Catal Lett
DOI 10.1007/s10562-014-1269-6

Iron and Palladium(II) Phthalocyanines as Recyclable Catalysts for Reduction of Nitroarenes

Praveen Kumar Verma · Manju Bala · Kavita Thakur · Upendra Sharma · Neeraj Kumar · Bikram Singh

Received: 11 February 2014 / Accepted: 30 April 2014

Abstract Iron(II) and palladium(II) phthalocyanines have been established as recyclable heterogeneous catalysts for the reduction of aromatic nitro compounds to corresponding amines using diphenylsilane/sodium borohydride as hydrogen sources in ethanol. Various reducible functional groups, such as acetyl, ester, cyano, amide, sulphonamide and carboxylic acid etc. were well tolerated, and the methods were applicable up to gram scale. Mechanistic studies showed that reduction of nitro group proceed through direct (nitroso) pathway and possibly iron or palladium phthalocyanines activates nitro group for reduction. FePc and PdPc also catalyzed the generation of hydrogen from the combination of diphenylsilane/sodium borohydride and ethanol.

CSIR-IHBT Communication No. 3564.

Electronic supplementary material The online version of this article (doi:10.1007/s10562-014-1269-6) contains supplementary material, which is available to authorized users.

P. K. Verma · M. Bala · K. Thakur · U. Sharma · N. Kumar · B. Singh (✉)
Natural Plant Products Division, CSIR-Institute of Himalayan Bioresource Technology, Palampur 176 061, Himachal Pradesh, India
e-mail: bikramsingh@ihbt.res.in; bikram_npp@rediffmail.com

P. K. Verma · M. Bala · B. Singh
Academy of Scientific & Innovative Research, CSIR-Institute of Himalayan Bioresource Technology, Palampur 176 061, Himachal Pradesh, India

U. Sharma
Department of Chemistry, Korea Advanced Institute of Science & Technology (KAIST), Daejeon 305-701, South Korea

Keywords Iron(II) phthalocyanine · Palladium(II) phthalocyanine · Diphenyl silane · Sodium borohydride · Nitro compounds

1 Introduction

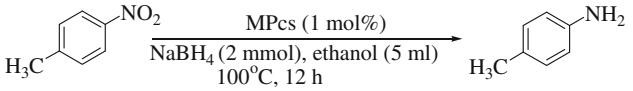
The hydrogenation of nitroarenes to amines is one of the important reactions in synthetic organic chemistry [1–3] and industrially applied for the synthesis of dyes, bioactive compounds and agricultural chemicals [4]. Total synthesis of numerous pharmaceuticals (Fig. S1, see supporting information) such as sildenafil [5], antibiotic linezolid [6], the HIV protease inhibitor amprenavir [7] and nimesulide [8] involve reduction of nitro group as the key step. Apart from the traditionally used non-catalytic processes like Bechamp or sulphide reduction [9], currently, transition metals are frequently used for the selective reduction of nitroarenes [10]. Transition metals such as Ni [11], Sn [12, 13], Cu [14], Co [14, 15], Zn [16–20], Au [21–29], Pd [30–33], Sm [34–36], Mo [37, 38], Re [39], Rh [40, 41] Ir [42] etc. has been widely explored for the reduction of nitroarenes. In recent years, iron due to its abundant availability has been extensively applied for various catalytic methods [43–50] and palladium complexes showed remarkable efficiency towards reduction reactions [51–55]. Moreover, iron compounds are relatively non-toxic, and inexpensive.

Although, combination of iron [43–49] and palladium [30–33] catalysts has been applied for this conversion, however, use of phosphine ligand, low yield of amines and lack of selectivity limit their scope.

