



ELSEVIER

Journal of Molecular Catalysis A: Chemical 124 (1997) 5–20

JOURNAL OF
MOLECULAR
CATALYSIS
A: CHEMICAL

Use of polystyrene bound orthometalated Schiff base complexes of palladium (II) as catalysts for the dihydrogen reduction of nitroalkanes, nitriles and ketones

S.M. Islam, B.K. Palit, D.K. Mukherjee, C.R. Saha *

Department of Chemistry, Indian Institute of Technology, Kharagpur 721302 W.B., India

Received 16 September 1996; accepted 10 March 1997

Abstract

Dihydrogen reduction of nitroalkanes, aliphatic and aromatic nitriles and ketones to their corresponding saturated products was successively achieved in DMF medium using polystyrene based acetato-bridged orthometalated Schiff base complexes of palladium (II) as catalysts, at 80–130°C and $6.0\text{--}14.0 \times 10^3$ (kN m⁻²) of P_{H₂}. The acetato-bridged Schiff base complexes are the catalyst precursors and the actual catalysts are the corresponding hydrogen activated orthometalated complexes with the acetate bridge replaced by H and DMF. The immobilization of the palladium (II) complexes in the polymer matrix slightly decreased their catalytic activities on the basis of metal content but improved the chemical and thermal stabilities and product selectivities relative to those of the corresponding homogeneous ones. The same specimen of the catalyst can be used repeatedly for the reduction of different substrates and stored for a long time without suffering any appreciable loss of activity. XPS data suggest the presence of palladium (II) in the fresh and used catalyst and kinetic studies indicate 1st order rate dependence on palladium (II) content, second order on P_{H₂} and independent of substrate concentration. A plausible mechanistic route has been suggested on the basis of kinetic data and experimental observations. © 1997 Elsevier Science B.V.

Keywords: Reduction; Polymer based; Orthometalated; Schiff base; Nitroalkanes; Nitriles; Ketones

1. Introduction

Among the numerous homogeneous catalysts used for the reduction of various unsaturated organic compounds [1–11], only few are stable enough to reduce nitro-compounds, ketones and nitriles under high temperature and high pressure conditions [12–15]. In most cases, catalysts undergo slow decomposition under stringent reaction conditions and the catalyst isolation from the product mixture poses serious problems. Immobilization of these complex catalysts on a suitable organic or inorganic polymer matrix increases their potentialities for industrial use due to their enhanced thermal and chemical stabilities and ease of isolation from the product mixture. The steric crowding around the

* Corresponding author. Tel.: +91-3222-55221; fax: +91-3222-55303.

metal-atom centre in the polymer matrix is mainly responsible for the increased product selectivity. Among the immobilized complex catalysts used for the successful reduction of substrates under drastic reaction conditions, 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] complexes supported on various polymers are worth being mentioned.

The excellent catalytic activities of some orthometalated palladium (II) complexes towards the reduction of organic nitrocompounds, alkenes, alkynes, aldehydes, ketones and Schiff bases in mild coordinating media [28,29] prompted us to extend our catalytic investigations with orthometalated complexes anchored to suitable polymers and to study the effect of the anchoring on their catalytic activities.

The objective of the present work is to investigate the catalytic activities of orthopalladated complexes with Schiff base ligands anchored to macroporous polystyrene beads towards the reduction of nitro compounds, nitriles and ketones under high pressure, high temperature conditions and to elucidate the reaction mechanisms by various physico-chemical means.

2. Experimental

Analytical grade chemicals and pure and dry hydrogen gas were used throughout the investigation. The solvents and liquid substrates were predistilled and dried by appropriate molecular sieve and the solid substrates were recrystallized before use. The metal and halogen were estimated by the usual procedures while C, H and N were analysed by semi-micro analytical methods. Dimethylformamide and the substrates were purified by the usual procedures [30] and the substrates were analysed by gas chromatographic analysis to determine the presence of any impurity in them.

Vibrational spectra, XPS study and thermal analysis were carried with Perkin Elmer 883, VG-Scientific ESCA Lab mark II and Shimadzu DT-40 instruments, respectively.

Gas chromatographic analysis was performed with a Chromopack CP-9000 with a FFAP capillary column using an appropriate temperature programming. The components in the product mixture were identified and estimated using authentic samples as standard.

Macroporous polystyrene beads crosslinked with 5% DVB (Art No. 22094-9) was supplied as hard insoluble 20–50 mesh spheres of average pore diameter 800 Å by Aldrich Chemical Co, USA.

2.1. Preparation of *p*-amino polystyrene

The material was prepared by following the method of King and Sweet [31]. The suspension of macroporous polystyrene beads (5 g) in a mixture of acetic anhydride (20 ml), nitric acid (~ 70%, 2 ml) and glacial acetic acid (4 ml) was constantly stirred for 30 min at 5°C and 5 h at 50°C. The corresponding *p*-nitro polystyrene thus obtained was washed successively with acetic acid, tetrahydrofuran, water and methanol and finally dried under vacuum.

A mixture containing acetic acid (20 ml), stannous chloride (5 g), concentrated hydrochloric acid (6 ml) and the suspension of *p*-nitropolystyrene (5 g) was stirred for 72 h at room temperature to reduce the nitro-compound to the corresponding aminehydrochloride. The residue after filtration was washed several times with a mixture of hydrochloric acid (12 M) and glacial acetic acid (1:4) and then successively with tetrahydrofuran and methanol. The product on repeated treatment with dilute alcoholic NaOH (5%) produces the corresponding free amine. This was washed with alcohol and dried under vacuum.

2.2. Preparation of the Schiff base ligands $P-(p-C_6H_4N=CRPh)$ and their corresponding palladium (II) complexes (A)

A suspension of *p*-aminopolystyrene (3 g) in dry toluene (30 ml) containing excess of the respective carbonyl compound, C_6H_5COR ($R = H, CH_3, C_6H_5$) was refluxed for 72 h under dry nitrogen using Dean–Stark apparatus [32,33]. A longer reflux period was needed for the preparation of *C*-substituted Schiff base ligands. The preparation of polymer based benzophenonanil using appropriate reagents required the presence of $POCl_3$ in the medium [34]. The polymer ligand was filtered, washed with benzene, tetrahydrofuran and ethanol in succession and then dried under vacuum.

The orthometalated complex of palladium(II) with polymer-Schiff base ligand was prepared following the method of Onoue et al. [35]. A suspension of the respective dried polymer Schiff base ligand (1.0 g) in acetic acid solution (15 ml) of palladium(II) acetate (0.75 g) was refluxed for 8 h when the yellow polymer slowly changed to deep brown and no further colour change occurred on further reflux. The resulting polymer complex (A) was filtered, washed with tetrahydrofuran and methanol in succession and dried under vacuum.

2.3. Preparation of the yellow brown activated complex (C)

The suspension of the respective polymer based deep brown palladium (II) complex (1 g) in deoxygenated DMF (20 ml) changed completely to yellow brown on continuous stirring at 80°C under normal pressure of pure and dry hydrogen for 1 h. It was filtered and washed thoroughly with dry acetone and finally dried under high vacuum. The G.C. analysis of the filtrate indicates the presence of acetic acid in it.

