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# Dihydrogen Reduction of Nitroorganics, Alkenes, Alkynes, and Schiff Bases Using Polymer-Anchored Orthometalated Schiff-Base Complexes of Palladium(II) as Catalysts

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**Complexation of Schiff bases derived from the condensation of aminopolystyrene and carbonyl compounds, PhCO$R$ ($R = $ H, $CH_3$, $C_6H_5$) with palladium(II) acetate results in the formation of acetato-bridged, dinuclear orthopalladated complexes anchored to macroporous polystyrene beads. Hydrogen activation of the material at 80°C in DMF suspension brings to the reduction of coordinated azomethine group with simultaneous replacement of the bridged acetate by H and DMF, producing the corresponding mononuclear secondary amine complexes. The activated species are highly active towards the dihydrogen reduction of aromatic nitro- and carbonyl compounds, alkenes, alkynes, and Schiff bases under normal pressure at ambient temperature in aprotic solvents like DMF, DMSO, ethyl acetate, and THF. The highest activity was observed with $R = $ H in a DMF medium. Similar polystyrene-based orthometalated secondary amine complexes of palladium(II) prepared by alternative methods exhibit comparable catalytic activities. The same specimen of the catalyst can be used repeatedly for the reduction of the same or different substrates under comparable reaction conditions and stored indefinitely without any loss of catalytic activity. A tentative reduction mechanism has been suggested on the basis of catalyst transformation, identification of the intermediates at various stages of reaction, and kinetic studies.**

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## INTRODUCTION

A large number of homogeneous catalysts have so far been used for the dihydrogen reduction of unsaturated organic compounds (1–7), but few are versatile enough to reduce a wide variety of functional groups like $-NO_2$, $>C{=}C<$, $-C{\equiv}C-$, $>C{=}N-$, and $>C{=}O$. The homogeneous catalysts generally possess higher efficiency and are suitable for study of the reaction mechanism but their higher susceptibility to drastic reaction conditions and the difficulties associated with their isolation from the product mixture restrict their reusability. Hence, their uses in organic synthesis and industry become very limited. The difficulties can be overcome by anchoring the homogeneous catalysts on some insoluble suitable polymer matrix. The resulting polymer-based immobilized catalysts may have a higher potential for industrial and synthetic use (8–14). The catalysts may develop higher specificity and product selectivity, depending on the environment of the metal complex in the polymer matrix. However, lower activity and metal leaching from the polymer framework due to decomplexation of the ligand, especially in acidic media, may create problems. These problems may be eliminated using functionalized polymers that are capable of forming strong complexes. Among such species, the complexes of iron[III] (15), palladium[II] (16–22), platinum[II] (23–25), rhodium[I] (26–31), ruthenium[II] (32–35), and nickel[II] (36–37) supported on inorganic or organic polymers are worthy of mention.

Orthometalated complexes of palladium(II) with various ligands (38), especially with Schiff bases (39), were found to be efficient homogeneous catalysts for the dihydrogen reduction of functional groups like $-NO_2$, $-NH_2OH$, $>C{=}C<$, $>C{=}N-$, and $>C{=}O$ under mild reaction conditions in moderate coordinating solvents. The results encouraged us to investigate the catalytic activities of polymer-anchored complexes and to understand the effect of such immobilizaiton on their catalytic activities. The paper presents the catalytic activities of orthometalated Schiff bases and secondary amine complexes of palladium(II) bonded to macroporous polystyrene beads and indicates the superiority of the heterogeneous system over the corresponding homogeneous ones. A mechanistic route has been proposed on the basis of characterization of the reaction intermediates at various stages of reduction.

## EXPERIMENTAL

### *Materials*

Air- and moisture-sensitive reactions were carried out under dry $N_2$. Palladium acetate was procured from Arora Matthey Ltd. and the macroporous polystyrene beads were

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crosslinked with 5% DVB (Art. No. 22094-9) was supplied as hard insoluble 20–50 mesh spheres of average pore diameter of 800 Å by Aldrich Chemical Co., USA. The chemicals used for the preparation of polymer-based catalysts were of analytical grade and purified before use. DMF, DMSO, ethyl acetate, toluene, and $CH_3OH$ were dried and purified by standard procedures (40). The analytical grade liquid substrates were purified by distillation while the solid ones were purified by recrystallization from the appropriate solvents. The purities of the substrates and solvents were checked by gas chromatography. In the case of alkenes, the percentage of different isomers were determined by gas chromatography. Both $H_2$ and $N_2$ were deoxygenated and dried by passing them successively through alkaline pyrogallol, fused $CaCl_2$, and silica gel towers.

### *Procedure*

*Preparation of p-nitropolystyrene (1A), p-aminohydrochloride polystyrene (1B), and p-aminopolystyrene (1C).* The preparation of the materials was according to the method of King and Sweet (41). The macroporous polystyrene beads (5 g) were para-nitrated by stirring them with a mixture of acetic anhydride (20 ml), nitric acid (70%, 2 ml), and glacial acetic acid (4 ml) for 30 min at 5°C and 5 h at 50°C using a magnetic stirrer. The resulting *p*-nitropolystyrene (*1A*) beads were then washed successively with acetic acid (20 ml), tetrahydrofuran (50 ml), deionized water (20 ml), and dry methanol (50 ml).

The dried *p*-nitropolystyrene (*1A*) was reduced to corresponding aminehydrochloride (*1B*) by $SnCl_2 + HCl$ procedure (41). The suspension of *1A* (5 g) in a mixture of glacial acetic acid (20 ml), stannous chloride (5 g) and concentrated hydrochloric acid (12 *M*, 6 ml) was magnetically stirred for 75 h at 30°C. The filtered beads were washed thrice with a mixture of hydrochloric acid (12 *M*) and glacial acetic acid (1 : 4, 10 ml) and then with tetrahydrofuran (20 ml) and dry methanol (50 ml) in succession.

The entire product (*1B*) was repeatedly washed with methanolic NaOH (5%) until the washings were chloride-free. The resulting *p*-aminopolystyrene (*1C*) was then repeatedly washed with dry methanol to free it from alkali and finally dried under vacuum.

*Preparation of p-Schiff-based polystyrene ligands (1D) and their corresponding palladium(II) complexes (1E).* The suspension of *1C* (12 g) in dry toluene (30 ml) containing excess of the desired carbonyl compound, $C_6H_5COR$ (0.05 mol, $R = H$, $CH_3$, $C_6H_5$) was refluxed for 72 h under dry nitrogen using Dean–Stark apparatus (42–44). Longer reflux period (90 h) was required when $R$ is $CH_3$ or Ph. The presence of a small amount of $POCl_3$ in the medium was necessary for preparation of the Schiff base when $R = Ph$. The refluxing was continued until the colour of the suspension changed to yellow. The filtered beads (*1D*) were washed with 20 ml each of benzene, tetrahydrofuran, and ethanol in succession and finally dried under vacuum.

The yellow suspension of *1D* (1.0 g) in glacial acetic acid solution of palladium acetate (0.75 g) was refluxed for 8 h when the suspension changed completely to brown. It was filtered and washed with tetrahydrofuran and methanol in order and the palladium(II) complex (*1E*) thus prepared was dried in a desiccator over fused $CaCl_2$.

*Preparation of yellow brown activated complex (1F).* The suspension of deep brown palladium (II) complex (*1E*) in dry DMF was continuously stirred under oxygen-free, dry hydrogen atmosphere at 80°C for 1 h when the suspension changed to yellow brown. The beads were separated, washed thoroughly with dry acetone, and finally dried.

*Preparation of p-secondary amine polystyrene ligand (2A or 2A′) and the corresponding palladium(II) complex (2B or 2B′).* The polystyrene-based secondary amine was prepared from *1D* ($R = H$) by two methods.

In the first method (45), the suspension of *1D* (3.0 g, $R = H$) in dry toluene (20 ml) was taken in a glass-lined stainless steel autoclave (100 ml) and the catalyst, $Co_2(CO)_8$ (0.20 g) was added to the reaction mixture under hydrogen. The mixture was then subjected to $CO + H_2$ (1 : 1) pressure of $10.0 \times 10^3$ $kNm^{-2}$ and kept stirred at 95°C for 1 h. The pressure was released after cooling the reaction mixture to room temperature and the secondary amine polystyrene (*2A*) were separated, washed with dry toluene and methanol in succession, and dried as usual.

In the second method (40), the suspension of *1C* (5 g) in dry DMF solution (20 ml) of pure sodium hydrogen carbonate (1.75 g) was taken in a round-bottom flask (100 ml). Freshly distilled benzyl chloride (1.9 ml) was added dropwise (about 1 h) into the reaction mixture kept at 90–95°C under a vigorous stirring condition. The reaction mixture was kept stirred for a period of 3 h more at the same temperature and filtered. The resulting beads (*2A′*) were washed successively with DMF (50 ml), alcoholic KOH (1 *M*, 40 ml), THF (30 ml), methanol, and finally dried under vacuum.

The yellow suspension of secondary amine, *2A* or *2A′* (1.0 g) in glacial acetic acid solution (15 ml) of palladium(II) acetate (0.75 g) was refluxed for 8 h when the suspension slowly changed to brown. The corresponding complex (*2B* or *2B′*) was filtered, washed successivley with glacial acetic acid and dry ethanol in succession, and dried under a vacuum.