Recently, metal phthalocyanines (MPcs) have been studied for their catalytic potential due to their cyclic tetradentate framework, which helps in electron transport mechanism for various redox reactions [56]. Additionally,

Published online: 23 May 2014

Table 1 Screening of MPcs and their corresponding salts for the reduction of 4-nitrotoluene



Entry	Catalyst	Conv.(%)[a]	Sel.(%)[a]
1	–	NR	–
2	Fe(II)Pc	66	61
3	$Fe(OAc)_2$	28[b]	51
4	Fe(III)Pc	41[b]	33
5	$FeCl_3$	46	>99
6	Co(II)Pc	99[b]	–
7	$Co(II)Pc(t\text{-}Bu)_4$	96[b]	1
8	$CoCl_2$	20	15
9	Ni(II)Pc	14	10
10	$NiCl_2$	37[b]	7
11	Cu(II)Pc	22[b]	2
12	$CuSO_4$	43	>98
13	Zn(II)Pc	35	95
14	$ZnCl_2$	NR	–
15	Mg(II)Pc	65[b]	2
16	$MgCl_2$	4	–
17	Al(III)PcOH	95[b]	–
18	$A1C1_3$	7	50
19	Pd(II)Pc	98	>99
20	$Pd(OAc)_2$	>99[b]	–

Reaction conditions: 4-nitrotoluene (1 mmol), $NaBH_4$ (2 mmol), catalyst (1 mol%), EtOH (5 mL), and 100 °C temperature for 12 h

[a] Determined by GC using *n*-hexadecane as internal standard; and also confirmed by GC–MS

[b] Intermediates were formed as major products (see Supporting information Table S1)

they are highly stable towards heat, moisture, acidic and/or basic conditions. More importantly MPcs works as heterogeneous recyclable catalysts without the need of any external ligands as they itself acts as fabulous ligands.

In this context, recently, apart from the synthesis of MPcs [57] we have reported their catalytic applications for various important organic transformations [14, 57–63]. In addition, during our studies, we observed iron and palladium phthalocyanines (FePc and PdPc) in combination with diphenylsilane and sodium borohydride, respectively, provided the best results for the reduction of aromatic nitro compounds to corresponding amines.

Herein, we disclose two new methods, first, selective reduction of nitro compounds using inexpensive, highly stable and abundantly available FePc with Ph_2SiH_2 in ethanol, and secondly, highly efficient PdPc with NaBH4 for the same reduction process. PdPc has been applied for the first time for reduction process.

2 Experimental

2.1 General Information

Metal salts used were purchased from Merck, Germany. Iron phthalocyanines, palladium phthalocyanine, nitro compounds, sodium borohydride and silanes were purchased from Sigma to Aldrich USA. Silica gel (60–120 mesh) used for column chromatography was purchased from Sisco Research Laboratories Pvt. Ltd. India and all other chemicals were purchased from Spectrochem, India, Merck, Germany, and Sigma-Aldrich, USA and were used without further purification. NMR spectra were recorded on a Bruker Avance-300 and Bruker Avance-600 spectrometer. Mass spectra were recorded on QTOF-Micro of Waters Micromass. The GC and GC–MS analysis was carried out on a Shimadzu (QP 2010) series Gas Chromatogram-Mass Spectrometers (Tokyo, Japan), AOC-20i auto-sampler coupled, and a DB-5MS capillary column, (30 m × 0.25 mm *i.d.*, 0.25 μm). The initial temperature of column was 70 °C held for 4 min and was programmed to 230 °C at 4 °C/min., then held for 15 min at 230 °C; the sample injection volume was 2 μL in GC grade dichloromethane. Helium was used as carrier gas at a flow rate of 1.1 mL min-1 on split mode (1: 50). Melting points were determined on a Barnstead Electrothermal 9100.

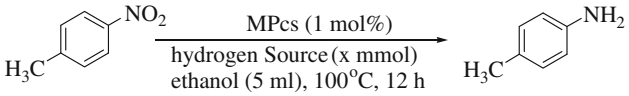
2.2 General Experimental Procedure for FePc Catalyzed Reduction of Nitro Compounds

To a stirred suspension of FePc (1 mol%) and diphenyl silane (3 mmol) in ethanol (5 mL) were added nitro compounds (1.0 mmol) at room temperature and then temperature was raised to 100 °C for 24 h. On completion of the reaction (as monitored by TLC), reaction mixture was filtered and passed through anhydrous Na_2SO_4 and dried under vacuum. The GC conversions and yields were determined by internal standard technique. The isolation of anilines was carried out by column chromatography on silica-gel (60–120) with appropriate mixture of *n*-hexane and ethyl acetate as an eluent.

