



# Polystyrene anchored orthometalated ruthenium(II) complex as catalyst for the dihydrogen reduction of unsaturated organic substrates

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## Abstract

The catalytically active orthometalated complex  $[\text{Ru}(\text{phpy})(\text{CO})_2\text{C1}]_2$  (phpy = phenylpyridine) was anchored to macroporous polystyrene beads through the binding of phenylpyridine moiety to the polymer backbone. The catalytic activity of the resulting species towards the reduction of organic nitro compounds, alkenes, alkynes, nitriles, Schiff bases, ketones and aldehydes under high pressure, high temperature conditions in mild coordinating media was found to be comparable to that of its homogeneous analogue in product selectivity but superior in stability and reusability. A tentative reduction mechanism was proposed on the basis of kinetic studies and the isolation of reactive intermediates.

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**Keywords:** Dihydrogen reduction; Polymer-anchored; Orthometalated ruthenium(II) complex; Nitroorganics; Nitriles; Ketone

## 1. Introduction

Among the numerous homogeneous catalysts used for the reduction of unsaturated organic compounds [1–11], only few are stable enough to reduce nitro compounds, ketones and nitriles under high temperature, high pressure conditions [12–15].

Homogeneous catalysts, in general, have limited applications due to their high susceptibility to reaction conditions and the problems encountered in their separation from the product mixture. Low thermal and chemical stabilities leads to their slow decomposition under stringent reaction conditions. Their utilities may be increased by immobilizing them on a suitable polymer matrix, which in addition to having higher chemical and thermal stabilities may easily be separated from the product mixture. The steric crowding around the metal atom centre in the polymer matrix may increase the substrate specificity and product selectivity. All these qualities, in addition to easy separation, make the polymer-anchored catalysts more attractive than their homogeneous counterpart.

Among the immobilized complex catalysts used for reduction purpose, the complexes of iron(III) [16], palladium(II) [17,18], platinum(II) [19,20], rhodium(I) [21,22], ruthenium(III) [23–25] and nickel(II) [26,27] supported on various polymers are worth being mentioned.

The excellent catalytic activities of some orthometalated ruthenium(II) complexes towards the reduction of unsaturated organic compounds in mild coordinating media [28,29] prompted us to investigate the catalytic activity of polystyrene-bound orthometalated phenylpyridine complex of ruthenium(II) towards the reduction of nitro compounds, alkenes, nitriles and ketones and to elucidate the reaction mechanism.

## 2. Experimental

Analytical-grade reagents and freshly distilled solvents, pure and dry hydrogen gas and dry and predistilled solvents were used throughout the investigation. The liquid substrates were predistilled and dried by an appropriate molecular sieve, and the solid substrates were recrystallized before use. The chemical analysis was done by the usual procedure [30]. The purities of solvents and substrates were checked by gas chromatography (GC).

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Vibrational, electronic, XPS studies and thermal analysis were carried out with Perkin-Elmer 833, Shimadzu MPC-3100, VG-Scientific ESCA Labmark II and Shimadzu DT-40 instruments, respectively. GC analysis was made with Chrompack CP-9000 instrument using SE-30 and 15% FFAP capillary columns with appropriate temperature programming. The components in the product mixture were identified and estimated using authentic samples as standard.

Macroporous polystyrene beads, crosslinked with 2% divinylbenzene (Art. No. 22094–9) were supplied as hard, insoluble 20–25 mesh spheres of average pore diameter 800 Å by Aldrich, USA. Ruthenium(III) chloride trihydrate was purchased from Arora Matthey. Bromine, 2-aminopyridine and *n*-butyl lithium were purchased from Aldrich, USA, and were used as such without further purification.

### 2.1. Hydrogenation procedure

In a typical experiment, DMF suspension of the catalyst was taken in the glass-lined autoclave which was first evacuated, flushed with dry and pure hydrogen and then allowed to attain the temperature of the oil bath. The substrates in DMF solution was introduced in the autoclave, which was quickly subjected to the desired hydrogen pressure. The reaction mixture was magnetically stirred during the reaction period and the experimental parameter were suitably adjusted and kept constant during the run. At the end, the reactor was quenched in an ice/salt mixture, and the components in the product mixture were identified and estimated by GC using authentic samples as standard. They were also identified by IR and PMR spectra whenever possible.

### 2.2. Preparation of catalyst

The outline for the preparation of polystyrene (1) anchored orthometalated ruthenium(II) complex, P-[phpy(CO)<sub>2</sub>RuCl]<sub>2</sub> (P = polystyrene backbone and phpy = phenylpyri-

dine), is shown in Scheme 1. The catalyst was prepared by reaction of polymer-anchored phenylpyridine moieties with [Ru(CO)<sub>2</sub>Cl<sub>2</sub>(2-methoxyethanol)<sub>2</sub>].

The species *p*-bromopolystyrene (2), *para*-lithiated polystyrene (3) and polystyrene-anchored 2-phenylpyridine (4) required for the synthesis of the present catalyst, P-[(phpy)(CO)<sub>2</sub>Ru-Cl]<sub>2</sub> (5), were prepared according to the literature methods [32–34].

### 2.3. Preparation of polymer-anchored dinuclear orthometalated ruthenium(II) complex, P-[(phpy)(CO)<sub>2</sub>Ru-Cl]<sub>2</sub> (5)