*Preparation of activated complex of secondary amine (2C or 2C′).* The activated species, *2C* or *2C′*, was prepared from the respective secondary amine complex of palladium(II), *2B* or *2B′*, by following the procedure analogous to that used for the preparation of *1F* from *1E*. The deep brown complex, *2B* or *2B′*, changed to yellow brown during hydrogen activation and the activated complex, *2C* or *2C′* was separated and dried as usual.

*Hydrogenation procedure.* The hydrogenation of the substrate was carried out in a conical-type glass reactor (100-ml capacity), equipped with a magnetic stirrer and provided with two high vacuum stopcocks at the diametrically opposite side. One stopcock is fitted with a rubber septum at the end to prevent any air leakage into the reactor, either during the introduction of the substrate or the periodical removal of the reaction mixture. The other stopcock is made into four terminals by suitable arrangements which are connected to (i) the hydrogen cylinder via a graduated gas burette, (ii) the nitrogen cylinder, (iii) the high-vacuum pump, and (iv) a manometer. The manometer always indicates the reactor pressure, and any excess pressure that develops in the reactor is released automatically by passing the excess gas out through the mercury reservior of the manometer. Arrangements are also provided for the deoxygenation and drying of the gasses before their introduction into the reactor. In a typical experiment, the suspension of the weighed amount of activated catalysts, *1F* or *2C* or *2C′* (0.032 mmol of Pd content) in deoxygenated DMF (20 ml) was taken in the reactor partially immersed in a thermostated silicon oil bath. It was first evacuated, flushed thrice with pure and dry nitrogen and twice with dry, deoxygenated hydrogen. The substrate (0.01 mol) was quickly introduced via syringe into the preequilibrated hydrogen flask through the septum and stopcock and the stirring rate was adjusted to have the maximum reaction rate. The periodic removal of the reaction mixture was done via syringe through the same stopcock and septum.

Hydrogen absorption started immediately with almost the maximum rate. The gas uptake was measured at 2-min intervals from the upward displacement of paraffin oil in a graduated gas burette. Sampling was done via microsyringe at 5-min intervals and the mixture was analysed with chrompack CP-9000 gas chromatograph using an FFAP column with appropriate temperature programming. For analysis of the reduction products of $PhNO_2$, the column temperature was raised from 100–240°C with a 10°C rise per minute.

Due to insolubilities of the polymer catalysts in organic or inorganic solvents, their characterization was limited to chemical analysis, IR spectra, XPS data, DTA analysis, and other physico-chemical properties. IR spectra were taken in Perkin–Elmer 883 spectrophotometer in the range of 4000 to 400 $cm^{-1}$ in kBr pellets and 400 to 200 $cm^{-1}$ in CsI disks. ESCA data were recorded with VG-scientific ESCA LAB-MARK-II using AlK$\alpha$ as the radiation source. DTA analyses were carried out using Schimadzu DT-40 instrument in the range of 30 to 600°C.

The polystyrene-anchored orthopalladated complexes were prepared per the following scheme:

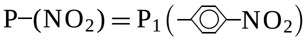
$$\mathrm{P} \xrightarrow{HNO_3+CH_3COOH} \underset{1A}{\mathrm{P{-}(NO_2)}} \xrightarrow[CH_3COOH]{SnCl_2+HCl} \underset{1B}{\mathrm{P{-}(NH_3Cl)}}$$

$$\xrightarrow[MeOH]{NaOH} \underset{1C}{\mathrm{P{-}(NH_2)}} \xrightarrow[R = H, CH_3, Ph]{C_6H_5COR} \underset{1D}{\mathrm{P{-}(N{=}CRC_6H_5)}}$$

$$\xrightarrow[CH_3COOH]{Pd(CH_3COO)_2} \underset{1E}{\mathrm{P{-}Pd(II)\ complex}}$$

$$\xrightarrow{H_2,\ DMF} \underset{1F}{\mathrm{P{-}Pd(II)\ activated\ complex}}$$

P = polystyrene framework



$$\mathrm{P{-}(NO_2) = P_1(-\bigcirc-NO_2)}$$

$$\underset{1D}{\mathrm{P{-}({-}N{=}CHC_6H_5)}} \xrightarrow[10.0 \times 10^3\ kNm^{-2}]{H_2+CO\ (1:1)} \underset{2A}{\mathrm{P{-}({-}NHCH_2C_6H_5)}}$$

$$\xrightarrow[CH_3COOH]{Pd(CH_3COO)_2} \underset{2B}{\mathrm{P{-}Pd(II)\ complex}}$$

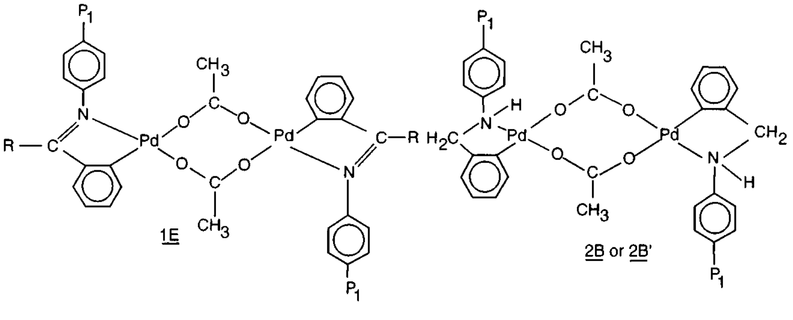
$$\xrightarrow{H_2,\ DMF} \underset{2C}{\mathrm{P{-}Pd(II)\ activated\ complex}}$$

$$\underset{1C}{\mathrm{P{-}({-}NH_2)}} + \mathrm{C_6H_5CH_2Cl} \xrightarrow[DMF]{NaHCO_3} \underset{2A'}{\mathrm{P{-}(NHCH_2C_6H_5)}}$$

$$\xrightarrow[CH_3COOH]{Pd(CH_3COO)_2} \underset{2B'}{\mathrm{P{-}Pd(II)\ complex}}$$

$$\xrightarrow{H_2,\ DMF} \underset{2C'}{\mathrm{P{-}Pd(II)\ activated\ complex}}$$

Although the formula and structural representation of *1F*, *2C*, and *2C′* in Scheme 1 and Table 1 appear identical,



**SCHEME 1.** Pd(II) complexes with functionalized polystyrene.

**TABLE 1**

**Analytical Data of the Functionalized Polymer and the Pd(II) Complexes**

| Compound | Colour | Cl% | C% | H% | N% | Metal% |
|---|---|---|---|---|---|---|
| $P-$ | Colourless | | 92.50 | 7.60 | | |
| *1A*. $P-NO_2$ | Light yellow | | 74.10 | 5.69 | 6.01 | |
| *1B*. $P-NH_3Cl$ | Yellow | 13.25 | 72.01 | 6.72 | 5.81 | |
| *1C*. $P-NH_2$ | Pale yellow | | 84.12 | 7.34 | 6.72 | |
| *1D* ($R = H$). $P-N:CHC_6H_5$ | Brownish yellow | | 87.09 | 6.60 | 5.01 | |
| *1D* ($R = CH_3$). $P-(N:C(CH_3)C_6H_5$ | Brownish yellow | | 85.98 | 6.80 | 4.90 | |
| *1D* ($R = Ph$). $P-N:C(C_6H_5)C_6H_5$ | Yellowish brown | | 85.11 | 6.12 | 4.13 | |
| *1E* ($R = H$). $P-[(N:CH(C_6H_4)Pd(OAc)]_2$ | Deep brown | | 71.12 | 5.02 | 4.00 | 12.25 |
| *1E* ($R = CH_3$). $P-[(N:C(CH_3)C_6H_4)Pd(OAc)]_2$ | Deep brown | | 74.46 | 5.88 | 4.10 | 11.00 |
| *1E* ($R = Ph$). $P-[(N:C(C_6H_5)C_6H_4)Pd(OAc)]_2$ | Deep brown | | 74.35 | 5.63 | 3.61 | 9.92 |
| *1F* ($R = H$). $P-[\{NHCH_2)C_6H_4\}Pd(H)(DMF)]$ | Yellowish brown | | 73.20 | 6.40 | 4.01 | 11.97 (11.95)[a] |
| *1F* ($R = CH_3$). $P-[\{NHCH(CH_3)C_6H_4\}Pd(H)(DMF)]$ | Yellowish brown | | 74.51 | 6.39 | 4.00 | 10.90 |
| *1F* ($R = Ph$). $P-[\{NHCH(Ph)C_6H_4\}Pd(H)(DMF)]$ | Yellowish brown | | 75.00 | 5.92 | 4.90 | 9.80 |
| *2A*. $P-[(NHCH_2)C_6H_5]$ | Yellowish brown | | 86.14 | 7.01 | 4.91 | |
| *2A′*. $P-[NHCH_2)C_6H_5]$ | Yellowish brown | | 85.62 | 7.21 | 5.60 | |
| *2B*. $P-[(NHCH_2)C_6H_4)Pd(OAc)]_2$ | Deep brown | | 76.65 | 6.43 | 4.38 | 8.01 |
| *2B′*. $P-[(NHCH_2)C_6H_4)Pd(OAc)]_2$ | Deep brown | | 80.40 | 7.45 | 5.30 | 4.31 |
| *2C*. $P-[(NHCH_2)C_6H_4)Pd(H)(DMF)]$ | Yellowish brown | | 77.54 | 6.81 | 5.38 | 7.92 |
| *2C′*. $P-[(NHCH_2)C_6H_4)Pd(H)(DMF)]$ | Yellowish brown | | 80.86 | 7.06 | 5.81 | 4.28 |

*Note*. P = polystyrene.