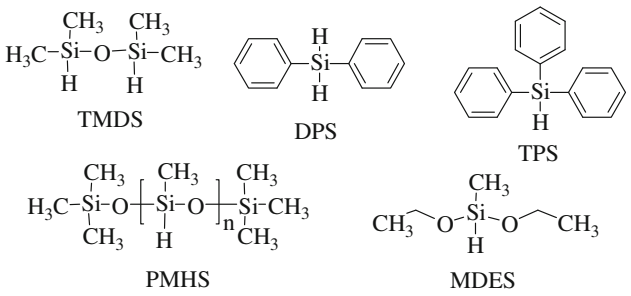
2.3 General Experimental Procedure for PdPc Catalyzed Reduction of Nitro Compounds

To a stirred suspension of PdPc (1 mol%) and $NaBH_4$ (2 mmol) in ethanol (5 mL) were added nitro compounds (1.0 mmol) at room temperature and then temperature was raised to 100 °C for 12 h. On completion of the reaction (as monitored by TLC), reaction mixture was filtered and passed through anhydrous Na_2SO_4 and dried under vacuum. The GC conversions and yields were determined by internal standard technique. The isolation of anilines was

Table 2 Screening of hydrogen sources with Pd(II)Pc and Fe(II)Pc for the reduction of 4-nitrotoluene



Entry	Hydrogen Source(mmol)	FePc		PdPc	
		Conv.(%)[a]	Sel.(%)[a]	Conv.(%)[a]	Sel.(%)[a]
1	–	NR	–	NR	–
2	CaH (2)	NR	–	NR	–
3	$Na(CN)BH_3$ (2)	10	64	<1	traces
4	$NaBH_4$ (2)	66	61	98	>99
5	NaH (2)	86	37	57	6
6	$NH_2–NH_2.H_2O$ (2)	59	>99	<1	traces
7	HCOOH (2)	NR	–	NR	–
8	HCOOK (2)	NR	–	27	>99
9	$HCOONH_4$ *(2)*	NR	–	NR	–
10	DPS (2)	54	>99	23	78
11	TPS (2)	3	>99	NR	–
12	PMHS (2)	7	>99	<1	traces
13	MDES (2)	12	>99	<1	traces
14	TMDS (2)	4	>99	NR	–



Reaction conditions: 4-nitrotoluene (1 mmol), hydrogen source (2 mmol), PdPc or FePc (1 mol%), EtOH (5 mL), and 100 °C temperature for 12 h

[a] Determined by GC using *n*-hexadecane as internal standard; and also confirmed by GC–MS

carried out by column chromatography on silica-gel (60–120) with appropriate mixture of *n*-hexane and ethyl acetate as an eluent.

3 Results and Discussion

3.1 Optimization Studies

Various combinations of catalysts, hydrogen sources and solvents were screened to access the best reaction conditions for the reduction of 4-nitrotoluene.

3.1.1 Catalysts Screening

Different MPcs and their corresponding metal salts were screened to find the best catalyst for the reduction of 4-nitrotoluene to corresponding amine with $NaBH_4$ in ethanol (Table 1). As expected reaction did not initiate without catalyst (Table 1, entry 1). Fe(II)Pc showed some promising results out of the tested iron catalysts (Table 1, entries 2–5). Excellent conversion was observed with Co(II)Pc and Co(II)Pc(*t*-Bu)$_4$, however, reaction halted at intermediate stage and did not provide the desired product (Table 1, entries 6–7). The corresponding cobalt salt ($CoCl_2$) was also not found to be effective for the reaction (Table 1, entry 8). Ni(II)Pc, Cu(II)Pc, Zn(II)Pc, Mg(II)Pc, Al(III)PcOH and their corresponding metal salts did not give the satisfactory conversions and selectivities for the desired product (Table 1, entries 9–18). In case of Pd(II)Pc excellent conversion and selectivity was observed (Table 1, entry 19). The corresponding salt, $Pd(OAc)_2$ of Pd(II)Pc also provided the excellent conversion, albeit, reaction stopped at intermediate stage without yielding the desired product (Table 1,

