preheated to the desired reaction temperature. The whole arrangement was then placed on a magnetic stirrer and the reaction mixture was subjected to the required pressure of pure carbon monoxide which was maintained constant throughout the run. At the end, the autoclave was rapidly cooled in an ice salt bath and blown off. The products were identified and analyzed after subsequent work up by GC and HPLC using authentic samples for comparison.

2.3. Preparation and isolation of the complexes

2.3.1. $[\text{RhA}(\text{CO})_2]$ (1)

The rhodium(I) complex was prepared according to the literature method [22]. The deep red solution mixture of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (0.26 g, 0.98 mmol) and anthranilic acid (0.2 g, 1.46 mmol) in dry, deoxygenated DMF was refluxed for 2 h. The cold solution diluted with 20 ml of distilled water produced yellow precipitate on keeping at 5 °C for 1 h. The precipitate after successive washing with water and acetone was dried under vacuum. The purity of the compound was checked by tlc, m.pt, chemical analysis, IR and UV-Vis spectral studies.

2.3.2. $[\text{Rh}(\text{OOC}_6\text{H}_4\text{NHCH}_2\text{-P})(\text{CO})_2]$ (2)

The polymer-supported complex having the same coordination environment as $[\text{Rh}(\text{A})(\text{CO})_2]$ (HA; $\text{C}_6\text{H}_4(\text{COOH})\text{NH}_2$) was prepared by refluxing the polymer acid ligand with $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in deoxygenated DMF under nitrogen [23,24]. Polystyrene beads with 5% cross linking of divinyl benzene were chloromethylated by the procedure adopted by Pepper et al. [25]. The chloromethylated polymer was treated with tetrahydrofuran solution of anthranilic acid for 24 h to replace 80% of the chlorines with the acid group. These beads were then refluxed with a twofold excess of DMF solution of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ for 6 h. At the end of the reflux period the brown colored beads were washed with water and acetone and dried under vacuum.

2.3.3. $[\text{RhA}(\text{CO})(\mu\text{-CO})_2]$ (3)

The yellow solution of $[\text{RhA}(\text{CO})_2]$ (0.3 g, 1.02 mmol) in dry deoxygenated DMF (10 ml) changed to deep green on stirring for 24 h under nitrogen. The

solution was reduced to 1 ml by vacuum evaporation at 60 °C, mixed with dry chloroform (5 ml) and kept at 0 °C for 24 h when the green crystalline precipitate separated out. This was washed with dry chloroform and dried under vacuum [26].

2.3.4. $[RhA(\mu-CO)(PhNO_2)]_2$ (**4**)

Dry $PhNO_2$ (0.5 ml) was added to the deep green solution obtained by stirring the DMF solution (10 ml) of $[RhA(CO)_2]$ (0.3 g, 1.02 mmol) for 24 h under nitrogen. The stirring was continued for 12 h more, dry chloroform (5 ml) was added and the mixture was kept at 0 °C for 24 h when the deep green precipitate separated out. This was washed with chloroform and finally dried under vacuum [26].

2.3.5. $[RhA(C(O)OCH_3)_2]$ (**5**)

A 50 ml stainless steel autoclave containing $[Rh(A)(CO)_2]$ was purged several times with CO. *o*-Nitrotoluene was dissolved in 15 ml of toluene and injected into the autoclave via an exhaust valve. After 5 min, 3 ml of methanol was injected in the same manner and the system was pressurized with CO (60 atm) and heated to 80 °C. After 24 h, the reactor was cooled, the pressure was released and the solution transferred to a two-necked 100 ml rb flask. Solvent was removed under vacuum and resulting brown oil was washed with 20 ml portions of diethyl ether and evacuated again. Light brown solid obtained was subjected to 1H NMR and IR studies for characterization [27,28]. Brown solid, 1H NMR (ppm, C_6D_6) 3.03

(s, OCH_3); 3.77 (s, OCH_3); 6.17 (m, ArH); 7.41 (m, ArH); 8.02 (m, ArH); IR (KBr, cm^{-1}) 1628, 1616; Anal: (Found: C, 36.38; N, 3.88; H, 3.24%; Calcd: C, 36.46; N, 3.98; H, 3.32%).