[a] Analytical data after fifth recycle of the catalyst.

the materials actually differ in their chemical composition. The same is applicable to (i) *2A* and *2A′* and (ii) *2B* and *2B′*.

It becomes clear from Table 1 that, *2A* and *2A′* differ in the amount of secondary amine content. Consequently (i) *2B* and *2B′* and (ii) *1F*, *2C*, and *2C′* should differ in the amount of metal loading, as is evidenced by their chemical analysis (Table 1).

## RESULTS AND DISCUSSION

The analytical and IR data of polystyrene, functionalised polystyrene, and the corresponding metal complexes are presented in Tables 1 and 2, respectively. The reaction of polystyrene with ($CH_3COOH + HNO_3$) resulted in nearly 56% nitration as evidenced by the chemical analysis of *1A* (Table 1) and the appearance of two strong and new IR peaks at 1520 and 1340 cm$^{-1}$ ($\nu NO_2$) in its spectra, in addition to the peaks in the region 3100–2800 cm$^{-1}$ ($\nu$C–H), ~1600, ~1500, and ~1460 cm$^{-1}$ (skeletal vibrations), 760 and 680 cm$^{-1}$ (C–H bending), observed in the spectra of macroporous polystyrene beads (Table 2). The appearance of another peak at 835 cm$^{-1}$ indicates para-nitration (41). The reduction of *1A* to the corresponding $P-NH_3Cl$ (*1B*) by the $SnCl_2 + HCl$ procedure was found superior to the Sn + HCl procedure. Elemental analysis of the aminohydrochloride, *1B*, indicates approximately 90% reduction of the $-NO_2$ group in *1A*. In *1B*, the $\nu NO_2$ peaks are reduced in intensity with the simultaneous apearance of a new peak at 2550 cm$^{-1}$ due to $-NH_3Cl$ (41). The species *1C* was completely chloride-free and exhibited strong multiple bands in the region 3400–3200 cm$^{-1}$ ($\nu NH_2$) and a shoulder at 1625 cm$^{-1}$ ($\delta NH_2$) with the simultaneous disappearance of the peak at 2550 cm$^{-1}$. The elemental analysis of *1D* and GC analysis for the unused PhCO*R* after the Schiff-base reaction suggests ~70–90% conversion of *1C* to *1D*, depending on the nature of *R*. The extent of reaction, however, varies in the order $H > CH_3 > C_6H_5$. The formation of a Schiff base is supported by the appearance of a new peak at ~1640 cm$^{-1}$ ($\nu$C=N). In the palladium(II) complexes of *1E* ($R = H, CH_3, C_6H_5$), the $\nu$C=N peak is split up, the original band at 1645 cm$^{-1}$ ($\nu$C=N, free) is reduced in intensity and a shoulder is observed at ~1615 cm$^{-1}$ ($\nu$C=N, coordinated). Three new medium intensity peaks at 1585 cm$^{-1}$, 1430 cm$^{-1}$ ($\nu$COO, bridged) (46, 38), and ~722 cm$^{-1}$ (orthometalation) (47) and a weak peak at 450 cm$^{-1}$ ($\nu$Pd–N) (48) appear in the spectra of *1E*. These spectral evidences suggest that a fraction of azomethine groups form dinuclear acetato-bridged orthometalated complexes of palladium(II). The secondary amines prepared by catalytic hydrogenation of *1D* ($R = H$) exhibits new IR peak at 1265 cm$^{-1}$ ($\nu$C–N) (49) with complete disapperance of the ($\nu$C=N) peak at ~1640 cm$^{-1}$, indicating 100% reduction of C=N groups. The complex *2B* or *2B′* exhibits the common IR peaks at 1265 cm$^{-1}$ ($\nu$C–N, free), 1250 cm$^{-1}$ ($\nu$C–N, coordinated), 1585 cm$^{-1}$, 1420 cm$^{-1}$ ($\nu$COO, bridged), 720 cm$^{-1}$ (orthometalation), and 450 cm$^{-1}$ ($\nu$Pd–N). According to chemical analysis (Table 1) only half of the Schiff base moieties in *1D* form orthometalated complexes with $Pd(OAc)_2$ to produce *1E* ($R = H$). In the case of secondary amine complexes only 30% of the ligand species in *2A*, obtained by

100% catalytic hydrogenation of the Schiff base moieties in *1D* ($R = \mathrm{H}$), form orthometalated complexes with palladium(II) (*2B*) (Scheme 1). In the case of the transformation of primary amines to secondary amines, only 50% of the primary amine species in *1C* react with $C_6H_5CH_2Cl$ to produce *2A′* and only 30% of the secondry amine moieties in *2A′* form orthopalladated complexes (Scheme 1). However, 100% of the palladium(II) complex species in *1E*, *2B*, and *2B′* form the corresponding activated complexes during hydrogen activation.

From the above observation it appears that 100% of ligand species in *1D*, *2A*, or *2A′* are never utilized to form palladium(II) complexes and only a fraction of the ligand species, depending on the nature of *1D*, *2A*, and *2A′*, is capable of complexation with the metal. Probably the disposition and geometry of these ligand species in the polymer framework control the formation of acetato-bridged dinuclear metal complexes. The ligand moieties with unsuitable distribution are incapable of forming the acetato-bridged complexes and thereby remain free. Chemical analysis of *1E* and *2B* or *2B′* suggests that less than 50% of the ligands coordinate with the metal. In the case of *1E*, the metal loading decreases with the bulkiness of *R* in the order $\mathrm{H} > CH_3 > C_6H_5$.

The IR spectra of *1F* and *2C* or *2C′* are comparable and show the presence of two new bands, a weak one at ~1980 $\mathrm{cm}^{-1}$ ($\nu$Pd–H) (50) and another of medium intensity at ~1655 $\mathrm{cm}^{-1}$ (coordinated DMF). The peaks due to a bridged aceto-group are absent, while the orthometalated peak at 722 $\mathrm{cm}^{-1}$ remains unaltered. Out of the two bands at 1615 and 1640 $\mathrm{cm}^{-1}$ in the spectra of *1E*, the latter one ($\nu$C=N, free) is retained while the former ($\nu$C=N, coordinated) is replaced by a peak at ~1250 $\mathrm{cm}^{-1}$ ($\nu$C–N, coordinated) in the spectra of *1F*. These facts indicate the following transformation occurs during hydrogen activation (Scheme 2). The liberation of acetic acid during hydrogen activation of *1E*, *2B*, and *2B′* has been confirmed by GC analysis of the corresponding DMF solution.

The IR spectra of all polystyrene-anchored palladium(II) complexes indicate the presence of a medium intensity peak at ~720 $\mathrm{cm}^{-1}$ (Table 2). The spectra of polystyrene, *1E*, *1F*, and the used catalyst are shown in Fig. 1. The ESCA results of all the species show well-resolved doublets with binding energies of Pd $3d_{5/2}$ in the region 338 to 339 eV (Table 3) and with full width at half maximum (FWHM) spread over 2.0 to 3.0. The spectra of *1E*, *1F*, and the used catalyst are presented in Fig. 2.

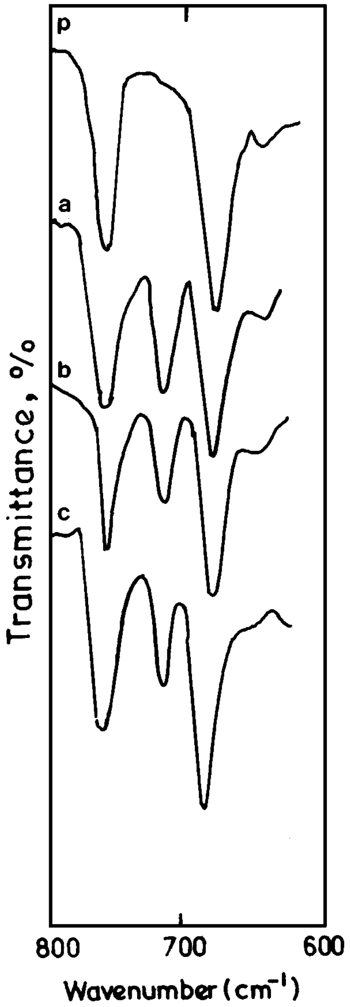
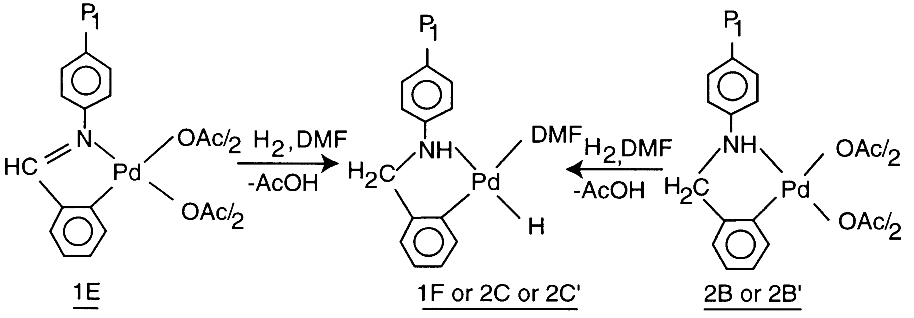


**FIG. 1.** IR spectra of (p) *1D*; (a) *1E*; (b) *1F*; (c) used catalyst.

The curve p in Fig. 1 is the IR spectra of macroporous polystyrene while the curves a, b, and c in Figs. 1 and 2