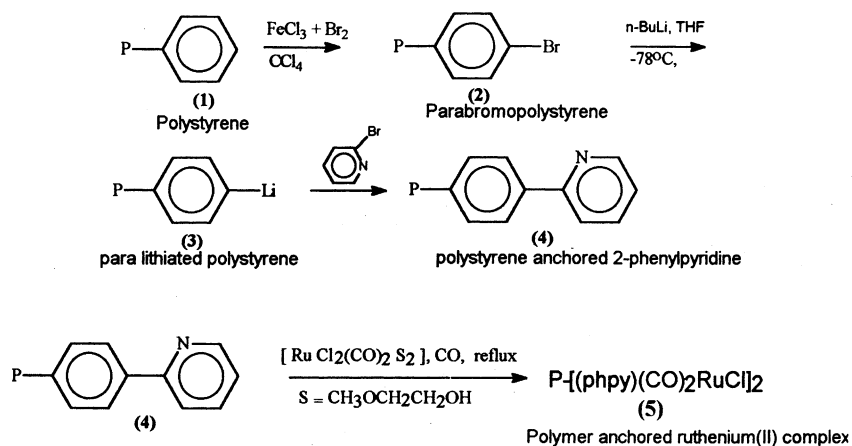
Carbon monoxide was bubbled for 6 h through a 2-methoxyethanol solution (20 ml) of RuCl<sub>3</sub>·3H<sub>2</sub>O (1.9 mmol) under reflux to produce the yellow solution of [Ru(CO)<sub>2</sub>Cl<sub>2</sub>S<sub>2</sub>] (S = 2-methoxyethanol) [31]. The anchored phenylpyridine (4) (2.0 g) was added to it and the yellow mixture was refluxed for 6 h when pale yellow catalyst (5) was formed. It was filtered, and washed first with ethanol and then with methanolic solution of NaOH (0.8%) to make it chloride-free. It was washed with 2-methoxyethanol, acetone and methanol in order and finally dried under high vacuum.

C (60.12%), H (5.26%), N (4.65%), Cl (6.51%), Ru (16.01%).

## 3. Results and discussion

### 3.1. Characterization of the complexes

The characterizations of insoluble functionalized polymers and their ruthenium(II) complexes were limited to chemical analysis, XPS, IR and electronic spectra, DTA and XRD. C, H and N analyses were made by semimicroanalytical procedure; halides were estimated by silver nitrate method and ruthenium was estimated according to the literature method [35].



Scheme 1.

The purities of the materials (1–4) were checked by chemical analyses, m.p. (wherever possible) and by IR spectra. The pale yellow polymer complex, P-[(phpy)(CO)<sub>2</sub>Ru-Cl]<sub>2</sub> (5), is diamagnetic and exhibits several IR peaks at 2050 cm<sup>-1</sup> (s), 1990 cm<sup>-1</sup> (sh), 1975 cm<sup>-1</sup> (sh), 1950 cm<sup>-1</sup> (s), 1885 cm<sup>-1</sup> (s), 1810 cm<sup>-1</sup> (s), 1740 cm<sup>-1</sup> (sh) and 1725 cm<sup>-1</sup> (s) in the carbonyl vibration region in addition to the bands at 1620 cm<sup>-1</sup> ( $\nu < \text{C}=\text{N}-$ ), 1440 cm<sup>-1</sup> ( $\nu < \text{C}=\text{C}>$ ), 720 cm<sup>-1</sup> (orthometalation) [36] and 260 cm<sup>-1</sup> (due to chloro-bridge). The appearance of several  $\nu$  CO bands indicates the presence of both linear and bridged CO groups in it [37]. The N-coordination of the phenylpyridine moiety to the metal was suggested from the high-frequency shifting of the  $\nu < \text{C}=\text{C}>$  band from 1420 to 1440 cm<sup>-1</sup> and  $\nu < \text{C}=\text{N}-$  band from 1600 to 1620 cm<sup>-1</sup> [38].

The diffuse reflectance spectra of [Ru(phpy)(CO)<sub>2</sub>Cl]<sub>2</sub> (456, 360 and 305 nm), and P-[Ru(phpy)(CO)<sub>2</sub>Cl]<sub>2</sub> (456, 342 and 306 nm) are very much comparable and suggest similar structures for both of them. XPS of the compounds were carried out in the range of 270–300 eV using Al K $\alpha$  as the target material. The data (compound 5:  $3d_{3/2} = 281.0$ ,  $3d_{5/2} = 276.8$  eV) confirms the presence of only Ru(II) and not Ru(0) in it.

Comparison of IR, DRS and XPS data of [Ru(phpy)(CO)<sub>2</sub>Cl]<sub>2</sub> and P-[Ru(phpy)(CO)<sub>2</sub>Cl]<sub>2</sub> suggests the latter to contain octahedral Ru(II) in it.

The species 5 is insoluble in all common solvents, thermally stable upto 200 °C and its XRD pattern suggests a noncrystalline nature. Chemical analysis suggests that nearly 60% of the ligand moieties form complexes with the metal. Rigid structure of the polymer matrix allows only suitably positioned phenylpyridine moieties to form chloro- or carbonyl-bridged complexes.

The metal in the polymer catalyst (5) does not leach out during catalytic run or when stirred with alcoholic or DMF solution of pyridine, bipyridine or PPh<sub>3</sub> for 12 h at room temperature. This suggests the strong bidentate characteristic of the polymer-bound phenylpyridine moieties.

#### 4. Reduction of substrates

The polystyrene-anchored complex (5) is effective for dihydrogen reduction of functional groups like -NO<sub>2</sub>,  $< \text{C}=\text{C}>$ ,  $< \text{C}=\text{O}>$ ,  $< \text{C}=\text{N}-$ ,  $-\text{C}\equiv\text{C}-$ ,  $-\text{C}\equiv\text{N}-$ , etc. only under relatively higher pressure and temperature.

DMF was the best reaction medium, followed by DMSO and ethylacetate. Higher reduction rates are observed in weak coordinating media while no reduction occurred in noncoordinating solvents. Reduction rate decreased in strong coordinating media as well as in presence of strong ligands like py, pic, dipy, PPh<sub>3</sub>, etc.

The substrates containing  $< \text{C}=\text{C}>$  and  $-\text{C}\equiv\text{C}-$  groups were rapidly and completely reduced at  $\sim 70$  °C under

30.0 bar of H<sub>2</sub> (Table 1). Based on the reduction rate, the substrates can be placed in the following order:

Styrene > isoprene > pent-1-ene > hex-1-ene  
> cyclohexene >  $\omega$ -nitrostyrene  
> maleic acid > fumaric acid.

Reduction of alk-1-enes yields only the corresponding alkanes and no isomerized products. The steric crowding around the metal atom in the polymer matrix probably restricts the 1-alkene coordination in a particular orientation, leading to the formation of alkanes only. Table 1 indicates easy reduction of alkenes with delocalized  $\pi$ -electron system compared to those having substitution or nondelocalized system. Probably both steric crowding of the substituted groups and the electronic effects are responsible for this difference. Nonsubstituted alkenes with delocalized  $\pi$ -electron system are expected to form stronger [metal-alkene] complex. Hence the concentration of the latter is increased at the intermediate stage.