2.4. Characterization

The compounds $[RhA(CO)_2]$, $[Rh(OOCC_6H_4NHCH_2-P)(CO)_2]$, $[RhA(CO)(\mu-CO)]_2$, $[RhA(\mu-CO)(PhNO_2)]_2$ and $[RhA(C(O)OCH_3)_2]$ were characterized on the basis of their analytical and vibrational spectral data (Table 1); electronic, PMR spectral and XPS data (Table 2).

Due to insolubility of the polymer-supported catalyst in common organic or inorganic solvents, its characterization was limited to IR spectra, XPS and DTA studies. IR peaks at 1580 cm^{-1} (νCO , as), 1360 cm^{-1} (νCO , s) and in the region $3000\text{--}3200\text{ cm}^{-1}$ (νNH_2) are present in the spectra of all the complexes indicating the presence of coordinated anthranilate in all of them. Compared to IR spectra of **1**, the spectra of **3** show the appearance of a new peak at 1810 cm^{-1} (νCO , bridged) at the cost of one νCO (terminal) peak at 2085 cm^{-1} . The other νCO peak at 2005 cm^{-1} remains almost unchanged. $[RhA(CO)_2]$ in DMF medium dimerises through CO bridging to form a penta-coordinated rhodium(I) complex containing both terminal and bridged carbonyl groups. The spectra of **4** exhibits two new peaks at 1510 and 1345 cm^{-1} due to coordinated $PhNO_2$ [29] and only the bridged carbonyl peak at 1810 cm^{-1} is present. In

Table 1
Analytical and vibrational data of the compounds

Compounds	νCO	νNH_2	νOCO	$\nu COOCH_3$	νNO_2	C%	H%	N%	Rh%
$[RhA(CO)_2]$ (1)	2085 2005	3175 (a) 3075 (s)	1580 (a) 1360 (s)			36.04	2.02	4.47	20.7
$[Rh(OOCC_6H_4NHCH_2-P)(CO)_2]$ (2)	2082 2008	3165 (a) 3070 (s)	1575 (a) 1350 (s)						1.38
$[RhA(CO)(\mu-CO)]_2$ (3)	2005 1810	3175 3075	1580 1360			36.44	2.01	4.72	20.2
$[RhA(\mu CO)(PhNO_2)]_2$ (4)	1810	3172 3072	1582 1358		1510 1345	40.92	3.81	6.29	18.8
$[RhA(C(O)OCH_3)_2]$ (5)		3172 (a) 3072 (s)	1585 (a) 1362 (s)	1628 1616		36.38	3.24	3.88	19.2

All ν values are given in cm^{-1} ; P = polystyrene.

Table 2
XPS and NMR data of the complexes

	Compounds	ESCA DATA (eV)		NMR spectral data (ppm, C ₆ D ₆)		
		3d _{5/2}	3d _{3/2}	Aromatic –H	–NH ₂	–COOCH ₃
(1)	[RhA(CO) ₂]	308.2	312	6.7–7.8 (m)	7.38 (s)	
(2)	[Rh(OOCC ₆ H ₄ NHCH ₂ -P)(CO) ₂]	308.6	312.8			
(3)	[RhA(CO)(μ-CO)] ₂	308.4	312.2	6.7–8.0 (m)	6.58 (s)	
(4)	[RhA(μ-CO)(PhNO ₂) ₂]	308.4	312.6	6.7–8.0 (m)	6.36 (s)	
(5)	[RhA(C(O)OCH ₃) ₂]	311.2	314.6	6.9–8.02 (m)	7.36 (s)	3.03 (s)/3.76 (s)

P = polystyrene.

case of complex **5** all peaks at the ν CO region disappear and the peak of 1616 (w) and 1628 in the ν CO region is characteristic of methoxy carbonyl ligand [30–32].

The rhodium content in each of the complexes was determined by refluxing them with concentration of HCl for 24 h and then estimating the metal concentration in the solution by atomic absorption spectrometry at wavelength 255.6 nm using air-acetylene flame. Analysis of the complex **2** after five catalytic runs indicated Rh content (1.19%) to be reduced by 13% compared to the original catalyst (1.38%). This modest loss does not appear to be metal elution as the complex showed similar catalytic activity and the beads showed no visible color change even after five catalytic runs under identical reaction conditions. The metal loss may be a consequence of changes in the bead structures as evident from slight shift in CO absorption peaks (Fig. 1). The structure and orientation of the beads in the polymer matrix shield the metal ion effectively reducing their loss during the process of leaching and estimation [27].