entry 20). Hence, out of the tested MPcs, Fe(II)Pc and Pd(II)Pc afforded the satisfactory results for the reduction of 4-nitrotoluene to corresponding amine and selected for further study.

3.1.2 Screening of Hydrogen Source

After MPcs screening, different hydrogen sources were tested for the reduction of 4-nitrotoluene with selected Pd(II)Pc and Fe(II)Pc (Table 2). As expected, reaction did not proceed without hydrogen source (Table 2, entry 1). CaH_2, HCOOH and $HCOONH_4$ were completely ineffective for the present reduction process (Table 2, entries 2, 7 and 9). Traces to moderate yields were observed with $Na(CN)BH_3$, NaH, NH_2-$NH_2.H_2O$, and HCOOK by both of the MPcs (Table 2, entries 3, 5, 6 and 8). Good yield was observed with $NaBH_4$ by Pd(II)Pc and moderate by Pd(II)Pc (Table 2, entry 4). Various silanes were also tested for the present reaction by both of the selected MPcs. Very low yields were observed with triphenyl silane (TPS), polymethylhydrosiloxane (PMHS), methyldiethoxysilane (MDES) and 1,1,3,3-tetramethyldisiloxane (TMDS) by both of the MPcs (Table 2, entries 11-14). Diphenyl silane (DPS) provided the low yield with Pd(II)Pc, while, moderate yield was observed with Fe(II)Pc for the present reaction (Table 2, entry 10). Hence, on the basis of the results obtained by screening of various MPcs and hydrogen sources it has been postulated that two methods including Pd(II)Pc with NaBH4 and Fe(II)Pc with DPS provided the best results for reduction of 4-nitrotoluene to corresponding amine.

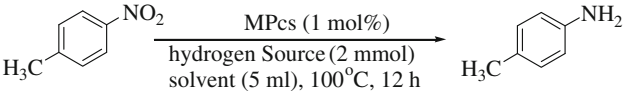
3.1.3 Solvent Screening

Various green solvents were tested for the FePc and PdPc catalyzed reduction of 4-nitrotoluene. Reaction did not proceed in water with both the catalysts (Table 3, entry 1), might be due to the insolubility of reactants. PEG-400, EG, and 1,4-dioxane did not provide the satisfactory results for the present reaction (Table 3, entries 4-6). Moderate conversion and excellent selectivity was observed with ethanol by FePc, while, PdPc provide the desired product with excellent conversion and selectivity (Table 3, entry 2). In the GC–MS analysis of FePc catalyzed reaction it was observed that DPS remains unutilised, hence, we further increased the reaction time up to 24 h that gave the desired product with high conversion and excellent selectivity (Table 3, entry 3).

3.1.4 Optimization of DPS and NaBH4 Quantity

In order to optimize the minimum amount of hydrogen sources required for FePc and PdPc catalyzed nitro reduction process, different amount of DPS and $NaBH_4$ were examined with the respective MPcs. It was observed that 3 mmol of DPS and 2 mmol of $NaBH_4$ were required for the reduction of 4-nitrotoluene to corresponding amine (Fig. S2, see supporting information).