The lowest reduction rates of maleic and fumaric acid may be due to their dissociation to produce H<sup>+</sup> and RCOO<sup>-</sup>. The former decreases the concentration of the active species [9] as per Eq. (1), while the latter coordinates with the metal and blocks the active sites in [9] (vide infra).

Among the Schiff bases, only benzylideneaniline and *N*-methylbenzaldiamine were reduced completely to the corresponding amines without any side products.  $< \text{C}=\text{N}-$  and  $< \text{C}=\text{C}>$  groups are reduced at comparable rates.

The present catalyst system is efficient for the reduction of various mono-nitroaromatics at 80 °C under a hydrogen pressure of 50 bar (Table 1). The final products in all cases were the corresponding anilines. They may be placed in the following order as per their reduction rates:

C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub> > *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub> > *p*-ClC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>  
> *o*-NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub> > *o*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>  
> 1-nitronaphthalene > *o*-ClC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>  
> *p*-NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub> > *p*-OHC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>.

Preferential reductions are possible in case of the mixture of nitrobenzene and *o*-chloronitrobenzene (Fig. 1). Both steric and electronic factors appear to be responsible for this preferential reduction. During the reduction of nitroaromatics, corresponding phenylhydroxylamines with very high reduction rates were detected at intermediate stages (Fig. 1). Partially reduced nitroaromatics or coupled products could not be detected at any stage of reduction. Attempts to selectively reduce nitrobenzene to corresponding phenylhydroxylamine by changing experimental parameters were unsuccessful.

Nitrobenzene and its *para*-substituted derivatives are reduced at the highest rate, followed by *meta*- and *ortho*-substituted ones in order. The steric factor probably dominates over the electronic factor to control the reduction rate. 4-Nitro-*o*-xylene was reduced at a very slow rate while the more sterically hindered 2-nitro-*m*-xylylene could not

Table 1  
Substrates and the corresponding products with catalyst P-[(phpy)(CO)<sub>2</sub> RuCl]<sub>2</sub>

Experiment no.	Substrate	Reaction time (h)	Initial turnover no. (min <sup>-1</sup> )	Product(s)	Yield (%)
1	Styrene <sup>a</sup>	6.0	6.38	Ethylbenzene	96
2	Isoprene <sup>a</sup>	6.5	5.73	2-Methylbutane	96
3	1-Pentene <sup>a</sup>	7.0	5.52	Pentane	92
4	1-Hexene <sup>a</sup>	7.4	5.29	Hexane	93
5	1-Heptene <sup>a</sup>	7.6	4.90	Heptane	91
6	Cyclohexene <sup>a</sup>	8.0	4.44	Cyclohexane	90
7	Maleic acid <sup>a</sup>	9.0	3.50	Succinic acid	88
8	Fumaric acid <sup>a</sup>	9.5	3.15	Succinic acid	86
9	Diphenylacetylene <sup>a</sup>	6.0	5.84	1,2-Diphenylethane	92
10	Phenylacetylene <sup>a</sup>	6.8	5.20	Ethylbenzene	90
11	<i>N</i> -Methylbenzaldimine	6.5	6.00	<i>N</i> -Methylbenzylamine	96
12	Benzylideneaniline <sup>a</sup>	6.0	6.35	<i>N</i> -Phenylbenzylamine	95
13	Nitrobenzene <sup>b</sup>	7.0	5.91	Aniline	92
14	<i>p</i> -Nitrotoluene <sup>b</sup>	7.4	4.78	<i>p</i> -Toluidine	90
15	<i>p</i> -Chloronitrobenzene <sup>b</sup>	7.8	4.53	<i>p</i> -Chloroaniline	91
16	<i>o</i> -Nitroaniline <sup>b</sup>	8.8	3.94	<i>o</i> -Phenylenediamine	88
17	<i>o</i> -Nitrotoluene <sup>b</sup>	9.2	3.62	<i>o</i> -Toluidine	90
18	1-Nitronaphthalene <sup>b</sup>	9.5	3.44	1-Aminonaphthalene	87
19	<i>o</i> -Chloronitrobenzene <sup>b</sup>	9.6	3.21	<i>o</i> -Chloroaniline	86
20	<i>p</i> -Nitroaniline <sup>b</sup>	9.8	2.85	<i>p</i> -Phenylenediamine	88
21	<i>p</i> -Nitrophenol <sup>b</sup>	9.9	2.85	<i>p</i> -Aminophenol	85
22	<i>p</i> -Dinitrobenzene <sup>c</sup>	8.5	3.25	<i>p</i> -Phenylenediamine	89
23	<i>m</i> -Dinitrobenzene <sup>c</sup>	9.0	2.95	<i>m</i> -Phenylenediamine	86
24	Nitromethane <sup>c</sup>	7.0	5.66	Methylamine	94
25	Nitroethane <sup>c</sup>	7.2	4.92	Ethylamine	90
26	1-Nitropropane <sup>c</sup>	7.5	4.61	1-Aminopropane	88
27	2-Nitropropane <sup>c</sup>	8.0	4.24	2-Aminopropane	89
28	Nitrocyclohexane <sup>c</sup>	9.0	3.58	Aminocyclohexane	86
29	Benzaldehyde <sup>d</sup>	6.0	5.26	Benzylalcohol	88
30	Benzophenone <sup>d</sup>	6.8	4.27	Diphenylmethanol	85
31	Acetophenone <sup>d</sup>	7.2	3.84	Phenylmethylmethanol	86
32	Benzoin <sup>d</sup>	7.9	3.65	Dihydrobenzoin	86
33	Benzil <sup>d</sup>	8.0	3.31	Dihydrobenzoin	84
34	Acetone <sup>d</sup>	8.0	2.92	2-Propanol	80
37	Benzonitrile <sup>e</sup>	9.5	2.90	Dibenzylamine	90
				Benzylamine	3
38	Acetonitrile <sup>e</sup>	9.5	2.80	Diethylamine	80
				Ethylamine	15

Reaction condition: [sub] = 0.5 M; [cat] = 2.0 × 10<sup>-4</sup> g atom lit<sup>-1</sup>; medium = DMF; total volume = 10 ml; yield refers to GC analysis.