2.4. Preparation of polystyrene based secondary amine ligand $P-(p-C_6H_4NHCH_2Ph)$ and the corresponding palladium (II) complex (B)

The polymer secondary amine ligand was prepared from the corresponding Schiff base ($R = H$) by (i) the reduction of the polymer-Schiff base in an autoclave using $H_2 + CO$ (1:1; $10.0 \times 10^3 \text{ kN m}^{-2}$) in a toluene suspension at 95°C using $Co_2(CO)_8$ as a catalyst [36], (ii) normal pressure hydrogenation of the corresponding Schiff base in the presence of $Pd_2(Bnpy)_2(OAc)_2$ ($Bnpy = \text{Benzoylpyridine}$) in DMF at ambient temperature [37], (iii) the reaction of polymer amine with benzylchloride (1:1) in DMF medium [38]. Almost complete reduction of the Schiff base occurred in the former case compared to $\sim 50\%$ reduction in the second case as evidenced by IR spectral data and the amount of H_2 absorbed.

The yellow suspension of the secondary amine (1.0 g) in glacial acetic acid solution (15 ml) of palladium (II) acetate (0.75 g) was refluxed for 8 h when the colour changed slowly and completely to brown. The brown palladium (II) complex (B) was washed first with acetic acid and then with dry ethanol and finally dried under high vacuum.

2.5. Preparation of the yellow-brown activated complex (C')

An activated species of palladium (II) secondary amine complex was prepared from the corresponding secondary amine complex (B) by following the identical procedure as that used for the preparation of (C) from (A). The deep brown complex (B) changed to yellow brown during

hydrogenation and the activated yellow brown species (C') was isolated and dried as usual. The presence of acetic acid in the filtrate was confirmed by G.C. analysis.

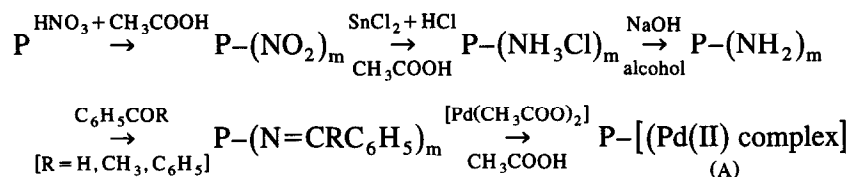
2.6. Hydrogenation procedure

Under high pressure and high temperature conditions, the catalytic activities of the activated species (C) and (C') are comparable in respect of the nature and yields of products, but the former is generally used in all catalytic investigations due to its easier method of preparation and higher efficiency. The species (A) or (B), though they produced identical products with comparable yields, required an induction period of nearly 40–45 min under the present experimental conditions. The induction period was, however, eliminated using (C) or (C'). In a typical experiment, DMF suspension of the activated catalyst (C) was introduced into the glass lined stainless steel autoclave equipped with a magnetic element. The reactor was first evacuated, flushed thrice with pure nitrogen and twice with pure and dry hydrogen and then immersed in the thermostated silicon oil bath preheated to experimental temperature. The substrate solution in deoxygenated DMF was introduced in the reactor and the hydrogen pressure was quickly raised to the desired value. The whole system was then placed on a magnetic stirrer and the reaction mixture was constantly stirred during the reaction period. The experimental temperature and pressure were kept constant during the run by suitable adjustment. The extent of reduction occurring during the attainment of desired pressure was found negligible. At the end, the mixture was quenched and the components in the product mixture were estimated by G.C.

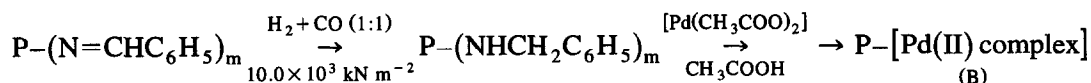
3. Results and discussion

3.1. Characterization of polymer complexes

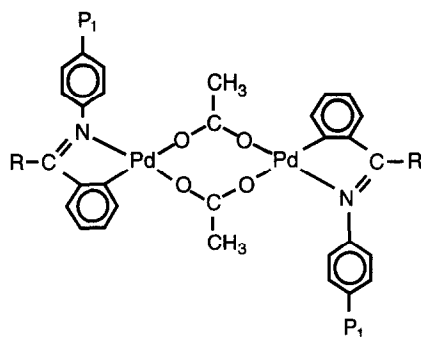
The orthometalated complexes of palladium (II) with the polymeric Schiff base ligands were prepared as follows (see also Scheme 1):



The polymer based orthometalated secondary amine complexes of palladium (II) was prepared as follows (see also Scheme 2):



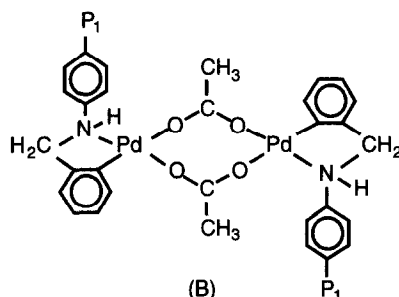
Due to insolubilities of the functionalised polymers and their palladium (II) complexes in different solvents, their structural investigations were limited to their physico-chemical properties, chemical analysis (Table 1) XPS (Table 3) and IR spectral data (Table 2) only. The polymer P exhibits IR peaks in the region $3100\text{--}2800 \text{ cm}^{-1}$ ($\nu\text{C-H}$), ~ 1600 , ~ 1500 and $\sim 1460 \text{ cm}^{-1}$ (skeletal



(A)

P = polystyrene framework,
 P - (NO₂)_m = P₁ (-C₆H₄-NO₂)_m

Scheme 1.



(B)

P-[Pd(II) complex
 (B)

Scheme 2.

vibration) and 760 and 680 cm⁻¹ (aromatic C–H bending). The chemical analysis of P–NO₂ suggest 56% nitration of the polystyrene ring which is supported by the appearance of two new medium intensity peaks at 1520 and 1340 cm⁻¹ (νNO₂). Another new peak at 835 cm⁻¹ suggest para-nitra-

Table 1
 Analytical data of the functionalized polymer and the Pd(II) complexes, P = polystyrene

Compound	Colour	Cl%	C%	H%	N%	Metal%
(1) P-	white		92.50	7.60		
(2) P–NO ₂	light yellow		74.10	5.69	6.01	
(3) P–NH ₃ Cl	yellow	13.25	72.01	6.72	5.81	
(4) P–NH ₂	pale yellow		84.12	7.34	6.72	
(5) P–N=CHC ₆ H ₅	brownish yellow		87.09	6.60	5.01	
(6) P–(N:C(CH ₃)C ₆ H ₅)	brownish yellow		85.98	6.80	4.90	
(7) P–N:C(C ₆ H ₅)C ₆ H ₅	yellowish brown		85.11	6.12	4.13	
(8) P–[NHCH ₂]C ₆ H ₅	yellowish brown		86.14	7.01	4.91	
(9) P–[(N:CH(C ₆ H ₄))Pd(OAc)] ₂	deep brown		71.12	5.02	4.00	12.25
(10) P–[(N:C(CH ₃)C ₆ H ₄)Pd(OAc)] ₂	deep brown		74.46	5.88	4.10	11.00
(11) P–[(N:C(C ₆ H ₅)C ₆ H ₄)Pd(OAc)] ₂	deep brown		74.35	5.63	3.61	9.92
(12) P–[(NHCH ₂)C ₆ H ₄)Pd(OAc)] ₂	deep brown		78.66	6.43	4.45	6.12