**SCHEME 2**

**TABLE 2**

**IR Spectral Data of the Compounds**

| Compounds | $\delta NH_2$ | $\nu NH_3Cl$ | $\nu NO_2$ cm$^{-1}$ | $\nu C{=}N$ | $\nu C{-}N$ | $\nu COO$ | $\nu Pd{-}H$ | Orthometalation | $\nu C{=}O$ Coord. (DMF) |
|---|---|---|---|---|---|---|---|---|---|
| *1A*. $P{-}NO_2$ | | | 1520(s)<br>1350(s) | | | | | | |
| *1B*. $P{-}NH_3Cl$ | | 2550 | 1520(w)<br>1350(m) | | | | | | |
| *1C*. $P{-}NH_2$ | 1625(sh) | | 1520(w)<br>1350(ms) | | | | | | |
| *1D* ($R = H$). $P{-}N{:}CHC_6H_5$ | 1625(sh) | | 1520(w)<br>1340(m) | 1640 | | | | | |
| *1D* ($R = Ph$). $P{-}N{:}C(C_6H_5)C_6H_5$ | 1628(w) | | 1520(w)<br>1340(m) | 1635 | | | | | |
| *1E* ($R = H$). $P{-}[(N{:}CH(C_6H_4)Pd(OAc)]_2$ | | | 1520(w)<br>1340(w) | 1615<br>1640 | | 1585<br>1420 | | 722 | |
| *1F* ($R = H$). $P{-}[(HNCH_2C_6H_4)Pd(H)(DMF)]$ | | | 1520(w)<br>1340(w) | 1640 | 1263 | | 1978 | 722 | 1655 |
| *2A*. $P{-}NHCH_2C_6H_5$ | 1626(sh) | | 1520(w)<br>1340(w) | | 1265 | | | | |
| *2B*. $P{-}[(NHCH_2C_6H_4)\ Pd(OAc)]_2$ | | | 1525(w)<br>1340(w) | | 1268 | 1580<br>1425 | | 720 | |
| *2C*. $P{-}[(NHCH_2C_6H_4)Pd(H)(DMF)]$ | | | 1525(w)<br>1340(w) | | 1262 | | 1980 | 722 | 1653 |

*Note*. P = polystyrene.

refer to nonactivated catalyst (*1E*, $R = H$), activated catalyst (*1F*, $R = H$) and the corresponding five-times-used catalyst, respectively. The IR spectra of all the species in the region 600–800 cm$^{-1}$ are comparable with the peak at ~720 cm$^{-1}$ (due to orthometalation), remaining almost

**TABLE 3**

**XPS Data of the Pd(II) Complexes**

| Compound | Pd | |
|---|---|---|
| | $3d_{3/2}$ | $3d_{5/2}$ |
| *1E* ($R = H$). $P{-}[(N{:}CHC_6H_4)Pd(OAc)]_2$<br>d.t. = 240°C | 343.75 | 338.25 |
| *1E* ($R = CH_3$). $P{-}[(N{:}C(CH_3)C_6H_4)Pd(OAc)]_2$<br>d.t. = 250°C | 343.60 | 338.20 |
| *1E* ($R = Ph$). $P{-}[(N{:}C(Ph)C_6H_4)Pd(OAc)]_2$<br>d.t. = 270°C | 343.85 | 338.40 |
| *1F* ($R = H$). $P{-}[(NHCH_2C_6H_4)Pd(H)(DMF)]$<br>d.t. = 230°C | 343.80 | 338.30 |
| *1F* ($R = CH_3$). $P{-}[(NHCH(CH_3)C_6H_4)Pd(H)(DMF)]$<br>d.t. = 235°C | 343.80 | 338.35 |
| *1F* ($R = Ph$). $P{-}[(NHCH(Ph)C_6H_4)Pd(H)(DMF)]$<br>d.t. = 260°C | 343.75 | 338.30 |
| *1F*[a] ($R = H$). $P{-}[(NHCH_2C_6H_4)Pd(H)(DMF)]$<br>d.t. = 230°C | 343.83 | 338.30 |
| *2B*. $P{-}[(NHCH_2{-}C_6H_4)Pd(OAc)_2]$<br>d.t. = 245°C | 343.70 | 338.20 |
| *2C*. $P{-}[(NHCH_2C_6H_4)Pd(H)(DMF)]$<br>d.t. = 230°C | 343.80 | 338.30 |

*Note*. d.t. = decomposition temperature; P = polystyrene.
[a] Used five times.

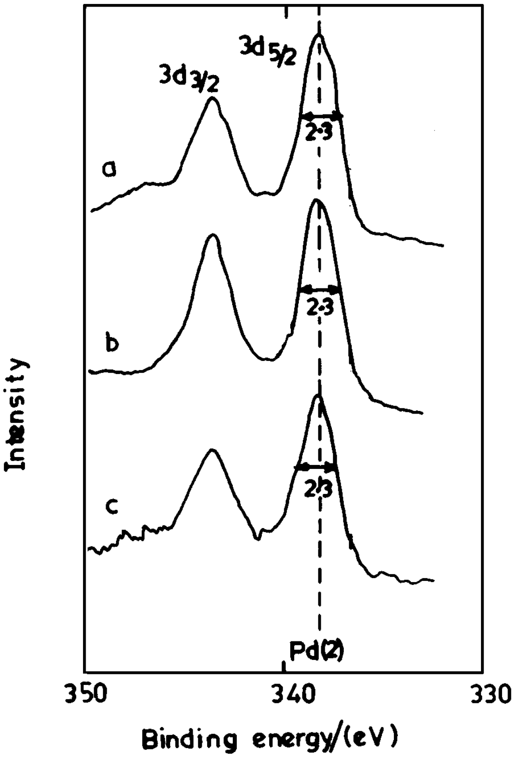


**FIG. 2.** XPS spectra of $3d_{5/2}$ and $3d_{3/2}$ level of Pd in the catalysts: (a) *1E*; (b) *1F*; (c) used catalyst.

unchanged in position and intensity (Fig. 1). This suggests that the orthometalated bonds remain intact during activation and catalytic hydrogenation of the substrate. The ESCA curves of *1E*, *1F* ($R = \mathrm{H}$), and the corresponding used catalyst as represented by a, b, and c, respectively (Fig. 2) are very comparable and suggest that all the species contained Pd(II). This further suggests that orthometalated palladium(II) does not suffer any reduction to $\mathrm{Pd}^0$ during activation or catalytic hydrogenation.

The species *1F*, *2B*, and *2C* may contain only orthopalladated complexes or a mixture of orthometalated and amine (only *N*-donor) types of complexes of palladium(II). The latter type may be formed due to complexation of free amine already present in the functionalized polymer or it may be formed during the complexation reaction (45). The species were separately stirred with alcoholic and DMF solutions of $PPh_3$ for 12 h at 80°C and filtered. Palladium(II) was found absent in the colourless filtrate in all cases. Any amine type of complex should be leached out by this treatment as the $Pd(II)–PPh_3$ bond is stronger than the $Pd(II)–NH_2C_6H_5$ bond. The *p*-aminopolystyrene (*1C*) reacts with $Pd(C_6H_5CN)_2Cl_2$ to produce a polymer-anchored Pd(II) complex containing the $Pd(II)–NH_2C_6H_5$ bond. The metal from this anchored complex was extracted by $PPh_3$ in a DMF medium (51). All this experimental evidence suggests the polymer contains only orthometalated complexes of palladium(II).

The ESCA and IR spectral data, the catalytic activities, and other physico-chemical properties of *1F* ($R = \mathrm{H}$), *2C*, and *2C′* suggest they contain the same catalytically active moieties, i.e. the mononuclear, four-coordinated orthometalated secondary amine complex of palladium(II).

*Catalytic activity.* All the complexes, *1F* ($R = \mathrm{H}$, $CH_3$, $C_6H_5$), *2C*, and *2C′* have comparable catalytic activities toward the reduction of nitroaromatics, aromatic aldehydes, alkenes, alkynes, and Schiff bases. The polymer compounds *1E* ($R = \mathrm{H}$, $CH_3$, $C_6H_5$), *2B*, and *2B′* are catalytically almost inactive at room temperature but their activities can be greatly enhanced and made comparable to that of the corresponding activated ones by initially heating the reaction mixture at 80°C for 45 min under hydrogen. The species *1F*, *2C*, and *2C′* do not require any activation period and start substrate reduction almost instantaneously with maximum speed. The catalysts *1F* ($R = \mathrm{H}$), *2C*, and *2C′* are comparable in their activities on the basis of Pd content (Table 4) but *1F* is superior due to its higher metal loading (Table 1). The activity of *2C′* is less than that of *2C* due to its very low metal loading. The detailed catalytic investigations were made with *1F* ($R = \mathrm{H}$) due to its highest efficiency (Table 4) and easy method of preparation. The highest activity of the catalysts was observed in DMF, followed by DMSO and ethyl acetate and the reduction rate slows down in stronger coordinated media like THF, $CH_3CN$, and PhCN, and the rate becomes immeasurably slow in noncoordinating media like $C_6H_6$, $C_6H_5CH_3$, $CHCl_3$, and $CCl_4$. Solvent coordination to the metal and its subsequent removal by a substrate molecule at intermediate stages appear essential for the reaction to proceed. The stronger and noncoordinating media cannot simultaneously satisfy the above two conditions and, hence, the reduction rate decreases in them.