<sup>a</sup> P<sub>H<sub>2</sub></sub> = 30.0 bar; T = 70 °C.

<sup>b</sup> P<sub>H<sub>2</sub></sub> = 50.0 bar; T = 80 °C.

<sup>c</sup> P<sub>H<sub>2</sub></sub> = 60.0 bar; T = 90 °C.

<sup>d</sup> P<sub>H<sub>2</sub></sub> = 70.0 bar; T = 105 °C.

<sup>e</sup> P<sub>H<sub>2</sub></sub> = 90.0 bar; T = 120 °C.

be reduced at all. The reduction rates of *p*-NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub> and *p*-OHC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub> are relatively low. Probably -NH<sub>2</sub> and -OH groups decreases the available sites for NO<sub>2</sub> coordination by partial blocking.

More stringent conditions were required for the reduction of dinitroaromatics to the corresponding diamines (Table 1). Corresponding mono- or dihydroxylamines could not be detected at any intermediate stage. Sequential hydrogenation also occurred in this case (Fig. 2).

The reductions of nitroalkanes were possible only at T ≈ 90 °C, P<sub>H<sub>2</sub></sub> = 60 bar (Table 1), and the order of their reduction rates are

Nitromethane > nitroethane > 1-nitropropane > 2-nitropropane > nitrocyclohexane.

Steric factor appears important in controlling the reduction rate. Both the increase of chain length and branching lower the reduction rate. Alkylhydroxylamines, which are very first reduced to the corresponding amines, are formed as intermediates (Fig. 3).

The carbonyl compounds are reduced to their corresponding alcohols (Table 1). On the basis of initial rates of reduction, they may be arranged as

Benzaldehyde > benzophenone > benzoin ~ benzil > acetophenone > acetone.

Benzaldehyde and benzophenone are reduced at the fastest rate probably due to their planarity and metal–substrate ring π-interaction. Nonplanar acetone without ring π-electrons is reduced at the slowest rate. The diketone compound,

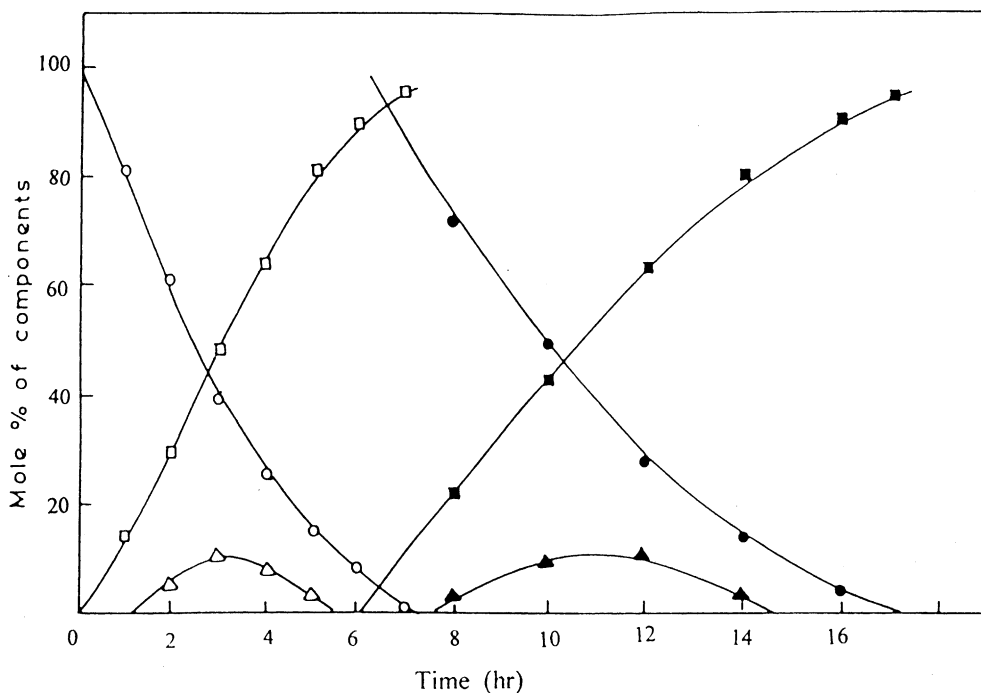


Fig. 1. Preferential hydrogenation of nitrobenzene in the presence of *o*-nitrotoluene with the catalyst P-[(phpy) Ru(CO)<sub>2</sub>Cl]<sub>2</sub>. [cat] =  $2.0 \times 10^{-3}$  g atom l<sup>-1</sup>;  $P_{H_2}$  = 50.0 bar; medium = DMF; total volume = 10 ml;  $T$  = 80 °C; [PhNO<sub>2</sub>] = 0.5 M; [*o*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>] = 0.5 M. (○) PhNO<sub>2</sub>; (□) PbNH<sub>2</sub>; (△) PhNHOH; (●) *o*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>; (◆) *o*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>; (△) *o*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>NHOH.

benzil, undergoes stepwise reduction, first to benzoin and then to dihydrobenzoin.