The electronic spectra of all the complexes in DMF medium except the polymer-supported one, show two common absorption bands at 280 nm (sh) and 336 nm. The former was assigned to intramolecular charge transfer of coordinated anthranilate anion [22], while the latter may be due to π – π^* transition of the ligand. Both the compounds **1** and **5** exhibit peaks at 380 nm indicating them to be square planar in nature [22]. The low intensity peaks at 620 and 510 nm observed in the spectra of **3** and **4** may be due to d–d transition in these five coordinated rhodium(I) complexes. The ¹H NMR spectra (ppm, C₆D₆) of complex **1**, exhibit multiple signals in the region 6.7–8.0 (phenyl protons) and a broad signal at 7.38 (NH₂) (Table 2). For complexes

3 and **4**, the NH₂ proton signals show upfield shift at 6.58 and 6.36 ppm, respectively, though the signal for the phenyl protons remain unchanged. This upfield shift may be due to increased electron density at the NH₂ group caused by the lowered number of terminal CO groups in these molecules or due to influence of metal d-orbitals in the changed coordination environment of the metal. Compound **5** exhibits new PMR signals at 3.03 and 3.76 ppm due to CH₃ protons of C(O)OCH₃ groups [27,33]. ¹H NMR signals in the methoxide and aromatic methyl regions of complex **5** are masked at higher concentrations of aromatic amine and CH₃OH.

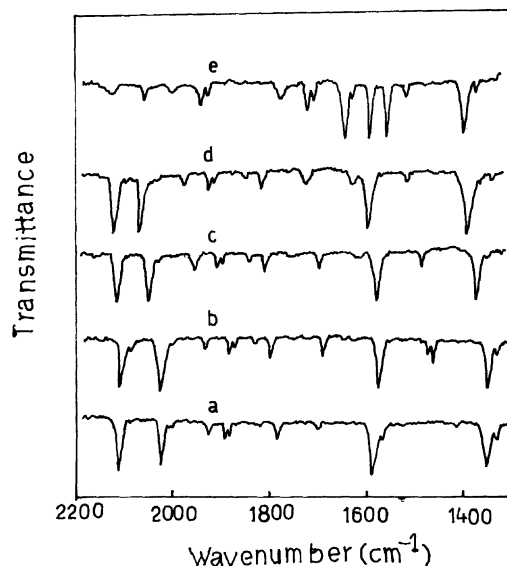


Fig. 1. IR spectra showing ν CO peaks of (a) complex **1**; (b) complex **2**; (c) used catalyst **2** after 3 runs; (d) used catalyst **2** after 5 runs; (e) complex **5**.

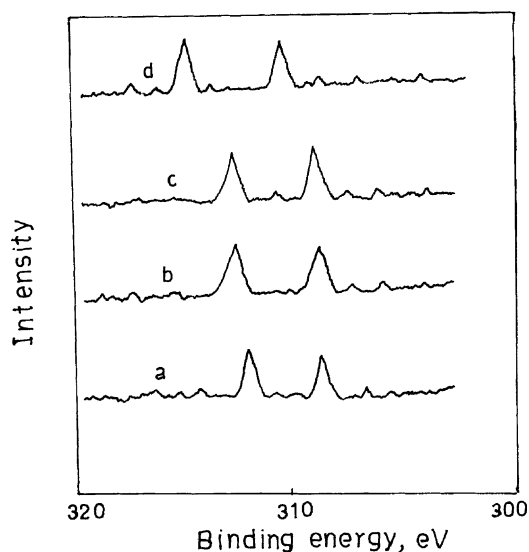


Fig. 2. XPS spectra of $3d_{5/2}$ and $3d_{3/2}$ levels of Rh in the catalysts: (a) complex **1**; (b) complex **2**; (c) used catalyst **2** after 5 runs; (d) complex **5**.