**TABLE 4**

**Comparison of Catalytic Activities of *F* (*R* = H, CH₃, Ph)**

| | Catalyst | Substrate | Reaction time (h) | Initial turnover number ($\mathrm{min}^{-1}$) | Product | % yield |
|---|---|---|---|---|---|---|
| a. | *F* ($R = \mathrm{H}$) | Nitrobenzene | 2.5 | 3.90 | Aniline | 97 |
| | *F* ($R = CH_3$) | | 3.0 | 3.25 | | 96 |
| | *F* ($R = \mathrm{Ph}$) | | 4.0 | 2.43 | | 93 |
| b. | *F* ($R = \mathrm{H}$) | Styrene | 0.70 | 14.70 | Ethylbenzene | 98 |
| | *F* ($R = CH_3$) | | 0.85 | 12.40 | | 98 |
| | *F* ($R = \mathrm{Ph}$) | | 1.10 | 9.18 | | 96 |
| c. | *F* ($R = \mathrm{H}$) | Phenyl-acetylene | 0.81 | 13.10 | Ethylbenzene | 97 |
| | *F* ($R = CH_3$) | | 0.95 | 11.00 | | 97 |
| | *F* ($R = \mathrm{Ph}$) | | 4.0 | 8.15 | | 94 |
| d. | *F* ($R = \mathrm{H}$) | Benzaldehyde | 1.85 | 5.30 | Benzylalcohol | 98 |
| | *F* ($R = CH_3$) | | 2.10 | 4.45 | | 97 |
| | *F* ($R = \mathrm{Ph}$) | | 3.00 | 3.10 | | 93 |

*Note.* [sub] = 0.50 *M*; [cat] = $1.60 \times 10^{-3}$ g · atom $\mathrm{liter}^{-1}$, medium = DMF; $T = 25$°C; $PH_2 = 1$ atm. Total volume = 10 ml; yields refer to G.C. analysis.

The present catalyst system does not visibly swell in a mild coordinating solvent like DMF, or DMSO. Slight swelling has been observed in the THF medium in which catalytic activity is poor. As all experiments have been performed in a DMF medium, swelling is not viewed as a major factor in the present catalyst system.

The results of dihydrogen reduction of different substrates using the catalyst *1F* ($R = \mathrm{H}$) are presented in Table 4. Aromatic nitro-compounds are completely reduced to the corresponding anilines via the intermediate formation of corresponding hydroxylamine, without the formation of any coupled products at any intermediate or final stage. Hydroxylamine is reduced at a much faster rate than nitrobenzene. Steric crowding around the metal atom in the polymer matrix surely prevents simultaneous *cis*-coordination of different partially reduced nitroaromatics to the metal necessary for coupled product formation. The planar azobenzene is reduced only to hydrazobenzene. The latter, due to its nonplanar geometry is unable to coordinate to the metal atom in the polymer framework. Nitrobenzene or its *p*-substituted derivatives are hydrogenated at much faster rates and can be preferentially reduced almost to 100% when present along with *o*-substituted nitrobenzenes or nitronapthalene. Sequential reduction of *m*- and *p*-dinitrobenzenes occur to the extent of 90 and 95%, respectively (Fig. 3).

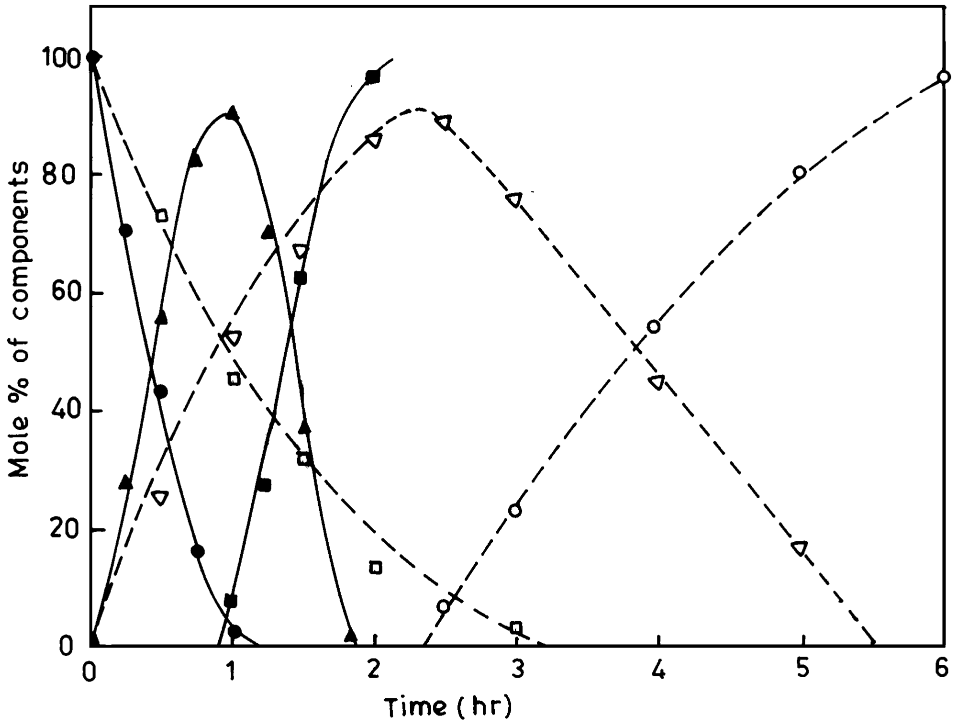


**FIG. 3.** Preferential reduction of phenylacetylene and *m*-dinitrobenzene. [cat] = $F$ ($R$ = H) = $1.60 \times 10^{-3}$ g · atom liter$^{-1}$. $PH_2$ = 1 atm; medium = DMF; total volume = 20 ml; $T$ = 25°C. [PhC≡CH] = 0.5 $M$; [$C_6H_4(NO_2)_2$] = 0.5 $M$. ● = Ph–C≡CH; ▲ = Ph–CH=$CH_2$; ■ = $PhCH_2CH_3$; □ = *m*-dinitrobenzene; △ = *m*-nitrohydroxylamine; ○ = *m*-phenelenediamine.

Hydrogenation of alk-1-enes occurs preferentially over isomerization. Preferential reductions of alk-1-enes to the extent of 90% are possible in presence of cyclic, internal, and branched chain alkenes and the latter ones are reduced at much slower rates. Isoprene is reduced stepwise first to 2-methyl 1-butene (98%) and finally to 2-methylbutane, indicating 1,2 addition at the initial stage. A double bond which is a part of delocalized system such as styrene is reduced more quickly than 1-hexene with a localized double bond. Maleic acid, fumeric acid, and *w*-nitrostyrene, containing vicinal electron withdrawing groups are reduced at much slower rates. These groups lower the electron density at >C=C<, thereby reducing its coordinating ability to metal atoms. This lowers the equilibrium concentration of metal-substrate complexes, resulting in decreased reduction rate. The sequential reduction of phenyl- and diphenylacetylene to the corresponding alkenes occurs to the extent of over 95% (Fig. 3). The reduction rates of the alkenes and alkynes do not differ much, but higher nucleophlicity of the alkynes favours their preferential binding to metal atoms. Only the aromatic aldehydes and ketones such as benzaldehyde and benzophenone could be reduced to the corresponding alcohol by this catalyst. The aliphatic carbonyl compounds could not be reduced to the corresponding alcohols by normal pressure hydrogen at varying temperatures. Benzaldehyde was reduced at a higher rate but its preferential reduction over benzophenone could not be observed to any appreciable extent when present in a mixture. Preferential reduction of *N*-methyl benzaldimine occurs to the extent of 100% in the presence of any nitroaromatics (Fig. 4). Probably >C=N– double bond of the planar Schiff base preferably coordinates to the metal more than the $-NO_2$ group and, hence, the former undergoes preferential reduction.

*Effect of acid and alkali on substrate reduction.* The reduction rate of nitrobenzene in the presence of acetic ($10^{-2}$ $M$) or hydrochloric acid ($10^{-3}$ $M$) decreased appreciably with the increased concentration of PhNHOH at intermediate stages. The cation, $PhNH_2^+OH$ formed in an acid medium cannot coordinate through the N atom and thus decreases the equilibrium concentration of an intermediate Pd(PhNHOH) adduct. The reduction rate is thereby decreased with the increased accumulation of (PhNHOH + $PhNH_2^+OH$) in the reaction mixture. The result suggests N coordination rather O coordination to the metal as the latter process should have no effect on the reduction rate and the concentration of the intermediate PhNHOH. Addition of alkali (~$10^{-3}$ $M$) has no noticeable effect. The reduction of any other substrate is not affected to any appreciable extent in the presence of dilute acid or alkali ($10^{-2}$ $M$).