Table 2

IR Spectral data of the compounds, P = polystyrene (data in cm^{-1})

Compounds	δNH_2	$\nu\text{NH}_3\text{Cl}$	νNO_2	$\nu\text{C}=\text{N}$	$\nu\text{C}-\text{N}$	νCOO	$\nu\text{Pd}-\text{H}$	Orthometalation	$\nu\text{C}=\text{O}$	Cord. (DMF)
(1) P- NO_2			1520(s) 1350(s)							
(2) P- NH_3Cl		2500	1520(s) 1350(m)							
(3) P- NH_2	1625(sh)		1520(w) 1350(m)							
(4) P-N:CHC $_6\text{H}_5$			1520(w) 1640 1340(w)							
(5) P-NHCH $_2\text{C}_6\text{H}_5$			1520(w) 1340(w)	1265						
(6) P-N:C(C $_6\text{H}_5$) $_2\text{C}_6\text{H}_5$	1628(sh,w)		1520(w) 1635 1340(m)							
(7) P-[(N:CH(C $_6\text{H}_4$))Pd(OAc)] $_2$ (A)			1520(w) 1615 1340(w) 1640	1585 1420			722			
(8) P-[(HNCH $_2\text{C}_6\text{H}_4$)Pd(H)(DMF)] (C)			1520(w) 1640 1340(w)	1263		1978	722		1655	
(9) P-[(NHCH $_2\text{C}_6\text{H}_4$)Pd(OAc)] $_2$ (B)			1525(w) 1340(w)	1268	1580 1425		720			
(10) P-[(NHCH $_2\text{C}_6\text{H}_4$)Pd(H)(DMF)] (C')			1525(w) 1340(w)	1262		1980	722		1653	

tion [31]. The polymer P- NO_2 is reduced to the corresponding P- NH_3Cl by the ($\text{SnCl}_2 + \text{HCl}$) procedure which is, however, found to be superior to the ($\text{Sn} + \text{HCl}$) procedure in the present case [31]. The estimation of chloride and nitrogen in P- NH_3Cl suggest approximately 90% reduction of P- NO_2 which is also supported by the reduced intensity of νNO_2 peaks and the appearance of a new peak at 2550 cm^{-1} due to NH_3Cl [31]. The base P- NH_2 obtained by washing P- NH_3Cl thrice with 5% alcoholic NaOH was completely chloride free and exhibits strong multiple bands in the region $3400\text{--}3200\text{ cm}^{-1}$ (νNH_2) with simultaneous disappearance of a peak at 2550 cm^{-1} . The peak at $\sim 1600\text{ cm}^{-1}$ present in all the above compounds is enhanced in this case, with a shoulder at $\sim 1625\text{ cm}^{-1}$ (δNH_2). The chemical analysis suggest that nearly 80–90% of the P- NH_2 groups react with the carbonyl compound, PhCOR to produce the corresponding Schiff base ligand, the extent of Schiff base formation varies with the nature of R in the order $\text{H} > \text{CH}_3 > \text{C}_6\text{H}_5$. This is revealed by the appearance of a $\nu(\text{C}=\text{N})$ peak at 1640 cm^{-1} and reduced intensity of the νNH_2 peak in their spectra. The deep brown P-palladium (II) complexes (A) decompose in the range of $240\text{--}270^\circ\text{C}$ (Table 3) with the consequent loss of their catalytic activities. The ($\nu\text{C}=\text{N}$) peak splits up in the case of all

Table 3

XPS data of the Pd(II) complexes P = polystyrene

Compound	Pd	
	$3d_{3/2}$	$3d_{5/2}$
P-[(N:CHC $_6\text{H}_4$)Pd(OAc)] $_2$ (d.t. = 240°C)	343.75	338.25
P-[(N:C(CH $_3$)C $_6\text{H}_4$)Pd(OAc)] $_2$ (d.t. = 250°C)	343.60	338.20
P-[(N:C(Ph)C $_6\text{H}_4$)Pd(OAc)] $_2$ (d.t. = 270°C)	343.85	338.40
P-[(NHCH $_2\text{C}_6\text{H}_4$)Pd(H)(DMF)] (d.t. = 230°C)	343.80	338.30
P-[(NHCH(CH $_3$)C $_6\text{H}_4$)Pd(H)(DMF)] (d.t. = 235°C)	343.80	338.35
P-[(NHCH(Ph)C $_6\text{H}_4$)Pd(H)(DMF)] (C) (d.t. = 260°C)	343.75	338.30
P-[(NHCH $_2\text{C}_6\text{H}_4$)Pd(OAc)] $_2$ (B) (d.t. = 245°C)	343.70	338.20
P-[(NHCH $_2\text{C}_6\text{H}_4$)Pd(H)(DMF)] (C') (d.t. = 230°C)	343.80	338.30

d.t. = decomposition temperature.

palladium (II) complexes, the original one at 1640 cm^{-1} is reduced in intensity while the other one due to a coordinated azomethine group appears as a shoulder at 1615 cm^{-1} on the enhanced peak at 1600 cm^{-1} (skeletal vibration). Two new peaks at ~ 1585 and $\sim 1420\text{ cm}^{-1}$ (νCOO bridged) and another at $\sim 722\text{ cm}^{-1}$ (orthometalation) [35] appear in the spectra of all the complexes (Table 2).

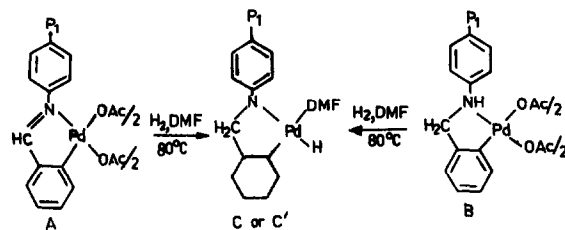
The presence of orthometalation is also supported from the fact that palladium (II) in these complexes could not be leached out by stirring them with alcoholic or DMF solution of PPh_3 in the absence or presence of HCl (10^{-2} M) for 12 h at ambient temperature. The metal in the polymer matrix can, however, be extracted by hot concentrated HNO_3 . The presence of both free and coordinated azomethine groups in these materials indicate the involvement of a fraction of Schiff base ligands in coordination with the metal atom. Probably the disposition and geometry of the Schiff base ligand moieties in the polymer framework control the formation of acetato-bridged palladium(II) complexes. The Schiff base moieties with unsuitable positions and geometry in the polymer matrix are unable to form such complexes and therefore remain free. Chemical analysis suggests the coordination of nearly 50% of the Schiff base to form orthopalladated complexes. The above experimental evidences suggest structure (A) for the complexes (Scheme 1).