XPS study of the compounds were carried out in the range 290–320 eV using Al $K\alpha$ as target material in order to determine the oxidation state of rhodium in them. The $3d_{5/2}$ and $3d_{3/2}$ levels of the metal in the complexes **1**, **2**, **3** and **4** have binding energies in the vicinity of ~ 308 and ~ 312 eV, respectively. The energies are comparable with +1 oxidation state of rhodium [34]. The binding energy for the isolated

complex **5** was found to be 311.2 ($3d_{5/2}$) and 314.6 eV ($3d_{3/2}$) which suggests the presence of Rh(III) in the species (Fig. 2). To avoid possible X-ray induced metal reduction in the polymer host, measurements were made with a reduced power of the X-ray source of 10 kV, 10 mA. Survey spectra were recorded for all samples in the binding energy range 0–1400 eV with a step of 0.5 eV.

3. Results and discussion

The catalyst $[\text{RhA}(\text{CO})_2]$ was found to be highly efficient for the reductive carbonylation of nitrobenzene in mild coordinating solvents and in presence of methanol. In absence of methanol, low conversion of nitrobenzene (15%) to aniline mainly, was recorded even when the carbon monoxide pressure was increased to 80 atm and temperature raised to 100 °C. Reaction at room temperature and low carbon monoxide pressure (20 atm) even in presence of methanol did not yield any product. Effect of carbon monoxide pressure and temperature on the carbonylation of nitrobenzene was therefore studied to optimize the yield of products. Highest conversion of PhNO_2 (100%) to diphenylurea (DPU) was achieved at 60 atm and 80 °C and at a methanol concentration of 6 M. Higher methanol concentration increased the yield of aniline at the cost of DPU. Comparable results were obtained with both the soluble and polymer-anchored rhodium complex (Table 3).

Table 3

Influence of $\text{PhNO}_2:\text{PhNH}_2$ molar ratio on the reductive carbonylation of PhNO_2^a in the presence of methanol

Run	Molar ratio ($\text{PhNO}_2:\text{PhNH}_2$)	Conversion ^b (%)	DPU ^c	Selectivity (%)		
				MPC ^d	PhNH_2	NPF ^e
1	1:0	100	59 (53)	16 (20)	9 (13)	10 (10)
2	0.5:1	40	74 (68)	4 (16)	–	17 (15)
3	1:0.5	100	69 (60)	9 (15)	7 (10)	12 (10)
4	1:1	100	70 (64)	9 (14)	8 (10)	13 (10)
5	1:2	100	71 (67)	13 (15)	(08)	14 (10)
6	1:4	100	70 (64)	13 (16)	(08)	14 (12)

Values in parentheses are those for the soluble rhodium catalyst.

^a Conditions: $\text{PhNO}_2 + \text{PhNH}_2 = 0.5$ mol, $\text{CH}_3\text{OH} = 2$ ml, Catal = Rh content = 2×10^{-4} mol, medium = DMF, $T = 80$ °C, $t = 4$ h, $P_{\text{CO}} = 60$ atm.

^b Calculated to the conversion of PhNO_2 (runs 1, 3–6) and PhNH_2 (run 2).

^c *N,N'*-Diphenylurea.

^d Methyl-*N*-phenyl carbamate.

^e *N*-Phenylformamide.

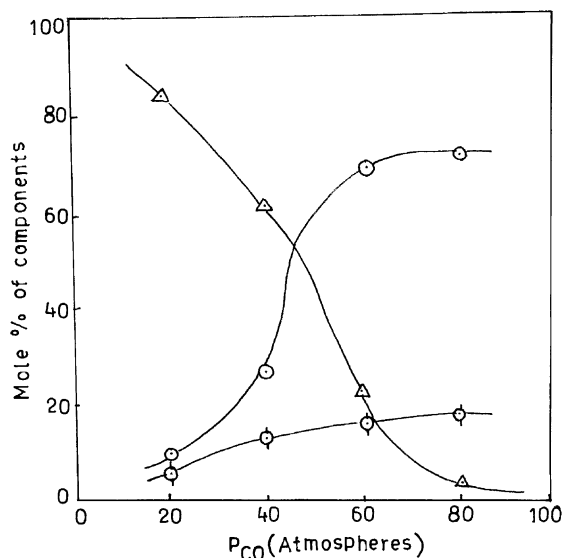


Fig. 3. Effect of P_{CO} on reductive carbonylation of $PhNO_2$. $T = 80^\circ C$, solvent = DMF, $t = 4$ h, (\odot) = $PhNH_2$, (\odot) = DPU, (Δ) = $PhNO_2$.