The present catalyst system can reduce styrene and nitrobenzene to ethylbenzene and aniline, respectively, in DMF under $N_2$ at an ambient temperature. The IR spectra

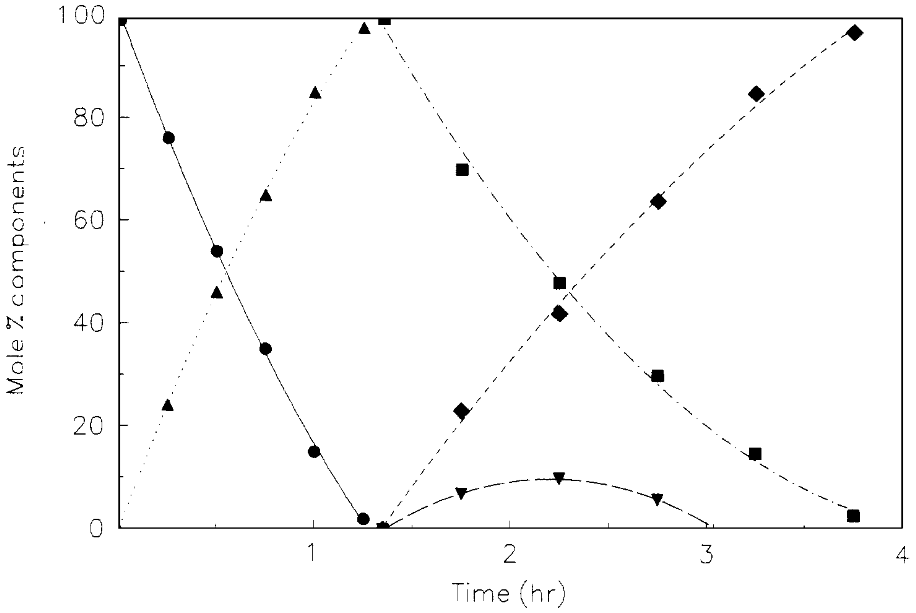
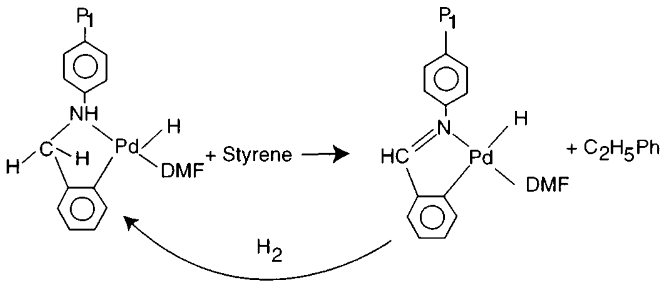


**FIG. 4.** Preferential hydrogenation of *N*-methylbenzaldimine and nitrobenzene. [cat] = $F$ ($R = \mathrm{H}$) = $1.60 \times 10^{-3}$ g · atom liter$^{-1}$. [Ph–CH=N–CH$_3$] = 0.5 *M*; PH$_2$ = 1 atm; medium = DMF; total volume = 20 ml; [PhNO$_2$] = 0.5 *M*; $T = 25$°C. ● = *N*-methylbenzaldimine; ▲ = *N*-methylbenzylamine; ■ = PhNO$_2$; ▼ = PhNHOH; ◆ = PhNH$_2$.

of the residual catalyst exhibit a shoulder at ∼1615 cm$^{-1}$ ($\nu$C=N, coordinated) at the cost of the peak at ∼1250 cm$^{-1}$ ($\nu$C–N, coordinated) present in IF. The bands at ∼1980 cm$^{-1}$ ($\nu$Pd–H), ∼1655 cm$^{-1}$ ($\nu$C=O, DMF), and ∼720 cm$^{-1}$ (orthometalation) remain unchanged. The observation suggests that during substrate reduction, the secondary amine complex is converted to a Schiff base complex with the transfer of hydrogen to the substrate. The Schiff base complex, in turn, may add a hydrogen molecule during hydrogenation to reform the secondary amine complex and, thus, complete the catalytic cycle as shown in Scheme 3.

The experimental observations suggest that the actual catalytic species to be secondary amine complexes of palladum(II), i.e., *1F*, *2C*, or *2C*′. During hydrogen activation the acetate bridges in *1E*, *2B*, and *2B*′ are replaced by Pd–H and Pd–DMF bonds while in *1E*, the >C=N– group is simultaneously reduced to >CH–NH–. The activity of the species *1F* varies with the nature of *R* in the order H > CH$_3$ > C$_6$H$_5$ (Table 4). The high dependence of activity on the nature of *R* suggests the involvement of –CR=N– group in the rate-determining step and it is sure that interconversion between –C*R*=N– and –CH*R*–NH– occurs during the reduction process as the catalyst after the run has been found to contain the –CH*R*–NH– group. The catalyst *1F* with $R = \mathrm{Ph}$ should be most stable due to extensive $\pi$-electron delocalization and the consequent planarity of the metal ligand ring, including the phenyl groups. Conversion of –CPh=N– to –CHPh–NH–, during hydrogenation will destroy the planarity with the simultaneous loss of $\pi$-electron delocalization. This will destabilize the resulting complex to a greater extent, compared to that when $R = \mathrm{H}$ or CH$_3$. Hence, the step involving H$_2$ addition to the –C*R*=N– group will be slowest for $R = \mathrm{Ph}$ and fastest for $R = \mathrm{H}$. This H$_2$ addition step is, therefore, considered to be the rate determining step.



**SCHEME 3**. Catalytic reduction of styrene and nitrobenzene under N$_2$.

The present system of catalysts, especially the species *1F*, appear to be very efficient and useful for organic synthesis and industrial reduction processes. The catalysts can be used repeatedly for the reduction of the same or different substrates or stored in a desiccator for a long time (kept more than 1 year in our laboratory) without any appreciable loss of activity. The system shows consistent activity in the reduction of substrates, even after the 10th recycle and the results for first, third, and fifth recycles are presented in Table 5. The results indicate the comparable activity of the fresh catalysts with the used ones.

The species *1F* appears to be superior to Pd–C (Arora Matthey) in the rate of reduction of substrates and percentage yields of products (Table 6). From the results in the table, the activities of *1F* and Pd–C appear to be comparable,

## TABLE 5

### Recycling of the Catalytic Species 1*F* (*R* = H) for Hydrogenation of Various Organic Substrates

| | | | | 1st recycle | | 3rd recycle | | 5th recycle | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Expt. no. | Substrate | Pd content (before run) g · atom · liter$^{-1}$ × $10^{-3}$ | Product(s) | Initial turnover number (min)$^{-1}$ | % yield | Initial turnover number (min)$^{-1}$ | % yield | Initial turnover number (min)$^{-1}$ | % yield | Pd content (after run) g · atom · liter × $10^{-3}$ |
| 1 | Nitrobenzene | 1.60 | Aniline | 3.90 | 97 | 3.89 | 97 | 3.89 | 97 | 1.60 |
| 2 | *p*-chloronitrobenzene | 1.60 | *p*-chloroaniline | 2.87 | 96 | 2.85 | 96 | 2.84 | 96 | 1.60 |
| 3 | *p*-dinitrobenzene | 1.60 | *p*-phenelenediamine | 1.68 | 95 | 1.67 | 95 | 1.64 | 95 | 1.60 |
| 4 | 1-nitronaphthalene | 1.60 | 1-aminonaphthalene | 1.45 | 94 | 1.43 | 94 | 1.40 | 94 | 1.60 |
| 5 | 6-nitrophthalide | 1.60 | 6-aminophthalide | 1.44 | 94 | 1.43 | 94 | 1.41 | 94 | 1.60 |
| 6 | Methyl 4,5-dimethoxy-2-nitrobenzoate | 1.60 | Methyl 4,5-dimethoxy-2-aminobenzoate | 1.50 | 96 | 1.48 | 96 | 1.47 | 96 | 1.60 |
| 7 | 1-hexene | 1.60 | Hexane | 7.70 | 96 | 7.70 | 96 | 7.65 | 95 | 1.60 |
| 8 | Cyclohexene | 1.60 | Cyclohexane | 5.70 | 98 | 5.69 | 98 | 5.69 | 97 | 1.60 |
| 9 | Benzaldehyde | 1.60 | Benzylalcohol | 5.30 | 98 | 5.25 | 98 | 5.24 | 98 | 1.60 |
| 10 | Fumaric acid | 1.60 | Succinic acid | 3.00 | 93 | 2.99 | 93 | 2.96 | 93 | 1.60 |
| 11 | Phenylacetylene | 1.60 | Ethylbenzene | 13.10 | 97 | 13.10 | 97 | 13.08 | 97 | 1.60 |
| 12 | *N*-methylbenzaldimine | 1.60 | *N*-methylbenzylamine | 6.60 | 100 | 6.59 | 100 | 6.59 | 100 | 1.60 |

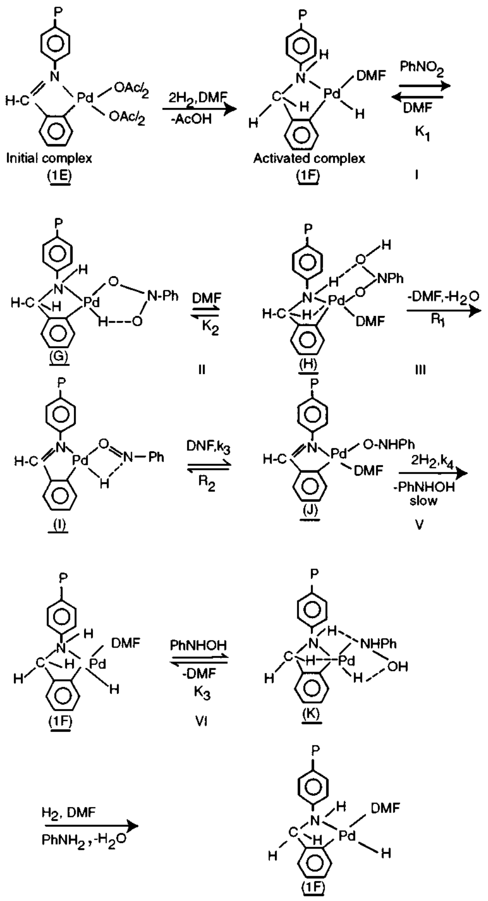
*Note*. [sub] = 0.50 *M*; [cat] = 1.60 × $10^{-3}$ g · atom liter$^{-1}$; medium = DMF; total volume = 10 ml; yields refer to G.C. analysis; $P_{H_2}$ = 1 atom.