The polystyrene based secondary amine complex of palladium (II) (B) prepared by reacting palladium (II) acetate with the secondary amine ($\text{R} = \text{H}$) exhibits strong multiple IR peaks in the range of $3200\text{--}3400$ ($\nu\text{N-H}$), a medium intensity peak at 1268 cm^{-1} ($\nu\text{C-N}$), two peaks at ~ 1580 and 1425 cm^{-1} (νCOO bridged) and a relatively weak peak at $\sim 720\text{ cm}^{-1}$ (orthometalation) [35] (Table 2). Though palladium (II) generally forms orthometalated complexes with tertiary amines, the formation of such complexes are known with sterically crowded primary or secondary amines [39,40]. In the present case, some secondary amine moieties directly bonded to the polystyrene framework may be sufficiently sterically crowded to form orthopalladated complexes. From the experimental evidences the probable structure (B) has been suggested for the orthopalladated species in the material (Scheme 2).

3.2. Characterization of the yellow brown activated catalyst (C)

The IR spectra of both the yellow brown activated catalysts (C) and the corresponding nonactivated ones (A and B) show the presence of orthometalated peaks at $\sim 722\text{ cm}^{-1}$. The activated species exhibit two new peaks at 1980 cm^{-1} ($\nu\text{Pd-H}$) and 1655 ($\nu\text{C=O}$ of DMF) at the cost of bridged νCOO peaks. No metal leaching occurs during hydrogen activation of (A) or (B) and the liberation of acetic acid (vide-infra) suggests the replacement of the bridged acetato groups by H and DMF. The shoulder at $\sim 1615\text{ cm}^{-1}$ ($\nu\text{C=N}$, coordinated) in the deep brown complexes (A) disappear completely in the activated species (C) with simultaneous appearance of a medium intensity peak at $\sim 1265\text{ cm}^{-1}$ ($\nu\text{C-N}$) [41] and a strong broad band at $3200\text{--}3400\text{ cm}^{-1}$ ($\nu\text{N-H}$). The polymer complex (A) was found to catalyse the hydrogenation of Schiff bases to the corresponding secondary amines [42] and the hydrogenation of the $>\text{C=N-}$ group to $-\text{CH-NH-}$ by palladium (II) in the same chelate moieties in (A) seems to be possible. Similar hydrogenation of the coordinated $-\text{N=N-}$ group coordinated to palladium (II) was reported earlier [29]. From the above facts and the comparable IR spectra of (C) and (C'), we propose the transformation in Scheme 3 to occur during hydrogen activation.

The catalytic activity of (B) is comparable with that of (A) ($\text{R} = \text{H}$) in respect to induction period and nature and yields of products. The species (B) was hydrogen activated by a procedure similar to that of (A) ($\text{R} = \text{H}$) and the activated species (C') is comparable to the complex (C) in catalytic activity (based on nature and yields of products). The higher efficiency of (C) may be due to its



higher metal content. The palladium (II) loading in (A) ($R = H$) is about 12% compared to that of $\sim 6\%$ in (B) (Table 1).

Using the activated complexes (C) as catalyst, the species left at the end of each catalytic run are identical to the corresponding ones used initially in catalytic activities, thermal stabilities, IR spectra and XPS data. It seems that the initial catalyst is reverted after the run.

Though the species (A) and (C) are highly active for the dihydrogen reduction of the substrates under the present experimental conditions, the activated complex (C) ($R = H$) is preferred and used for detailed catalytic investigation because of its highest activity in the series ($R = H, CH_3, C_6H_5$). The highest activity of (C) ($R = H$) was observed in DMF medium followed by DMSO and the reduction rate slowed down in stronger coordinating solvent like THF, dioxan and is immeasurably slow in noncoordinating solvents like $C_6H_6, C_6H_5CH_3, CCl_4$, etc. The addition of strong coordinating agents like pyridine or PPh_3 in the reaction media retards the reaction rate. DMF and DMSO are sufficiently strong coordinating media to cleave the acetate bridge in (A) or (B) to produce (C) under H_2 at $80^\circ C$. The coordinated DMF or DMSO molecule may be displaced moderately easily from the metal centre by the substrate molecule. In presence of stronger coordinating media, the substrate coordination to the metal atom in the species (C) is hindered resulting in the decreased concentration of metal–substrate complex with the consequent slowing down of the reduction rate. The poor or non-coordinating media are probably unable to produce the different intermediates involved in the reaction sequence (Scheme 5).

Nitroalkanes could be reduced very efficiently at $120^\circ C$ under a hydrogen pressure of $\sim 10.5 \times 10^3$ $kN m^{-2}$. Reduction at a lower temperature ($\sim 60^\circ C$) and pressure ($\sim 4.0 \times 10^3$ $kN m^{-2}$) required a longer reaction time yielding identical products. Nitroalkanes were reduced probably via the formation of alkyhydroxylamines as the latter were always detected in appreciable amounts at intermediate stages (Fig. 1). Alkyhydroxylamines were reduced completely to the corresponding amines but the present catalytic systems were inactive towards the reduction of alkyloximes. The reduction rate depends appreciably on the nature of nitroalkanes and the latter may be arranged in the order: nitromethane $>$ nitroethane $>$ 1-nitropropane \gg 2-nitropropane. Nitromethane is preferentially reduced to the extent of 95% when present along with 2-nitropropane at $100^\circ C$ under $P_{H_2} = 8.0 \times 10^3$ $kN m^{-2}$. In general, the reduction rate decreases with an increasing chain length of alkyl groups and α -branching greatly retards the reaction rate. The reason may be steric in origin.

Dihydrogen reduction of nitriles, RCN ($R = CH_3, Ph$) led to the simultaneous formation of both secondary $(RCH_2)_2NH$ (major) and primary amines RCH_2NH_2 (minor) at intermediate stages and the final products in both cases were mainly the corresponding secondary amines ($\sim 95\%$) (Fig. 2). The low selectivity for the formation of RCH_2NH_2 is probably due to the catalytic reaction of the latter with RCN leading to the formation of $(RCH_2)_2NH$ and liberation of NH_3 , the latter was, however, always detected in the gas phase.