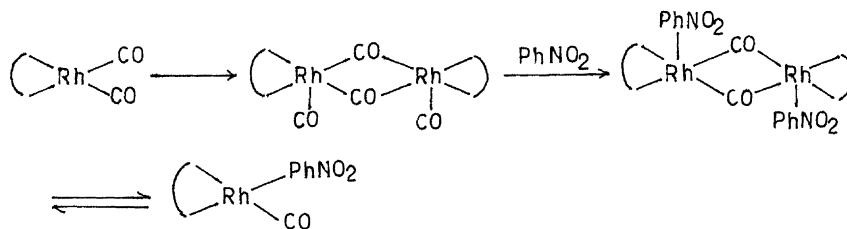
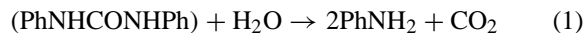
At carbon monoxide pressure of 20 atm or below, no carbonylation reaction takes place as nitrobenzene concentration remain unchanged and no reaction products were observed even after 16 h exposure to catalytic run (Fig. 3). Both the group of catalysts in homogeneous and heterogeneous phase exhibit similar behavior though with slightly different rates. The DMF solution of the isolated complexes **3** and **4** were also subjected to carbonylation of nitrobenzene under identical set of conditions as employed for rhodium complexes **1** and **2**. No product formation occurred even with these complexes at low temperature (less than $20^\circ C$) and at carbon monoxide pressure maintained below 20 atm.

The DMF solution of the starting complex **1** was next kept at a carbon monoxide pressure of 60 atm and

$80^\circ C$ for 6 h and intermittent IR analysis of the withdrawn samples show the presence of both terminal and bridged carbonyl groups. These sets of reactions suggest that the starting catalyst $[RhA(CO)_2]$ must undergo transformation into its bridged dimer and this transformation is not feasible at room temperature and low pressure of carbon monoxide. In order to find out any transformation of $[RhA(PhNO_2)(\mu-CO)]_2$ that may occur in solution at higher temperature, IR spectra of the DMF solution of the compound at $80^\circ C$ was taken. The spectra exhibit a new peak at 2008 cm^{-1} (ν_{CO} terminal) in addition to the peak at 1810 cm^{-1} suggesting the existence of the following equilibria in DMF solution (Scheme 1).

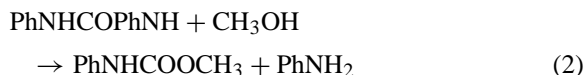
$[RhA(CO)PhNO_2]$ is believed to be the catalytically active species formed under the given set of conditions though all attempts to isolate it in the pure state were unsuccessful.

With regard to the formation of aniline as the by-product during reductive carbonylation of nitrobenzene in presence of methanol to carbamate (run 1, Table 3), the influence of $PhNO_2$ to $PhNH_2$ molar ratio in the reductive carbonylation process was also the subject of study. It is clear from the result that though the molar ratio ($PhNO_2:PhNH_2$) decreased, the percentage conversion to DPU and MPC remains unaltered. When no aniline was added to the system, conversion of $PhNO_2$ to DPU and formation of $PhNH_2$ ($\sim 15\%$) suggests the role of methanol as hydrogen provider (the system was degassed to free it from air and moisture). With $PhNH_2$ as substrate, the product distribution changed substantially with the highest recorded yield of DPU (70%). Presence of moisture in the system greatly hinders the catalytic conversion to DPU and almost 90% aniline was recorded. High aniline formation may be due to hydrolysis of any DPU formed (reaction (1)):



Scheme 1.

High alcohol content in the system greatly reduced the extent of DPU formation with simultaneous rise in the percentage of MPC and PhNIH₂. Reactions (2) and (3) seem to be the most probable reason for low conversion to DPU:



Formation of NPF in the system (detected in all the six runs: Table 3) is believed to be due to direct interaction of CO and PhNH₂.