## TABLE 6

### Comparison of Catalytic Activities of *1F* (*R* = H) and Pd–C under Normal Pressure Conditions

| | | | *1F* | | Pd–C | |
|---|---|---|---|---|---|---|
| Expt. no. | Substrate | Product(s) | Initial turn over number (min)$^{-1}$ | % yield | Initial turn over number (min)$^{-1}$ | % yield |
| 1 | Nitrobenzene | Aniline | 3.90 | 97 | 2.62 | 96 |
| 2 | *o*-chloronitrobenzene | *o*-chloroaniline | 2.37 | 94 | 1.26 | 93 |
| 3 | *o*-nitrotolune | *o*-toluidine | 2.06 | 92 | 1.06 | 90 |
| 4 | *p*-dinitrobenzene | *p*-pheneledíamine | 1.69 | 95 | 0.85 | 89 |
| 5 | *m*-dinitrobenzene | *m*-phenelenediamine | 1.40 | 95 | 0.74 | 88 |
| 6 | *p*-chloronitrobenzene | *p*-chloroaniline | 2.87 | 96 | 1.30 | 95 |
| 7 | *p*-nitrotolune | *p*-toluidine | 2.70 | 96 | 1.26 | 90 |
| 8 | 1-nitronaphthalene | 1-aminonaphthalene | 1.45 | 94 | 1.32 | 88 |
| 9 | 6-nitrophthalide | 6-aminophthalide | 1.44 | 94 | 0.66 | 86 |
| 10 | Methyl 4,5-dimethoxy-2-nitrobenzoate | Methyl 4,5-dimethoxy-2-aminobenzoate | 1.50 | 96 | 0.68 | 60 |
| 11 | Styrene | Ethylbenzene | 14.70 | 98 | 10.30 | 98 |
| 12 | 1-hexene | Hexane | 7.70 | 96 | 4.43 | 95 |
| 13 | Cyclohexene | Cyclohexane | 5.70 | 98 | 2.58 | 92 |
| 14 | *ω*-Nitrostyrene | *ω*-Nitroethylbenzene | 5.80 | 96 | 2.73 | 90 |
| 15 | Maleic acid | Succinic acid | 3.30 | 93 | 1.50 | 89 |
| 16 | Fumaric acid | Succinic acid | 3.00 | 93 | 1.48 | 88 |
| 17 | Isoprene | 2-methylbutane | 14.70 | 97 | 7.10 | 91 |
| 18 | Diphenylacetylene | 1,2-diphenylethane | 6.20 | 94 | 3.11 | 90 |
| 19 | Phenylacetylene | Ethylbenzene | 13.10 | 97 | 9.98 | 96 |
| 20 | Benzaldehyde | Benzylalcohol | 5.30 | 98 | 3.30 | 95 |
| 21 | Benzylidineaniline | *N*-phenylbenzylamine | 4.30 | 100 | 1.83 | 92 |
| 22 | *N*-methylbenzaldimine | *N*-methylbenzylamine | 6.60 | 100 | 2.7 | 92 |

*Note*. [sub] = 0.50 *M*; [cat] = [F, *R* = H] = [Pd–C] = 1.60 × $10^{-3}$ g · atom liter$^{-1}$; medium = DMF; total volume = 10 ml; yields refer to G.C. analysis; $P_{H_2}$ = 1 atom. Let the percentage of Pd in the catalyst be *X*; let the no. of g · atom of Pd per g. of catalyst = $X/100 \times 107$. Let the number of moles of substrate reduced by 1 g of catalyst per minute = *Y*. The turnover number = $Y/(X/100 \times 107) = Y \times 100 \times 107/X$.



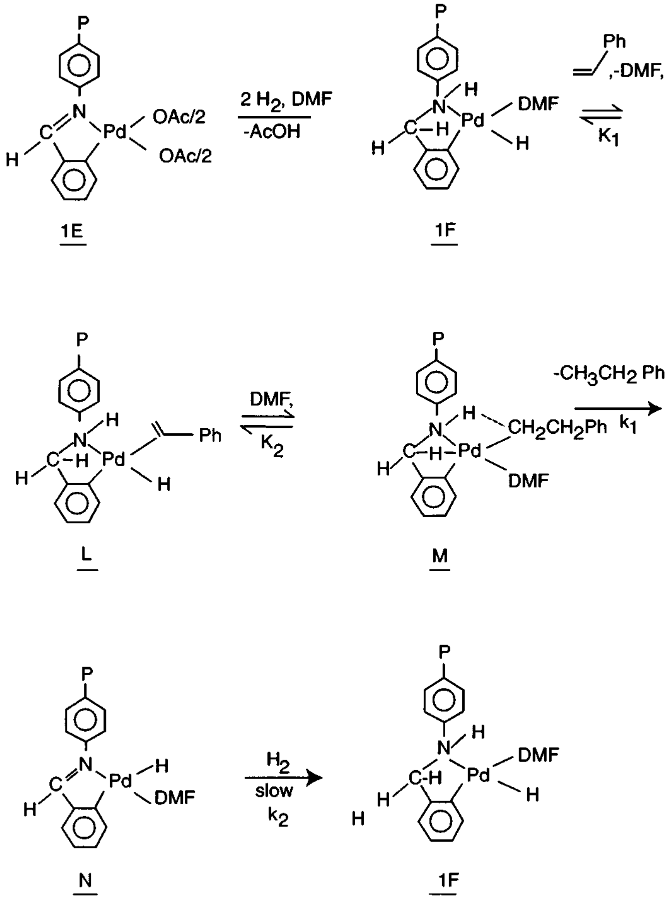
**SCHEME 4.** Reduction of nitrobenzene.

so far as the product selectivity is concerned, but *1F* is superior to Pd–C in the reduction rate and percentage yields of products. The superiority of *1F* is clearly discernible from entry 10 (Table 6) in which the methoxy substituted nitroester is shown to be reducible to its amine in high yields. The conventional hydrogenation of the nitroester over Pt or Pd–C provides variable yields of corresponding amines (52) and here we got only 60% yield using Pd–C.

*Kinetic studies.* The kinetic studies were done with *1F* ($R = H$) in DMF for the reductions of nitrobenzene, phenylhydroxylamine, and styrene at room temperature. The initial rate of hydrogen absorption was determined from the graphical extrapolation of the rate curve to $t = 0$ and the results were verified by GC analysis of the reaction mixture at different time intervals. In the case of nitrobenzene, the initial rate followed the first-order dependence on Pd content of the polymer-catalyst in the range of $1.00–5.00 \times 10^{-3}$ g atom/liter (Fig. 5), second-order dependence on $P_{H_2}$ in the range 200–1000 mm of Hg (Fig. 6) and independent of substrate concentration in the range 0.5–3.0 *M*. In the case of phenylhydroxylamine and styrene, the initial rate was first-order dependent on Pd content and $P_{H_2}$ and independent of the substrate concentration within the above-mentioned experimental parameters.

On the basis of kinetics and other experimental data the tentative mechanisms for the reduction of nitrobenzene and styrene have been presented in Schemes 4 and 5 respectively.

According to Scheme 4, the aceto-bridged orthometalated complex *1E*, reacts with hydrogen in DMF, producing the activated complex *1F* in which the bridge is replaced by hydrogen and DMF. The coordinated Schiff base in *1E* is reduced to form the corresponding secondary amine without any cleavage of the orthometalated bonds. Nitrobenzene combines with *1F* via oxygen donors, producing the species *G*. In DMF medium, *G* and *H* are in equilibrium. Interaction among the various atoms in *H* finally leads to the elimination of DMF and $H_2O$ reforming the orthometalated Schiff base complex *I*. Simultaneous abstraction of hydrogens from coordinated secondary amine in *H* by substrates and metal is responsible for this conversion. The transformation of *1F* to the corresponding Schiff base complex *N*, by $PhNO_2$ in DMF has been found by an isolated experiment (Scheme 3). The species *J* which is in equilibrium



**SCHEME 5.** Reduction of styrene.

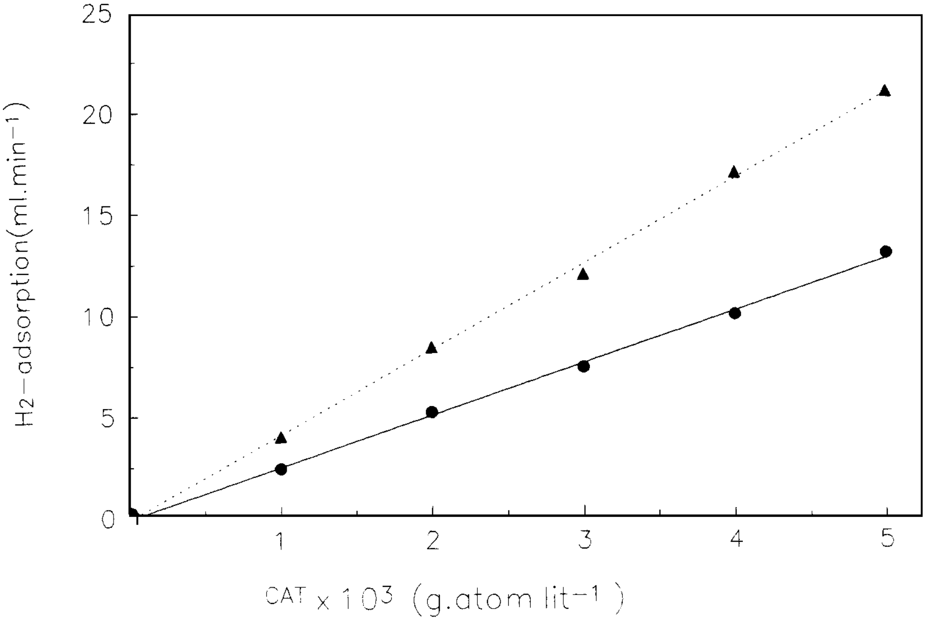


**FIG. 5.** Initial rate dependence on catalyst concentration: [cat] = F(*R* = H); [Ph–CH=CH$_2$] = 0.5 *M*; [PhNO$_2$] = 0.5 *M*; $P_{H_2}$ = 1 atm; medium = DMF; total volume = 10 ml; *T* = 25°C. ▲ = Ph–CH=CH$_2$; ● = PhNO$_2$.