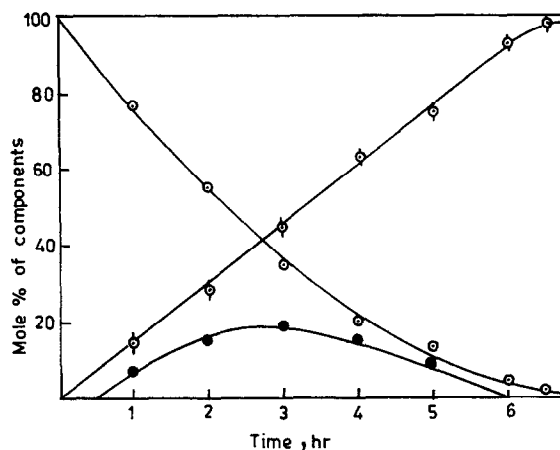
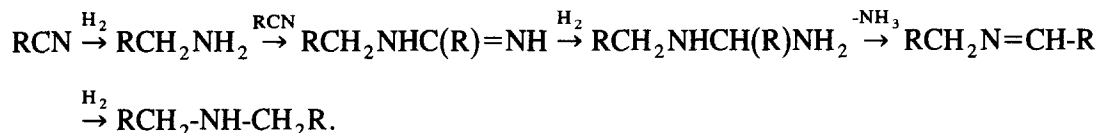


Fig. 1. Reduction of 1-nitropropane with: [Cat] = $P-[p-(NHCH_2C_6H_4)Pd(OAc)]_2 = 1.70 \times 10^{-3}$ g atom l^{-1} , [1-nitropropane] = 1.50 M. $P_{H_2} = 10.5 \times 10^3$ kN m^{-2} , medium = DMF, total volume = 10 ml. Temp. = 120°C. (○) = 1-nitropropane, (∅) = 1-aminopropane, (●) = propylhydroxylamine.

Initial addition of excess RCH_2NH_2 along with RCN reduced the reaction time slightly but the concentration of primary amine in the final product mixture was considerably lower compared to that added initially. On this basis, we suggest the reaction to proceed according to the scheme as proposed by Holy et al. [43].



The reduction of acetonitrile occurs at a much slower rate relative to that of benzonitrile and it is possible to selectively reduce benzonitrile to the extent of 90% when both the substrates are present together. Benzonitrile is known to form a more stable complex with palladium (II) compared to that of acetonitrile and hence a higher concentration of intermediate metal-benzonitrile complex probably

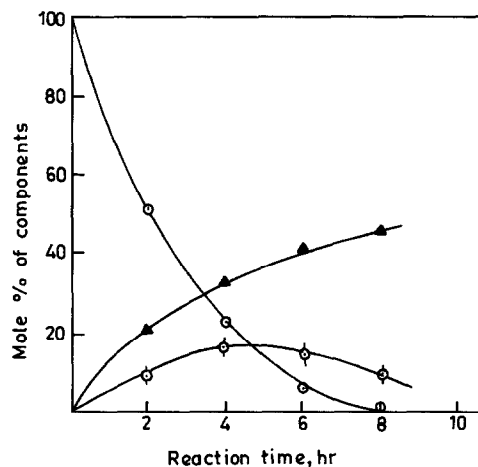


Fig. 2. Reduction of acetonitrile with: [Cat] = $P-[p-(NHCH_2C_6H_4)Pd(OAc)]_2 = 1.90 \times 10^{-3}$ g atom l^{-1} , [acetonitrile] = 0.50 M. $P_{H_2} = 12.5 \times 10^3$ kN m^{-2} , medium = DMF, total volume = 10 ml. Temp. = 130°C. (○) = acetonitrile, (∅) = ethylamine, (▲) = diethyl amine.

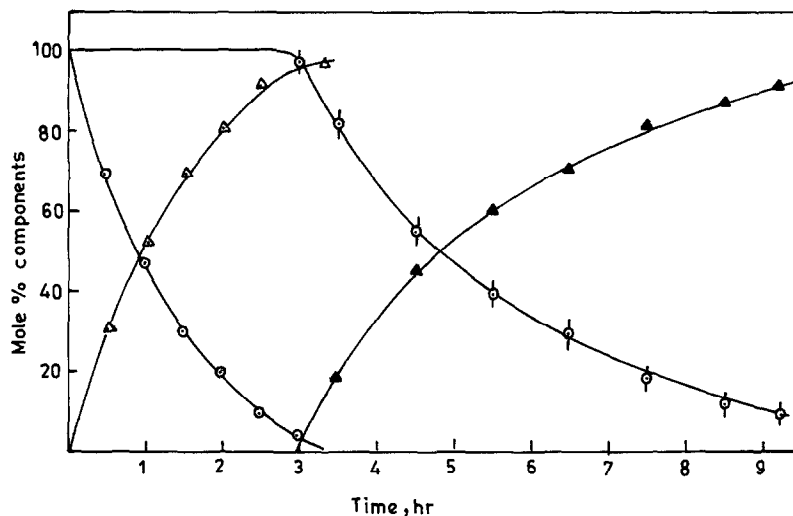


Fig. 3. Reduction of benzophenone-acetone mixture. [Cat] = $P-[p-(NHCH_2C_6H_4)Pd(OAc)_2] = 1.82 \times 10^{-3} \text{ g atom l}^{-1}$, [PhCOPh] = 1.50 M, [CH₃COCH₃] = 1.50 M, $P_{H_2} = 9.0 \times 10^3 \text{ kN m}^{-2}$. Medium = DMF, total volume = 10 ml. Temp = 100°C. (○) = PhCOPh, (∆) = PhCH(OH)Ph, (▲) = CH₃CHOH(CH₃).

leads to a higher reduction rate. Selective formation of RCH₂NH₂ from the corresponding RCN was not possible under varying experimental conditions.

The efficient reduction of ketones RCOR (R = CH₃, Ph) to the corresponding secondary alcohols to the extent of 90–95% occurs in the presence of the activated complexes in DMF medium. The optimum reduction conditions for all the three substrates are comparable but the reduction rates and yields of products vary in the order: benzophenone > acetophenone ≫ acetone. Benzophenone could be reduced almost completely to the corresponding alcohol before the starting of the reduction of acetone when both are present together (Fig. 3). Steric and electronic factors are possibly responsible for this variation of reduction rates and yields (Table 4). Due to the planar structure and the presence of extensive π electron delocalization, the >C=O group of benzophenone is supposed to coordinate

Table 4
Substrates and the corresponding products with catalyst (C, R = H)

Substrate	Reaction Time (h)	Initial turn over No. (min ⁻¹)	Product(s)	% Yield
(1) Nitromethane ^a	6.0	3.69	methylamine	(98)
(2) Nitroethane ^a	6.2	3.56	ethylamine	(98)
(3) 1-Nitropropane ^a	6.5	3.33	1-aminopropane	(97)
(4) 2-Nitropropane ^a	7.2	2.93	2-aminopropane	(96)
(5) 1-Nitroheptane ^a	6.8	3.11	1-aminoheptane	(94)
(6) Benzophenone ^b	3.0	6.06	diphenylmethanol	(96)
(7) Acetophenone ^b	4.2	4.60	phenylmethylmethanol	(94)
(8) Acetone ^b	6.2	3.06	2-propanol	(92)
(9) Benzonitrile ^c	5.5	3.44	dibenzylamine	(95)
(10) Acetonitrile ^c	8.6	2.12	diethylamine ethylamine	(90) (8)

Medium = DMF, [substrate] = 1.50 mol l⁻¹, total volume = 10.0 ml.

^a [Cat] = $1.70 \times 10^{-3} \text{ g atom l}^{-1}$, $P_{H_2} = 10.5 \times 10^3 \text{ kN m}^{-2}$, $T = 120^\circ\text{C}$.