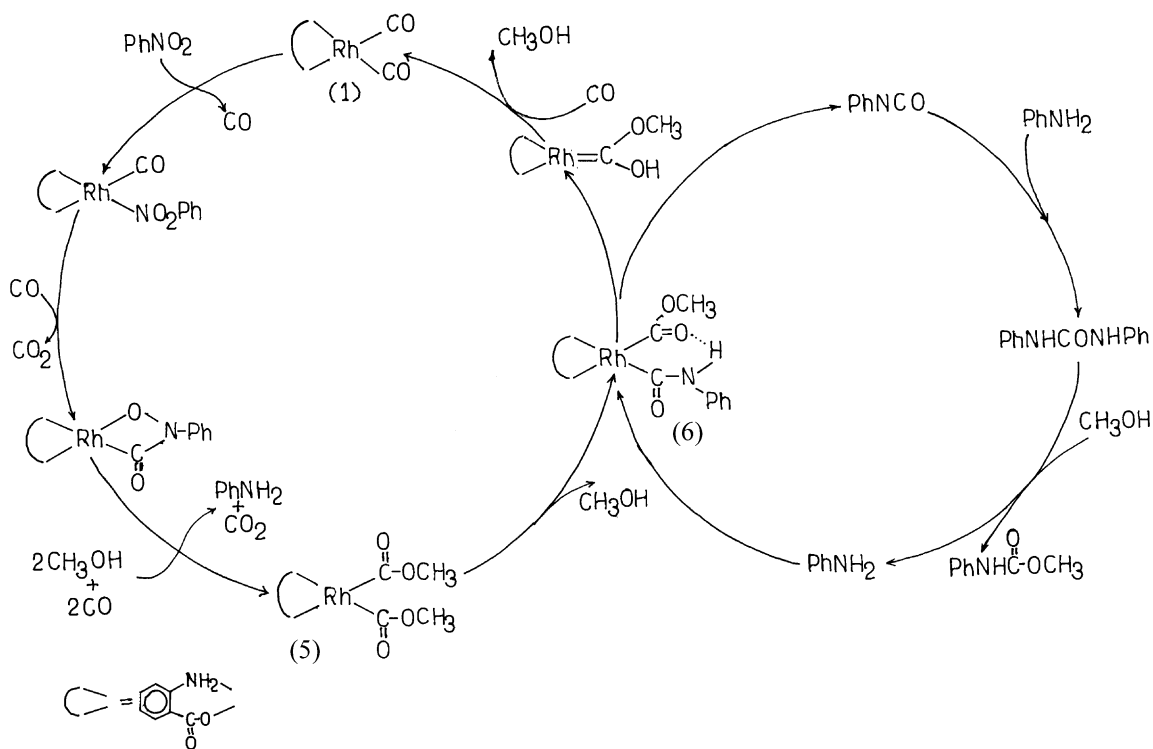


Increase in aniline concentration however results in no significant change in NPF formation (runs 3–6).

Monitoring the IR and ¹H NMR spectra of the solutions during catalytic run did not show the formation of intermediate metal hydride species. Carbonylation

of nitrobenzene was conducted in DMF containing either 1-hexene or phenylacetylene under optimum reaction conditions. The alkene and the alkyne remained unchanged during the entire carbonylation process. Formation of metal hydride species has therefore been ruled out as its formation should reduce alkene or alkyne to the corresponding saturated products.

Several authors restored to nitrene mechanism in rationalizing the products such as isocyanates, carbamates, urea, etc. formed during reductive carbonylation of nitrobenzene [35–37]. Attempts were therefore made to trap any phenyl nitrene if formed at the intermediate stage using diphenylacetylene in the reaction medium. The phenylnitrene derivatives could not be detected under the optimum reaction conditions using both the soluble and the polymer-supported complex. Spectroscopic studies however showed that the reaction proceeds through a species [RhA(C(O)OCH₃)₂] and the isocyanate formed at an intermediate stage is immediately scavenged by excess amine to



Scheme 2.