The nitriles were reduced mainly to the corresponding secondary amines under more severe reaction conditions, i.e.  $T$  = 120 °C,  $P_{H_2}$  = 90 bar. The final reduction products of CH<sub>3</sub>CN are ethylamine (~15%) and diethylamine

(~80%), while those for C<sub>6</sub>H<sub>5</sub>CN are (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)<sub>2</sub>NH (>90%) and C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>NH<sub>2</sub> (<3%). The formation of R<sub>2</sub>NH (R = C<sub>2</sub>H<sub>5</sub>/C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>) and liberation of NH<sub>3</sub> suggest the occurrence of some secondary reaction at intermediate stages. The nitriles, RCN (R = CH<sub>3</sub>, Ph), do not react with RCH<sub>2</sub>NH<sub>2</sub> in the presence of catalyst at 120 °C. The initial

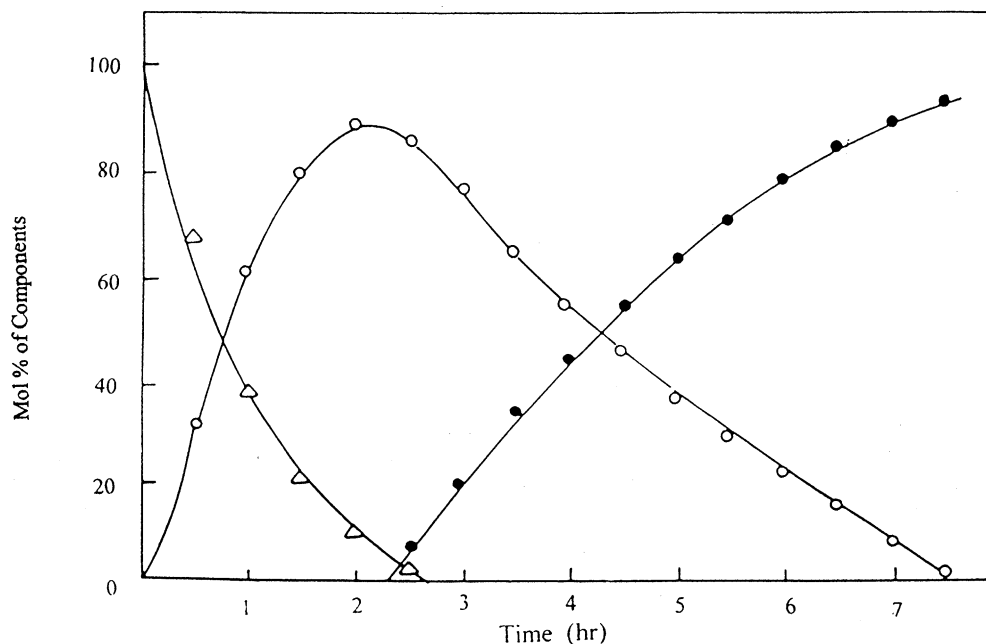


Fig. 2. Sequential reduction of *p*-dinitrobenzene with the catalyst P-[(phpy)Ru(CO)<sub>2</sub>Cl]<sub>2</sub>. [cat] =  $2.0 \times 10^{-3}$  g atom l<sup>-1</sup>;  $P_{H_2}$  = 90.0 bar; medium = DMF; total volume = 10 ml;  $T$  = 120 °C; [*p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>] = 0.5 M. (△) *p*-dinitrobenzene; (○) *p*-nitroaniline; (●) *p*-phenylenediamine.

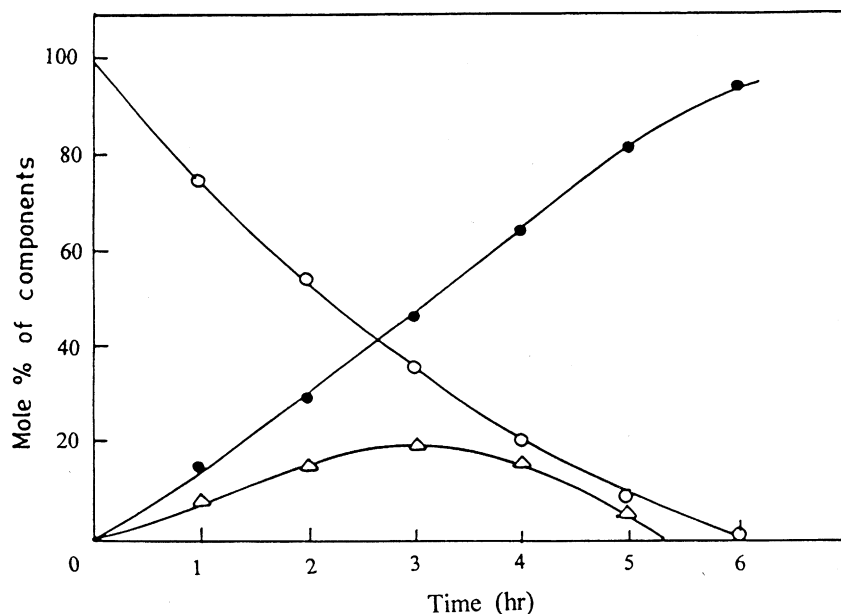


Fig. 3. Reduction of 2-nitropropane with the catalyst  $P-[(\text{phpy})\text{Ru}(\text{CO})_2\text{Cl}]_2$ .  $[\text{Cat}] = 2.0 \times 10^{-3}$  g atom  $\text{lit}^{-1}$   $\text{P}_{\text{H}_2} = 80.0$  bar;  $[2\text{-nitropropane}] = 0.5$  M, medium = DMF; total volume = 10 ml;  $T = 100^\circ\text{C}$ ; (○)=2-nitropropane, (△) = N-propylhydroxylamine, (●) = 2-aminopropane.

addition of  $\text{RCH}_2\text{NH}_2$  ( $\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$ ) during the reduction of RCN always increased the proportion of corresponding  $(\text{RCH}_2)_2\text{NH}$  in the product mixture. Ethylamine or benzylamine (in absence of corresponding nitriles) remained unchanged and do not dimerize to produce the corresponding secondary amines under catalytic hydrogenation condition.

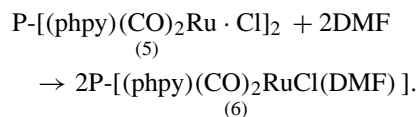
To understand the reaction mechanism, the reduction of  $\text{C}_6\text{H}_5\text{CN}$  was carried out in presence of acetic anhydride and sodium acetate so that  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$  if formed will be trapped as its acetylate and therefore not allowed to react with the probable intermediate,  $\text{C}_6\text{H}_5\text{CH} = \text{NH}$ , to yield  $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{NH}$ . The product mixture contained only the acetylate and no secondary amine. The result suggests the formation of intermediate imine, which reacts with the primary amine to produce secondary amine and ammonia. This is supported by the fact that reduction of  $\text{C}_6\text{H}_5\text{CN}$  in the presence of  $\text{C}_2\text{H}_5\text{NH}_2$  produced benzylamine (minor), *N*-ethylbenzylamine (major) and dibenzylamine (trace) and ammonia.