^b [Cat] = $1.82 \times 10^{-3} \text{ g atom l}^{-1}$, $P_{H_2} = 9.0 \times 10^3 \text{ kN m}^{-2}$, $T = 100^\circ\text{C}$.

^c [Cat] = $1.90 \times 10^{-3} \text{ g atom l}^{-1}$, $P_{H_2} = 12.5 \times 10^3 \text{ kN m}^{-2}$, $T = 130^\circ\text{C}$.

strongly to palladium (II) in the polymer matrix resulting in the formation of a greater proportion of metal–substrate complex compared to that of acetone. This results in a higher reduction rate with the consequent greater yield of product. The carbonyl group of acetone forms a weak metal–substrate complex due to its nonplanar structure and the presence of localized double bonds. This leads to a lower concentration of intermediate palladium (II)–acetone complex with the consequent lowering of reduction rate and yields of 2-propanol.

XPS studies of different catalytic species related to the present investigation were carried out in the range of 330–350 eV using Al-K α as target material in order to determine the oxidation state of palladium in them and the data are presented in Table 3. The results suggest the presence of palladium (II) in all these species and there is no reduction of palladium (II) in the deep brown polymer material during hydrogen activation or catalytic run. The very small difference of XPS values ($3d_{5/2}$ and $3d_{3/2}$) among these species (A, B and C) may be due to a change of coordination environment around the metal-atom in them (Table 3). However, the identical XPS values of the initial catalyst (C) and the used ones suggest the presence of palladium (II) with the same co-ordination environment in both of them.

3.3. Kinetics and mechanism

The kinetic studies were made with the activated catalyst (C) ($R = H$) in DMF medium for the reduction of nitroalkanes under high pressure, high temperature conditions. The rate was determined by GLC estimation of products and substrates at 15 min intervals and the initial rate was calculated by graphical extrapolation of the rate curve to zero time. For the reduction of nitroalkanes the initial rate was found to follow first order dependence on the Pd content of the catalyst in the range of $1.00\text{--}6.0 \times 10^{-3}$ g atom l^{-1} (Fig. 4), second order dependence on hydrogen pressure in the range of $7.0\text{--}14.0 \times 10^3$ kN m^{-2} (Fig. 5) and independent of substrate concentration in the range of 0.5–3.0 M. The rate of reduction of alkylhydroxylamine was first order dependent on palladium (II) content and P_{H_2} and independent of substrate concentration.

Styrene and nitrobenzene are reduced to ethylbenzene and aniline, respectively, by the activated species C($R = H$) in DMF medium under nitrogen at ambient temperature. The IR spectra of the

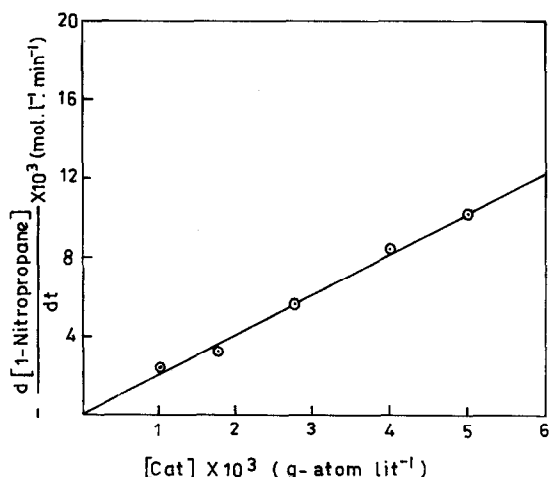


Fig. 4. Rate dependence on catalyst concentration. [Cat] = $P-[p-(NHCH_2C_6H_4)Pd(OAc)_2]$. Medium = DMF, [1-nitropropane] = 1.50 M. Temp. = 120°C. $P_{H_2} = 10.5 \times 10^3$ kN m^{-2} . Time = 6.5 h. Total volume = 10 ml.

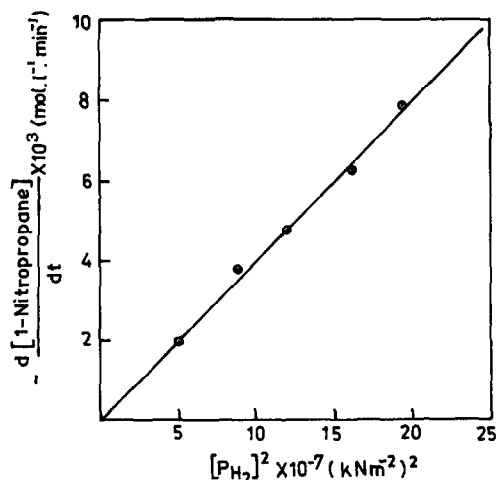
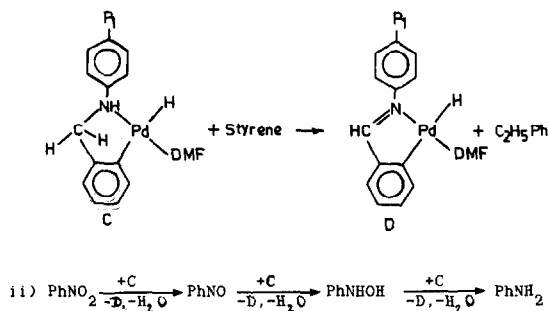


Fig. 5. Rate dependence on hydrogen pressure. [Cat] = $P-[p\text{-}(\text{NHCH}_2\text{C}_6\text{H}_4)\text{Pd}(\text{OAc})_2] = 1.70 \times 10^{-3} \text{ g atom l}^{-1}$. [1-nitropropane] = 1.50 M. Temp. = 120°C. Time = 6.5 h. Medium = DMF, total volume = 10 ml.

residual catalyst after thorough washing with dry acetone and drying under high vacuum showed the disappearance of a peak at 1268 cm^{-1} ($\nu\text{C-N}$) which was already present in the spectra of (C) and the appearance of a new shoulder at 1615 cm^{-1} ($\nu\text{C=N}$). The peaks at 1980 cm^{-1} ($\nu\text{Pd-H}$) and 1655 cm^{-1} ($\nu\text{C=O}$ of DMF), however, remained unchanged. These observations suggest Scheme 4 for the reduction.

From the experimental observations it appears that the actual catalytic species in all the cases are the secondary amine complexes (C) ($R = \text{H}, \text{CH}_3, \text{Ph}$) and heating of the acetato-bridged catalyst (A) or (B) in DMF under H_2 is required mainly to cleave the acetate bridge in them with the consequent formation of the active species (C) with a Pd-H bond. The activity of the catalyst (C) varies on the nature of the substituent R in the order $\text{H} > \text{CH}_3 > \text{C}_6\text{H}_5$ (Table 5). The high dependence of activity on the nature of the substituent R, suggests the involvement of a $-\text{CR=N}-$ group in the rate determining step and it was already found that a $-\text{CHR-NH}-$ group is transformed to a $\text{CR=N}-$ group at some step during substrate reduction.