Table 3 Screening of solvent for the reduction of nitro compounds



Entry	Solvent	Conv./Sel.(%)[a] FePc/DPS[b]	Conv./Sel.(%)[a] PdPc/$NaBH_4$
1	Water	NR	NR
2	Ethanol	54/> 99	98/> 99
3	Ethanol	84/> 99[b]	
4	PEG-400	80/38	75/1
5	EG	50/99	72/63
6	1,4-Dioxane	75/70	21/< 1

Reaction condition: 4-nitrotoluene (1 mmol), $NaBH_4$ or DPS (2 mmol), FePc or PdPc (1 mol%), solvent (5 mL), and 100 °C temperature for 12 h

PEG-400 polyethylene glycol-400, *EG* ethylene glycol

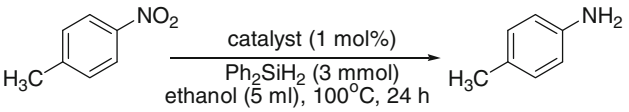
[a] Determined by GC using *n*-hexadecane as internal standard; and also confirmed by GC–MS

[b] Reaction time 24 h

3.2 Fe(II)Pc/DPS Catalyzed Reduction of Nitro Compounds

After the screening of MPcs, hydrogen sources and solvents, we also investigated the effect of other iron based catalysts for their comparison with FePc under the optimized conditions (Table 4). It was observed that various iron salts gave

Table 4 Comparison of Fe(II)Pc with other iron based catalysts for reduction of 4-nitrotoluene



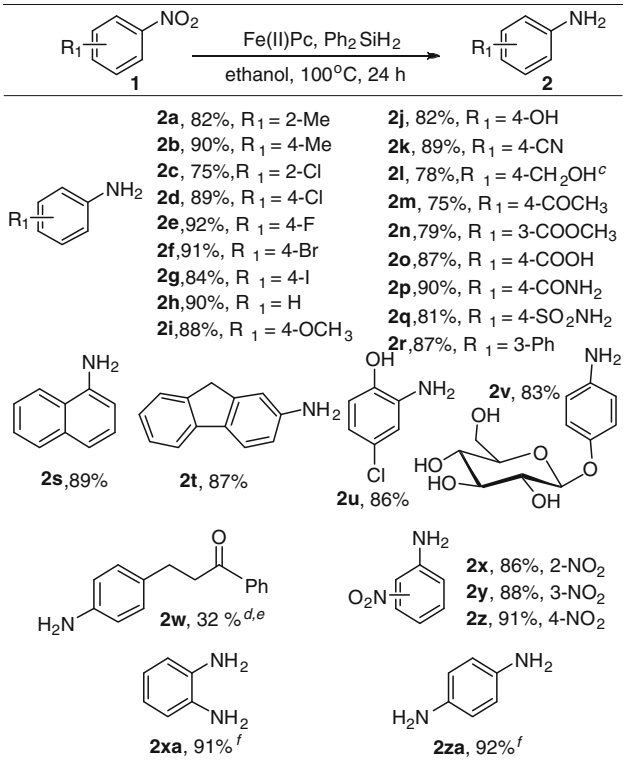
Entry	Catalyst	Yield (%)[a]
1	$FeSO_4$	38
2	$FeCI_3$	10
3	Fe metal	2
4	K_3FeCN_6	5
5	Fe_2O_3	7
6	$Fe(OAc)_2$	36
7	Fe(ll)Pc	91
8	Fe(lll)Pc	8

Reaction conditions: 4-nitrotoluene (1 mmol), DPS (3 mmol), catalyst (1 mol%), EtOH (5 mL), and 100 °C temperature for 24 h

[a] Determined by GC using *n*-hexadecane as internal standard; and also confirmed by GC–MS

low yields of the desired product as compared to excellent yield by Fe(II)Pc (Table 4, entries 1-7). Fe(III)Pc also provided the desired product in low yield (Table 4, entry 8). With the optimized conditions in hand, the scope of the FePc catalyzed method was investigated for the reduction of various substituted nitro compounds (Table 5). 2- and 4-Nitrotoluenes was effectively reduced to corresponding anilines with high yields (Table 5, entries 2a and 2b). Halogen substituted nitroarenes (F, Cl, Br, I) were efficiently reduced to corresponding anilines in high yields (Table 5, entries 2c–2 g). Importantly, no dehalogenation or decomposition was observed in any case, often encountered with several reduction methods [64–66]. Nitrobenzene was hydrogenated to aniline in good yield (Table 5, entry 2 h). The methoxy and hydroxyl substituted nitroarenes were reduced to corresponding amines in high yields (Table 5, entries 2i–2j). Interestingly, in contrast to some previous reports, high yield [39, 43] and selectivity [67] of