N,N'-diphenylurea. The complex **5** was isolated (refer Section 2) and the isolated complex was subjected to carbonylation reaction under identical reaction conditions as maintained for the starting catalyst **1**. GC analysis showed >50% DPU formation within 1 h of catalytic run. Several runs were conducted in DMF using PhNO as substrate and the similar product distribution suggests that PhNO₂ was deoxygenated to PhNO at some earlier stage of the catalytic cycle (Scheme 2).

¹H NMR spectra of a CH₃OH/C₆D₆ solution of **5** and *p*-toluidine were monitored for a period of 24 h. After 12 h, the spectrum collected revealed resonances from **5**, CH₃OH, *p*-toluidine and three new signals. There was a singlet at 10.72 ppm, similar in chemical shift to the hydrogen bonded amide proton [38], a singlet at 2.55 ppm, characteristic of a methoxy carbonyl proton [27], and a singlet at 2.04 ppm, a shift similar to methyl resonance from the *p*-tolyl moiety. The integration of these three signals was 1:3:3, respectively. ¹H NMR signals are masked at higher concentration of aromatic amine and methanol. The result describes the formation of the methoxy carbonyl–carbamoyl species **6** in the reaction medium and all attempts were made to isolate the solid sample but without success. During the experiments described above, the concentration of **6** increased to a constant ratio with **5** suggesting that an equilibrium was achieved. The reaction quotient [6]/[5] decreased in a linear fashion as CH₃OH concentration was increased from 1.0 to 8.0 M at constant concentration of *p*-toluidine. Formation of the intermediate species **6** by the reaction of *p*-toluidine with **5** and simultaneous liberation of one equivalent of methyl alcohol as predicted in the catalytic cycle has therefore been established (Scheme 2).

An effort was also made to identify the reaction pathway by treating a solution of *p*-toluidine and methanol in a septum sealed vial with *p*-tolylisocyanate. Visible amounts of *N,N'*-ditolylurea were noticed within 5 min at ambient temperature. After 30 min the solution in the vial was analyzed using gas chromatography. The belief that the isocyanate formed at an intermediate stage is immediately taken up by the amine resulting in the formation of urea is therefore substantial and no trace of carbamate could be detected at any stage of the reaction [39]. Reaction (3) leading to the formation of carbamate seemed unlikely due to lower basicity of CH₃OH than PhNH₂.

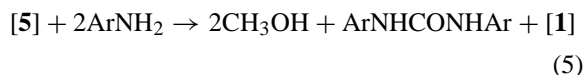
Table 4

Rate constant for the reaction of [RhA(C(O)OCH₃)₂] with *p*-toluidine

Temperature (°C)	[ArNH ₂] (M)	[Rh] (mM)	<i>k</i> (M ⁻¹ min ⁻¹)
80	0.20	30.2	0.24
80	0.44	30.2	0.21
80	0.56	30.2	0.23
80	0.15	30.2	0.23
80	0.15	14.4	0.20
80	0.15	44.2	0.21

3.1. Kinetic analysis of the reaction of [RhA(C(O)OCH₃)₂] with *p*-toluidine at 80 °C

These reactions were carried out in high pressure cell designed for spectroscopic studies under high gas pressure [40] in order to simulate the conditions of the actual catalytic process. Various volumes of the isolated complex **5** and *p*-toluidine in toluene-*d*₈ and CD₃OD were taken in a 5 mm NMR tube to give a total volume of 0.5 ml. The initial concentrations of **5** and *p*-toluidine in these solutions are listed in Table 4. The valve of the high pressure tube was connected to the pressure line and the cell was pressurized with carbon monoxide (60 atm). The solution in the cell was shaken to insure that a reasonable amount of CO dissolved in solution. The pressure was released and the tube was placed in an NMR spectrometer with the probe warmed to the desired temperature. The organic product observed from the reaction of **5** and *p*-toluidine under all conditions was *N,N'*-di-*p*-tolylurea (Eq. (5)).