The palladium (II) complex of Schiff base moieties with $R = \text{C}_6\text{H}_5$ should be most stable due to planarity and extensive π -electron delocalization in the orthometalated part including R. Addition of H_2 to $\text{CPh}_2=\text{N}-$ group will destroy the planarity with simultaneous loss of π -electron delocalization. This will destabilize the resulting complex to a greater extent compared to that with $R = \text{H}$ or CH_3 .



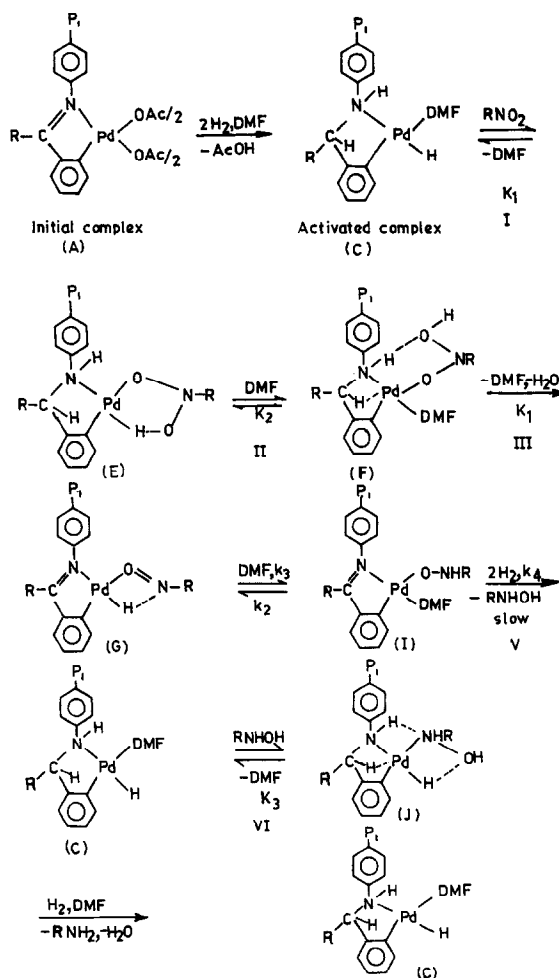
Scheme 4.

Table 5

Catalytic activities of $P-[p\text{-NHCHR}C_6H_4]Pd(OAc)_2$ for varying R (R = H, CH_3 , C_6H_5)

Substrate	R	Reaction time (h)	Initial turn-over No. (min^{-1})	Product	% Yield
(1) Nitro-methane	H	6.0	3.69	methyl-amine	98
	CH_3	6.4	3.31		96
	C_6H_5	7.8	2.62		93
(2) Acetone	H	6.2	3.06	2-propanol	92
	CH_3	6.5	2.91		92
	C_6H_5	7.5	2.47		90
(3) Benzonitrile	H	5.5	3.44	dibenzyl-amine	95
	CH_3	6.1	3.00		93
	C_6H_5	7.6	2.31		90

Medium = DMF, total volume = 10 ml.

Reaction condition: (1) Nitromethane: (1.5 M), [cat] = 1.70×10^{-3} g atom l^{-1} , $P_{H_2} = 10.5 \times 10^3$ kN m^{-2} , $T = 120^\circ\text{C}$.Reaction condition: (2) Acetone: (1.5 M), [cat] = 1.82×10^{-3} g atom l^{-1} , $P_{H_2} = 9.0 \times 10^3$ kN m^{-2} , $T = 100^\circ\text{C}$.Reaction condition: (3) Benzonitrile: (1.5 M), [cat] = 1.90×10^{-3} g atom l^{-1} , $P_{H_2} = 12.5 \times 10^3$ kN m^{-2} , $T = 130^\circ\text{C}$.

Scheme 5.

Hence the rate of H₂ addition to the >C=N- group of the orthopalladated part must be slowest when R = C₆H₅ compared to that when R = H or CH₃. Addition of H₂ to the >C=N- group will be easiest for R = H than for R = CH₃ due to the steric factor. Most probably the slowest step in the reduction process involves the addition of H₂ to the >C=N- group of the orthopalladated ring. According to Scheme 5,

$$\text{Rate} = k_4[\text{I}][\text{H}_2]^2$$

$$[\text{Cat}]_{\text{T}} = [\text{C}] + [\text{E}] + [\text{F}] + [\text{G}] + [\text{I}] + [\text{J}]$$

$$[\text{C}] = \frac{[\text{E}][\text{DMF}]}{K_1[\text{RNO}_2]} \quad (1)$$

$$[\text{E}] = \frac{[\text{F}]}{K_2[\text{DMF}]} \quad (2)$$

$$[\text{J}] = \frac{K_3[\text{C}][\text{RNHOH}]}{[\text{DMF}]} \quad (3)$$

Considering the steady state equilibrium of [G] and [I]

$$k_1[\text{F}] + k_2[\text{I}] = k_3[\text{G}][\text{DMF}] \quad (4)$$

$$k_3[\text{G}][\text{DMF}] = k_2[\text{I}] + k_4[\text{I}][\text{H}_2]^2 \quad (5)$$

From Eqs. (4) and (5)

$$[\text{F}] = K_6[\text{I}][\text{H}_2]^2, \quad K_6 = \frac{k_4}{k_1} \quad (6)$$

$$[\text{G}] = K_7[\text{I}] + K_8[\text{I}][\text{H}_2]^2, \quad K_7 = \frac{k_2}{k_3[\text{DMF}]}, \quad K_8 = \frac{k_4}{k_3[\text{DMF}]}$$

From Eqs. (1), (2) and (6)

$$[\text{C}] = \frac{K_4[\text{I}][\text{H}_2]^2}{[\text{RNO}_2]}, \quad K_4 = \frac{K_6}{K_1K_2} \quad (7)$$

From Eqs. (2) and (6)

$$[\text{E}] = K_5[\text{I}][\text{H}_2]^2, \quad K_5 = \frac{K_6}{K_2[\text{DMF}]}$$

From Eqs. (3) and (7)

$$[\text{J}] = \frac{K_9[\text{I}][\text{H}_2]^2[\text{RNHOH}]}{[\text{RNO}_2]}, \quad K_9 = \frac{K_3K_4}{[\text{DMF}]}$$

$$\begin{aligned} [\text{Cat}]_{\text{T}} &= \frac{k_4[\text{I}][\text{H}_2]^2}{[\text{RNO}_2]} + K_5[\text{I}][\text{H}_2]^2 + K_6[\text{I}][\text{H}_2]^2 + K_7[\text{I}] + K_8[\text{I}][\text{H}_2]^2 + [\text{I}] \\ &+ \frac{K_9[\text{I}][\text{H}_2]^2[\text{RNHOH}]}{[\text{RNO}_2]} = \frac{K_4[\text{I}][\text{H}_2]^2}{[\text{RNO}_2]} + K_{10}[\text{I}][\text{H}_2]^2 + K_{11}[\text{I}] + \frac{K_9[\text{I}][\text{H}_2]^2[\text{RNHOH}]}{[\text{RNO}_2]} \end{aligned}$$