Table 5 Fe(II)Pc catalyzed reduction of various aromatic nitro compounds[a,b]



[a] Reaction condition: nitro compound (1 mmol), Ph_2SiH_2 (3 mmol), Fe(II)Pc (1 mol%), EtOH (5 mL), and 100 °C temperature for 24 h

[b] Isolated yields

[c] Both aldehyde and nitro group were reduced

[d] Both carbon-carbon double bond and nitro group were reduced

[e] 61 % Only carbon-carbon double bond reduced product obtained

[f] Both nitro groups were reduced using 6 equiv. of DPS

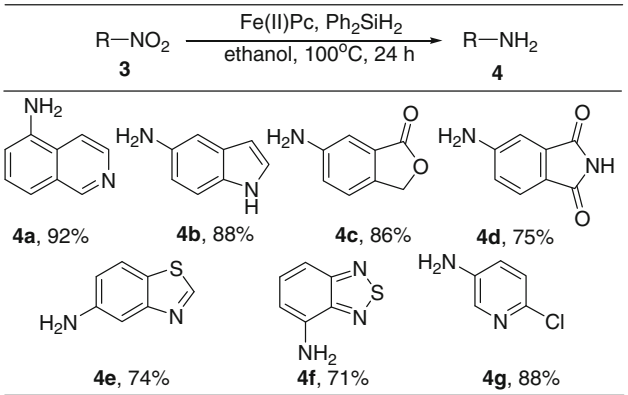
4-cyanoaniline were observed under the present reaction condition (Table 5, entry 2 k). In case of 4-nitrobenzaldehyde, both nitro and aldehyde functional groups were reduced by present protocol (Table 5, entry 2 l). Notably, the other reducible functionalities such as acid, ketone, ester, amide and sulfonamide remain intact during the reduction (Table 5, entries 2 m-2q). The reduction of m-phenylnitrobenzene gave desired product in good yield (Table 5, entry 2r). The reduction of 1-nitronaphthalene, 2-nitrofluorene [43] and 4-chloro-2-nitrophenol afforded the corresponding amines in good yields (Table 5, entries 2s–2u). The present protocol was also applicable for complex nitro compounds. The reduction of 4-nitrobenzene-β-D-glucopyranoside provided the corresponding amine in good yield (Table 5, entry 2v). In case of 4-nitrochalcone, mixture of product was observed corresponding to double bond reduction along with nitro group (Table 5, entry 2w). Regioselective reduction of dinitro compounds is one of the challenging tasks for the development of reduction methodologies. Under present reaction conditions, *o*-, *m*- and *p*-dinitrobenzenes were regioselectively reduced to corresponding mono amines [20, 68–73] in good to high yields (Table 5, entries 2x–2z). Interestingly, when reaction of dinitro compound was carried out with the doubled of the optimized amount of DPS, both nitro groups were reduced to corresponding diamines in excellent yields (Table 5, entries 2xa and 2za). Unfortunately, in case of aliphatic nitro compounds, promising results were not observed for the reduction of nitro group under present reaction conditions (Table S2, entries 1 and 2, see supporting information).

Present reaction conditions are also applicable for the reduction of nitro-substituted heteroaromatics (Table 6). The reduction of 5-nitroisoquinoline and 5-nitroindole gave the desired products in high yields (Table 6, entries 4a and 4b). Also, high chemoselectivity was observed for nitro group over carbonyl group in case of 5-nitrophthalide and 4-nitrophthalimide (Table 6, entries 4c and 4d). The deoxygenation of 6-nitrobenzothiazole and 4-nitrobenzothiadiazole was achieved in good yields (Table 6, entries 4e and 4f) to afford the biologically important precursors [74–76] 6-aminobenzothiazole and 4-aminobenzothiadiazoles. The reduction of 2-chloro-5-nitropyridine afforded the desired product in high yield (Table 6, entry 4 g).