Higher susceptibility of  $\text{PhCH} = \text{NH}$  to nucleophilic attack by  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$  resulted in the absence of  $\text{PhCH}_2\text{NH}_2$  in the final product mixture of  $\text{PhCN}$  reduction. In case of  $\text{CH}_3\text{CN}$  reductions, lower susceptibility of  $\text{CH}_3\text{CH} = \text{NH}$  to nucleophilic attack by  $\text{C}_2\text{H}_5\text{NH}_2$  is responsible for the presence of small amounts of  $\text{CH}_3\text{CH}_2\text{NH}_2$  in the final product mixture.

#### 4.1. The following two complexes were isolated during catalytic run. $P-[(\text{phpy})\text{Ru}(\text{CO})_2\text{Cl} \cdot \text{DMF}]$ (6)

The suspension of the pale yellow polymer complex (5) (1.0 g), in deoxygenated DMF (20 ml), was stirred for 72 h under  $\text{N}_2$  at  $\sim 100^\circ\text{C}$  when it changed colour to light brown.

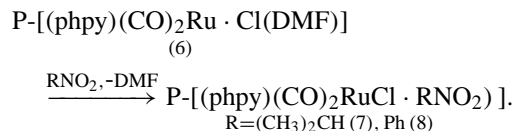
It was filtered and washed several times with dry acetone to make it DMF-free. The material 6 is suggested to be formed as



For 6: C, 55.62%; H, 4.32%; N, 6.05%; Cl, 6.58%; Ru, 18.72%.

#### 4.2. $P-[(\text{phpy})\text{Ru}(\text{CO})_2\text{Cl} \cdot \text{RNO}_2]$ , $\text{R} = (\text{CH}_3)_2\text{CH}$ (7), $\text{Ph}$ (8)

A mixture of the suspension of 6 (2.0 g) in dry deaerated alcohol (20 ml) and pure  $\text{RNO}_2$  [ $\text{R} = (\text{CH}_3)_2\text{CH}, \text{C}_6\text{H}_5$ ] (5 ml) was refluxed under  $\text{N}_2$  for 12 h, when the colour of the suspension slightly deepens. This was filtered, washed successively with methanol and chloroform and dried under vacuum.

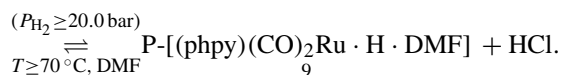
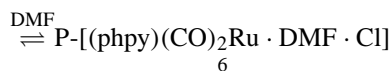
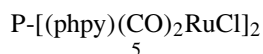


For 7: C, 55.32%; H, 3.85%; N, 6.19%; Cl, 6.72%; Ru, 19.14%.

For 8: C, 56.67%; H, 4.02%; N, 6.10%; Cl, 6.47%; Ru, 19.01%.

The deep brown polymer material (9) left after alkene reduction was different from 5. The filtered DMF solution exhibited lower pH, higher conductance values, liberated  $\text{CO}_2$  from  $\text{NaHCO}_3$  and contained  $\text{Cl}^-$ . The species

P-[(phpy)(CO)<sub>2</sub>RuCl·DMF] (**6**) turns deep brown at ~80 °C under  $P_{H_2} > 20$  bar in DMF suspension. The filtered DMF possesses similar characteristics. The deep brown material (**9**) probably formed as



Compound **9** could not be properly characterized due to its nonreproducible analytical data. Compound **6** exhibits strong IR peaks at 2040 and 1985  $cm^{-1}$  ( $\nu$  CO, terminal) [31] and a new peak at 1650  $cm^{-1}$  ( $\nu$  CO, coordinated DMF) [39] with simultaneous disappearance of 260  $cm^{-1}$  peak (chloro-bridge). Compound **7** shows peaks at 2055 and 1990  $cm^{-1}$  ( $\nu$  CO, terminal) and strong new peaks at 1540 and 1410  $cm^{-1}$  ( $\nu$  NO<sub>2</sub>) [40]. The brown material (**9**) exhibits a new peak at 1890  $cm^{-1}$  ( $\nu$  Ru–H) in addition to peaks due to  $\nu$  CO (t) and  $\nu$  CO (DMF). The peaks at 720  $cm^{-1}$  (orthometalation) is present in all of them. The

IR, DRS (compound **6**: 450, 345, 315 nm; compound **7**: 448, 342 and 304 nm) and XPS (compound **6**:  $3d_{3/2} = 280.2$ ,  $3d_{5/2} = 276.6$  eV; compound **7**:  $3d_{3/2} = 280.5$ ,  $3d_{5/2} = 276.6$  eV; compound **9**:  $3d_{3/2} = 280.6$ ,  $3d_{5/2} = 276.5$  eV) data indicate the presence of octahedral Ru(II) in all of them.

The catalyst is moderately stable in dry atmosphere, and can be recycled several times for the reduction of same or different substrates without loss of catalytic activity. The activity of the catalyst does not decrease on storing for a period of up to 1 year.

#### 4.3. Reaction kinetics and mechanism

The kinetics for the reduction of substrates were studied in DMF medium. All reaction parameters except the varied one were kept constant during any set of runs. The initial rate in each case was determined from graphical extrapolation of the rate curve to zero time.