Where $K_{10} = K_5 + K_6 + K_8$, $K_{11} = K_7 + 1$,

$$[I] = \frac{[\text{Cat}]_T [\text{RNO}_2]}{[\text{H}_2]^2 \{K_4 + K_{10} [\text{RNO}_2] + K_9 [\text{RNHOH}]\} + K_{11} [\text{RNO}_2]}$$

Under the experimental conditions, $[\text{H}_2]^2 \approx 10^{-3} \text{ M}$ and $[\text{RNO}_2] = 1.5 \text{ M}$. So the equation reduces to

$$[I] = \frac{[\text{Cat}]_T [\text{RNO}_2]}{K_{11} [\text{RNO}_2]} = \frac{[\text{Cat}]_T}{K_{11}}$$

$$\text{Rate} = k_4 [I] [\text{H}_2]^2 = K [\text{Cat}]_T [\text{H}_2]^2, \quad K = \frac{k_4}{K_{11}}$$

4. Conclusion

The polymer based orthopalladated complex catalysts used in the present investigation have slightly lower activity than the corresponding homogeneous ones [28] but are superior to the latter as (i) the same specimen of the catalyst can be used repeatedly for the reduction of substrates of different nature without suffering any appreciable loss of activity, (ii) the isolation of the used catalyst from the product mixture encounters no difficulty, (iii) the catalytic activities of the corresponding homogeneous systems were limited to aromatic ketones and nitriles only while the present systems are active towards a wide range of ketones and nitriles including aromatic, aliphatic or mixed ones and (iv) the fresh or used catalysts can be stored under a dry condition for a long time without any appreciable loss of its catalytic activities. Hence the present system may find wide applications in the synthesis of fine organic chemicals either in the laboratory or on an industrial scale.

References

- [1] M.O. Albers, E. Singleton, M.M. Viney, *J. Mol. Catal.* 30 (1985) 213.
- [2] J.L. Zuffa, M.L. Blohm, W.L. Gladfelter, *J. Am. Chem. Soc.* 108 (1986) 552.
- [3] A.M. Tafesh, M. Beller, *Tetrahedron. Lett.* 36 (1995) 9305.
- [4] K.D. Kallinen, T.T. Pakkanen, T.A. Pakkanen, *J. Mol. Catal.* 99 (1995) 29.
- [5] U. Möhring, M. Schäfer, F. Kukla, M. Schlaf, H. Werner, *J. Mol. Catal.* 99 (1995) 55.
- [6] J.F. Knifton, *J. Org. Chem.* 41 (1976) 1200.
- [7] J.F. Knifton, *J. Org. Chem.* 40 (1975) 519.
- [8] E.G. Chepalkin, M.L. Khidekel, *J. Mol. Catal.* 4 (1978) 103.
- [9] R.A. Sanchez-Delgado, N. Valencia, R.L. Morquez-Saliva, A. Audrillo, M. Medina, *Inorg. Chem.* 25 (1986) 1106.
- [10] D.K. Mukherjee, B.K. Palit, C.R. Saha, *J. Mol. Catal.* 88 (1994) 57.
- [11] R.A. Sanchez-Delgado, O.L. Ochoa, *J. Organomet. Chem.* 202 (1980) 427.
- [12] F. Hochard, H. Jobic, J. Massardier, A.J. Renouprez, *J. Mol. Catal.* 95 (1995) 165.
- [13] C. Viceute, G.B. Shulpen, B. Moreno, S. SaboEienne, B. Chaudret, *J. Mol. Catal.* 98 (1995) 25.
- [14] S. Ram, R.E. Ehremkanfer, *Tetrahedron Lett.* 25 (1984) 3415.
- [15] A. Bose, C.R. Saha, *J. Mol. Catal.* 49 (1989) 271.
- [16] P. Morys, J. Schlieper, *J. Mol. Catal.* 95 (1995) 27.
- [17] D.E. Bergbreiter, B. Chem, T.J. Lynch, *J. Org. Chem.* 48 (1983) 4179.
- [18] E. Baralt, N. Holy, *J. Org. Chem.* 49 (1984) 2626.
- [19] C.R. Saha, S. Bhattacharya, *J. Chem. Tech. Biotechnol.* 37 (1987) 223.
- [20] B. Log, A. Tijani, R. Dataste, F. Figueras, *J. Mol. Catal.* 79 (1993) 253.
- [21] Z. Jaworska, S. Gobas, W. Mistra, J. Wrzyzy, *J. Mol. Catal.* 88 (1994) 13.

- [22] D.T. Gokak, R.N. Ram, *J. Mol. Catal.* 49 (1989) 285.
- [23] J.N. Shah, R.N. Ram, *J. Mol. Catal.* 83 (1993) 67.
- [24] J.N. Shah, D.T. Gokak, R.N. Ram, *J. Mol. Catal.* 60 (1990) 141.
- [25] J.N. Shah, R.N. Ram, *J. Mol. Catal.* 77 (1992) 235.
- [26] J.M. Compelo, R. guardeno, W. Luna, J.M. Marino, J. Morales, J.L. Tirado, *J. Mol. Catal.* 85 (1993) 305.
- [27] N.L. Holy, *J. Org. Chem.* 45 (1980) 1418.
- [28] D.K. Mukherjee, B.K. Palit, C.R. Saha, *Indian J. Chem.* 31A (1992) 243.
- [29] P.K. Santra, C.R. Sara, *J. Mol. Catal.* 39 (1987) 279.
- [30] Vogel, (Text book of Practical Organic Chemistry).
- [31] R.B. King, E.M. Sweet, *J. Org. Chem.* 44 (1979) 385.
- [32] Fieser, Fiser, Reagent for Organic Synthesis, vol. 3, p. 291.
- [33] S.F. Wendell, *Tetrahedron* 19 (1963) 445.
- [34] A.W. Weston, R.J. Michael, *J. Am. Chem. Soc.* 73 (1951) 1381.
- [35] H. Onoue, I. Moritani, *J. Organomet. Chem.* 43 (1972) 431.
- [36] I. Baraniyai, F. Urvary, L. Marko, *J. Mol. Catal.* 82 (1985) 343.
- [37] A. Bose, C.R. Saha, *Indian J. Chem.* 29A (1990) 461.
- [38] L. Velluz, G. Amiard, R. Heymes, *Bull. Soc. Chim. Fr.* (1954) 1012.
- [39] J. Dehand, M. Pfeffer, *Coord. Chem. Rev.* 18 (1976) 327.
- [40] B.N. Cockburn, D.V. Howe, T. Keating, B.F.G. Johnson, J. Lewis, *J. Chem. Soc. Dalton Trans.* (1973) 404.
- [41] R.M. Silverstein, *IR Spectroscopy*, 5th ed., Wiley, 1991, p. 124.
- [42] M. Islam, A. Bose, D. Mal, C.R. Saha, in preparation.
- [43] N.L. Holy, *J. Org. Chem.* 44 (2) (1979) 239.