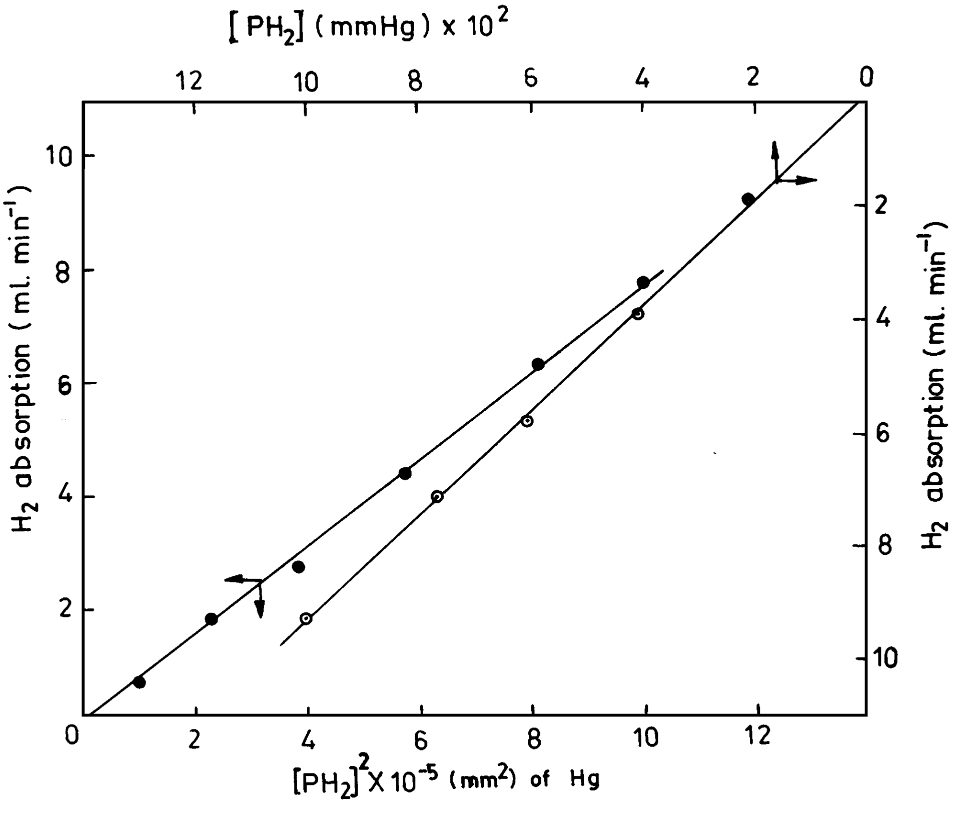


**FIG. 6.** Initial rate dependence on hydrogen pressure: [cat] = *F* (*R* = H) = 1.60 × $10^{-3}$ g · atom liter$^{-1}$; [Ph–CH=CH$_2$] = 0.5 *M*; [PhNO$_2$] = 0.5 *M*; medium = DMF; total volume = 10 ml, *T* = 25°C. ○ = Ph–CH=CH$_2$; ● = PhNO$_2$.

with *I* in a DMF medium reacts with hydrogen, regenerating *1F* with the simultaneous elimination of PhNHOH. This is probably the most complicated and slowest step of the present catalytic system. Phenylhydroxylamine is finally reduced to aniline in the presence of hydrogen as shown in Scheme 4.

During the reduction of styrene, the orthometalated Pd(II) in the activated complex *1F*, form the $\pi$-complex *L*, with styrene (Scheme 5). The species *L* is in equilibrium with *M* via DMF. Interaction of hydrogen atoms of the secondary amine with the substrate and metal as shown in *M* lead to the formation of the corresponding orthometalated Schiff base complex *N*, with the simultaneous elimination of $C_6H_5C_2H_5$. Slow hydrogenation of *N* regerates *1F* with the completion of the catalytic cycle. In both schemes, the hydrogenation of the Schiff base to the corresponding secondary amine is suggested to be the most complicated and slowest one.

According to Scheme 4,

$$\text{Rate} = k[\text{J}][\text{H}_2]^2$$
$$[\text{Cat}]_\text{T} = [\text{F}] + [\text{G}] + [\text{H}] + [\text{I}] + [\text{J}] + [\text{K}].$$

Putting the values of [F], [G], [H], [I], and [K] in terms of J, we have

$$[\text{Cat}]_\text{T} = \frac{\text{K}_1[\text{J}][\text{H}_2]^2}{[\text{PhNO}_2]} + \text{K}_2[\text{J}][\text{H}_2]^2 + \text{K}_3[\text{J}][\text{H}_2]^2 + \text{K}_4[\text{J}] + \text{K}_5[\text{J}][\text{H}_2]^2 + [\text{J}] + \text{K}_6\frac{[\text{J}][\text{H}_2]^2[\text{PhNHOH}]}{[\text{PhNO}_2]},$$

where $\text{K}_1, \text{K}_2, \ldots, \text{K}_6$ are all constants,

$$[\text{Cat}]_\text{T} = [\text{J}]\left[\frac{\text{K}_1[\text{H}_2]^2}{[\text{PhNO}_2]} + \text{K}_6\frac{[\text{H}_2]^2[\text{PhNHOH}]}{[\text{PhNO}_2]} + \text{K}_7 + \text{K}_8[\text{H}_2]^2\right]$$

where $\text{K}_7 = \text{K}_4 + 1$, $\text{K}_8 = \text{K}_2 + \text{K}_3 + \text{K}_5$;

$$[\text{J}] = \frac{[\text{Cat}]_\text{T}[\text{PhNO}_2]}{[\text{H}_2]^2\{\text{K}_1 + \text{K}_8[\text{PhNO}_2] + \text{K}_6[\text{PhNHOH}]\} + \text{K}_7[\text{PhNO}_2]}.$$

In the present investigation,

$$[\text{H}_2]^2 \approx 10^{-5}\,M, \quad [\text{PhNO}_2] = 0.5\,M$$
$$\text{J} = \frac{[\text{Cat}]_\text{T}}{\text{K}_7}$$
$$\text{Rate} = \text{K}'[\text{Cat}]_\text{T}[\text{H}]^2.$$

According to Scheme 5,

$$\text{Rate} = k_2[\text{N}][\text{H}_2]$$
$$[\text{Cat}]_\text{T} = [\text{F}] + [\text{L}] + [\text{M}] + [\text{N}].$$

Considering the steady-state equilibrium of [N],

$$[\text{Cat}]_\text{T} = \frac{\text{K}_5[\text{N}][\text{H}_2]}{[\text{S}]} + \frac{\text{K}_4[\text{N}][\text{H}_2]}{[\text{DMF}]} + \text{K}_3[\text{N}][\text{H}_2] + [\text{N}];$$

S = styrene;

$$[\text{N}] = \frac{[\text{Cat}]_\text{T}[\text{S}][\text{DMF}]}{[\text{H}_2]\{\text{K}_5[\text{DMF}]+\text{K}_4[\text{S}]+\text{K}_3[\text{S}][\text{DMF}]\}+[\text{S}][\text{DMF}]},$$

as $[\text{H}_2] = 10^{-3}\,M$, $[\text{Styrene}] = 1.0\,M$, $[\text{DMF}] \approx 13.0\,M$. So

$$[\text{N}] = \frac{[\text{Cat}]_\text{T}[\text{S}][\text{DMF}]}{[\text{S}][\text{DMF}]} = [\text{Cat}]_\text{T}$$
$$\text{Rate} = k_2[\text{Cat}]_\text{T}[\text{H}_2].$$

## CONCLUSION

The materials used in the present investigation are polystyrene-anchored orthometalated complexes of palladium(II) as evidenced from the appearance of the IR peak at ~720 cm$^{-1}$ and ESCA peaks at 338.25 ($3d_{5/2}$) and 343.75 ($3d_{3/2}$).

The specimen palladium can be repeatedly used for the reduction of the same or different substrates without diminished catalytic activity or metal content. The catalyst appears to be superior to Pd–C in (i) the reduction rate of the substrate and (ii) the reduction of methyl 4,5-dimethoxy 2-nitrobenzoate. These properties make the present catalyst system superior to palladium charcoal used for the reduction of organic substrates.

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