In case of 2-nitropropane, the reductions were carried out at  $90 \pm 0.1$  °C keeping the substrate concentration fixed. The initial reduction rates of the substrate were plotted against varying metal content in the range of  $1.0$ – $10.0 \times 10^{-3}$  g atom  $l^{-1}$  at four different fixed hydrogen pressures,

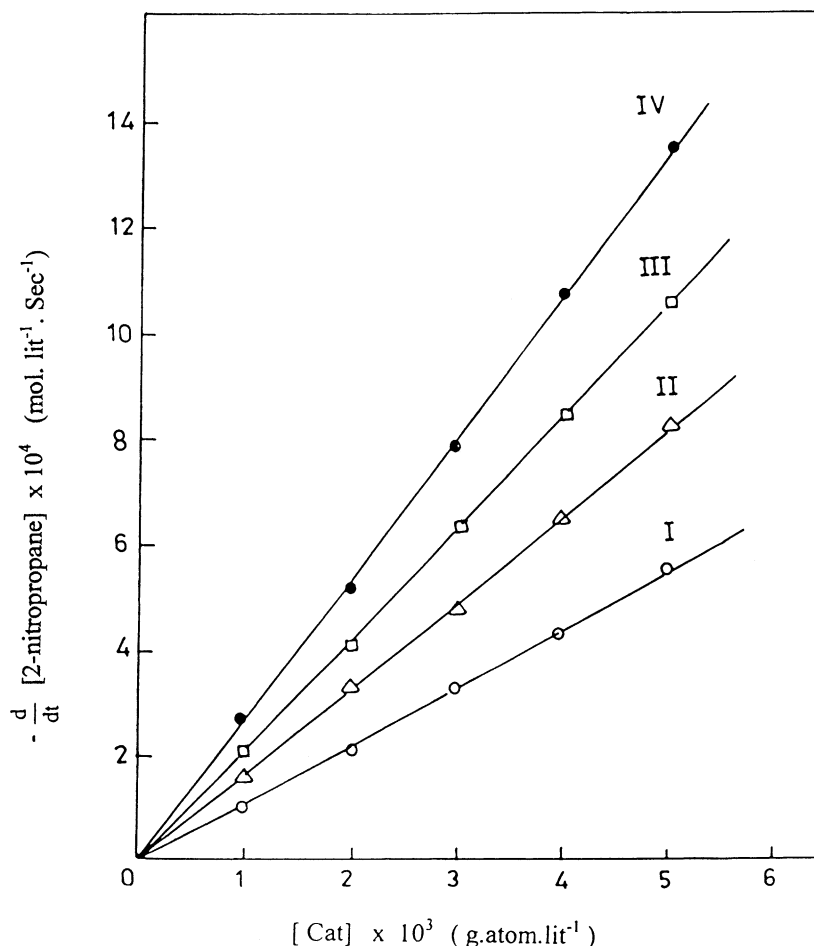


Fig. 4. Rate dependence on catalyst concentration for the reduction of 2-nitropropane with P-[(phpy) Ru(CO)<sub>2</sub>Cl]<sub>2</sub> as catalyst under various hydrogen pressure. [2-nitropropane] = 0.5 M; total volume = 10 ml;  $T = 80^\circ C$ ;  $P_{H_2}$ : (○) = 40.0 bar; (△) = 60.0 bar; (□) = 80.0 bar; (●) = 100.0 bar.

i.e. (i) 40.0 bar, (ii) 60.0 bar, (iii) 80 bar and (iv) 100.0 bar. The plot of initial rates versus (i) metal content of the catalyst at fixed  $P_{H_2}$  and (ii)  $P_{H_2}$  at constant catalyst concentration were linear in both cases, indicating the reaction to be first-order with respect to metal content of the catalyst and  $P_{H_2}$ .

The reaction kinetics of nitrobenzene reduction were studied at  $80 \pm 0.11^\circ\text{C}$  at fixed substrate concentrations. The initial reduction rates were plotted against (i)  $1.0 \times 10^{-3} \text{ g atom l}^{-1}$ , (ii)  $2.0 \times 10^{-3} \text{ g atom l}^{-1}$ , (iii)  $3.0 \times 10^{-3} \text{ g atom l}^{-1}$  and (iv)  $4.0 \times 10^{-3} \text{ g atom lit}^{-1}$  at different fixed  $P_{H_2}$  of (i) 40.0 bar, (ii) 60.0 bar, (iii) 80 bar and (iv) 100.0 bar. The rates were first-order-dependent on (i) metal content of catalyst per litre and (ii)  $P_{H_2}$ . The initial reduction rates of both nitrobenzene and 2-nitropropane, which were found to be independent of substrate concentration in the range of 0.5–3.0 M, may be expressed as:  $\text{Rate} = k_1[P_{H_2}][\text{cat}]$ .

The rates of reduction of 2-nitropropane with the catalyst concentration at various hydrogen pressures and with hydrogen pressure at different catalyst concentrations are plotted in Figs. 4 and 5, respectively. The rate constant  $k$  was calculated from the slope of the curves obtained by (i) plotting rate versus  $[\text{cat}]$  at different fixed hydrogen pressures (Fig. 4) and (ii) plotting rate versus  $P_{H_2}$  at different fixed catalyst concentrations (Fig. 5). The nearly constant values of  $k$  in these two cases support the above rate equation.

From Fig. 4,

$$\text{slope} = \frac{\text{rate}}{[\text{cat}]} \quad \text{and} \quad k = \frac{\text{slope}}{P_{H_2}}$$

The  $k$  values lie between  $1.96 \times 10^{-6}$  and  $2.09 \times 10^{-6} (\text{s bar})^{-1}$  in the range of hydrogen pressure of 40–100 bar and between  $1.93 \times 10^{-6}$  and  $2.10 \times 10^{-6} (\text{s bar})^{-1}$  in the concentration range from  $2.0 \times 10^{-3}$  to  $6.0 \times 10^{-3} \text{ g atom l}^{-1}$ .

From Fig. 5,

$$\text{slope} = \frac{\text{rate}}{P_{H_2}} \quad \text{and} \quad k = \frac{\text{slope}}{[\text{cat}]}$$

The following tentative mechanism was suggested on the basis of experimental facts. ( $K_1, K_2, K_3$  and  $K_4$  are equilibrium constants and  $k_1, k_2$  and  $k_3$  are rate constants.) According to the Scheme 2

$$\text{Rate} = k_1[10][H_2]$$

Let  $[\text{cat}]_T = \text{Total catalyst concentration}$ .

$$[\text{cat}]_T = [9] + [10] + [11] + [12] + [13]$$

$$[\text{cat}]_T = \frac{[10][\text{DMF}]}{K_1[\text{RNO}_2]} + [10] + \frac{k_1[10][H_2]}{k_2[H_2O] + k_2[H_2]} + \frac{K_3[10][\text{RNOH}]}{K_1[\text{RNO}_2]} + \frac{[10][\text{RNH}_2]}{K_1K_4[\text{RNO}_2]}$$