The rate was followed by the study of the 3.03 and 3.76 signals characteristic of CH₃ protons of C(O)OCH₃ group of **5** and the peak areas were evaluated with the integration for all species normalized to the initial concentration of **5**. The reaction was complete within 90 min at 80 °C and upon standing for an additional 24 h, crystals of *N,N'*-di-*p*-tolylurea were visible in the reaction tube and **1** was the major metal species present in the reaction solution. It was imperative that the kinetic reaction was strictly performed

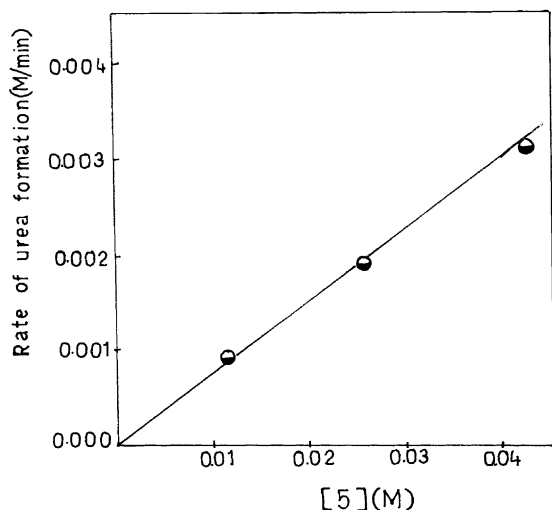
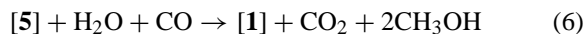


Fig. 4. Initial rate of urea formation from the reaction of **5** with *p*-toluidine at 80 °C. First order rate dependence is shown with respect to metal-complex concentration.

under dry conditions as smallest measurable concentration of water caused an erroneous result due to the hydrolysis of complex **5** with liberation of the starting catalyst **1**, CO₂, and two equivalents of CH₃OH (Eq. (6)):



The kinetics outlined in the paper was conducted in different temperature regimes. Although the final products were identical, the kinetic work in the low temperature region was complicated by the appearance of peaks corresponding to the intermediate **6**. The effects of the varying concentration of **5** and *p*-toluidine on the initial rate of urea formation are shown in Figs. 4 and 5, respectively. The observed rate constants shown in Table 4 were determined by the rate law:

$$\text{Rate} = k[\text{ArNH}_2][\text{RhA}(\text{C}(\text{O})\text{OCH}_3)_2]$$

Based on the above observations and identification of the reactive intermediates, the mechanism shown in Scheme 2 has been proposed for the carbonylation process using both the soluble and polymer-supported rhodium catalyst. The in situ spectroscopic studies of the high pressure catalysis established that the principal species observed in solution was [RhA(C(O)OCH₃)₂] and that several intermediate

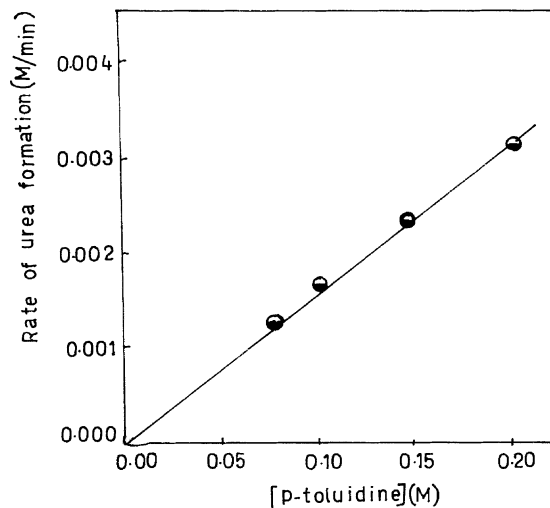


Fig. 5. A first order rate dependence is shown with respect to the concentration of *p*-toluidine from the reaction of **5** with *p*-toluidine at 80 °C and $P_{\text{CO}} = 60$ atm.

steps were involved in the conversion of nitrobenzene to useful diarylurea in presence of alcohol.

4. Conclusion

The reaction conducted under catalytic conditions produced either diarylurea or the carbamate depending upon the conditions. Even in those runs that produced carbamates, urea was still proposed to be the intermediate. Intramolecular elimination of aryl isocyanate is the mechanism which releases the organic product from the catalyst and in all of the stoichiometric reactions, the isocyanate is immediately trapped by ArNH₂ to form the observed product, diarylurea. A sample of the polymer-supported catalyst even after five catalytic runs behaved very much like the unused catalyst with no sign of metal decomposition or bead fragmentation.

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