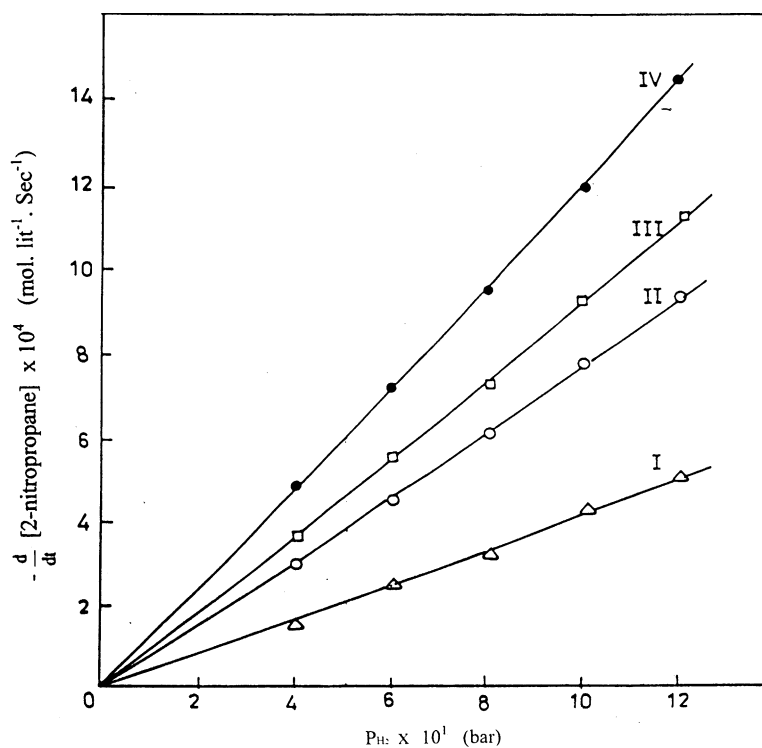
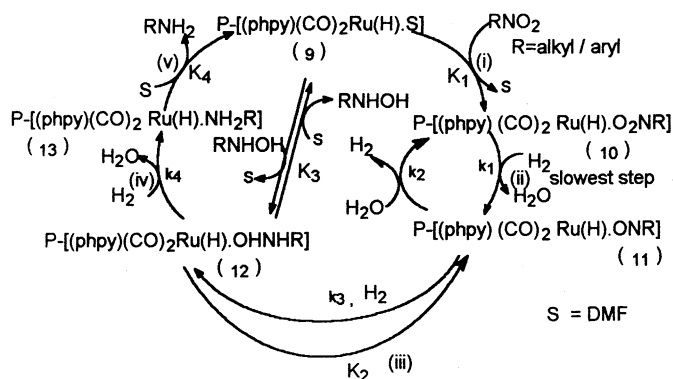
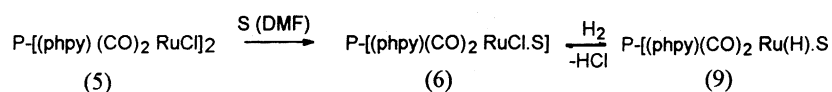


Fig. 5. Rate dependence on  $P_{H_2}$  for the reduction of 2-nitropropane under various catalyst concentrations with P-[(phpy) Ru(CO)<sub>2</sub>Cl]<sub>2</sub> as catalyst. [2-nitropropane] = 0.5 M; medium = DMF;  $T = 105^\circ\text{C}$ , [Cat]: (O) =  $2.0 \times 10^{-3} \text{ g atom lit}^{-1}$ ; ( $\Delta$ ) =  $4.0 \times 10^{-3} \text{ g atom lit}^{-1}$ ; ( $\square$ ) =  $5.0 \times 10^{-3} \text{ g atom lit}^{-1}$ ; ( $\bullet$ ) =  $6.0 \times 10^{-3} \text{ g atom lit}^{-1}$ .





Scheme 2.

At the initial stage,



and the equation becomes

$$\begin{aligned} [\text{cat}]_T &= \frac{[10][\text{DMF}]}{K_1[\text{RNO}_2]} + [10] + \frac{k_1[10]}{k_2} \\ &= \frac{[10](\text{DMF} + (1 + k')K_1[\text{RNO}_2])}{K_1[\text{RNO}_2]}; \end{aligned}$$

where  $\frac{k_1}{k_2} = k'$ ,

$$\text{or } [10] = \frac{K_1[\text{cat}]_T[\text{RNO}_2]}{[\text{DMF}] + (1 + k')K_1[\text{RNO}_2]}.$$

Therefore,

$$\text{rate} = \frac{k_1 K_1 [\text{cat}]_T [\text{RNO}_2] [\text{H}_2]}{[\text{DMF}] + (1 + k')k_1 [\text{RNO}_2]} = \frac{k_5 [\text{cat}]_T [\text{RNO}_2] [\text{H}_2]}{K_6 + k_7 [\text{RNO}_2]},$$

where  $k_1 K_1 = k_5$ ,  $[\text{DMF}] = K_6$ ,  $1 + k' = k_7$

If  $K_6 \ll k_7 [\text{RNO}_2]$ ,

$$\text{rate} = \frac{k_5 [\text{cat}]_T [\text{RNO}_2] [\text{H}_2]}{k_7 [\text{RNO}_2]} = k_8 [\text{cat}]_T [\text{H}_2], \quad k_8 = \frac{k_5}{k_7}.$$

## 5. Conclusion

The polystyrene-anchored catalyst is comparable to its homogeneous counterpart in activity and product selectivity. The advantages are that it can withstand more stringent reaction conditions and can be easily separated and recycled. The recycled one can be stored under  $\text{N}_2$  without appreciable loss of catalytic activity.

The species 5–9 have comparable catalytic activities, but the first four (5–8) require induction period ranging from 10 to 15 min, but the hydride (9) starts reduction of substrates

immediately. Hence the species 9 appears to be involved in the catalytic cycle.

The magnitude of the value of rate constant  $k_1$  indicates high activity of the catalyst and its constancy over a range of  $P_{\text{H}_2}$  and catalyst concentration confirms the rate equation.

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