3.3 Pd(II)Pc/$NaBH_4$ Catalyzed Reduction of Nitro Compounds

Various palladium salts and complexes were screened to compare their catalytic activity with Pd(II)Pc catalyzed nitro reduction process (Table 7). Excellent conversion and selectivity was observed with $PdCl_2$ (Table 7, entry 2), however, $Pd(OAc)_2$ from which PdPc was prepared

Table 6 Fe(II)Pc catalyzed reduction of various heteroaromatic nitro compounds

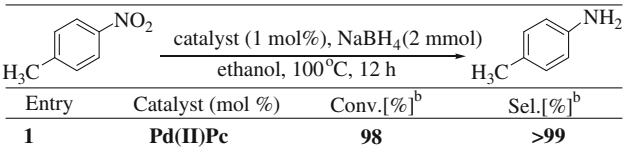


Reaction conditions: nitro compound (1 mmol), Ph_2SiH_2 (3 mmol), Fe(II)Pc (1 mol%), EtOH (5 mL), and 100 °C temperature for 24 h. Isolated yields

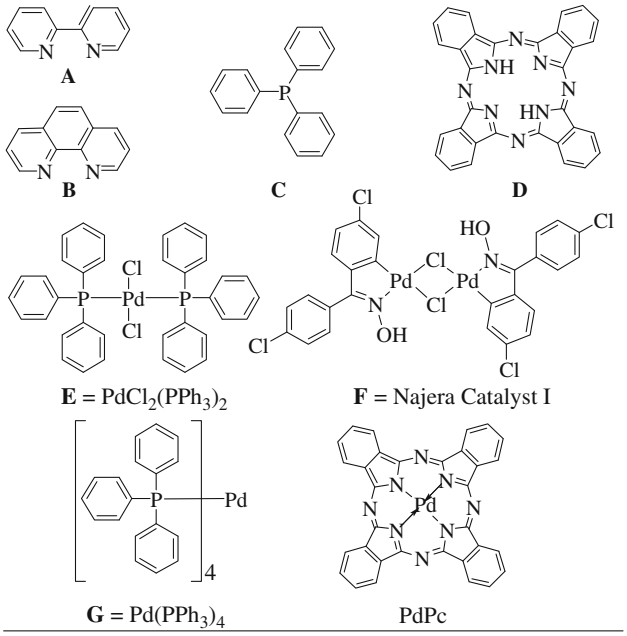
afforded the reaction intermediates as major products (Table 7, entry 3). Excellent conversion and selectivity were observed with PdPc (Table 7, entry 1). The combination of $Pd(OAc)_2$ with other ligands (A–D) provided the excellent conversion and high selectivity for the desired product (Table 7, entries 4–7). Reaction was also carried out with three palladium complexes (E–G) to compare with PdPc, however, acceptable results were not observed (Table 7, entries 8–10). Hence, PdPc was selected for the further study.

The scope of PdPc catalyzed method was investigated by the reaction of various substituted nitro compounds (Table 8). Excellent yields were observed for the reduction of nitrobenzene and 4-nitrotoluene (Table 8, entries 6a and 6b). In case of nitro benzaldehydes, both carbaldehyde and nitro groups were reduced to corresponding amino alcohols (Table 8, entries 6c and 6d). The high yields for amino alcohols proposed the present method to be well suited for the one step double reduction of nitro benzaldehydes. The methoxy, cyano and amide substituted nitro benzenes afforded the desired products in good to excellent yields (Table 8, entries 6e–6g). Good yield of corresponding product was observed for tri-substituted chloronitrophenol (Table 8, entry 6h). The reduction of 2-nitrofullerene gave the desired product in moderate yield (Table 8, entry 6i). In case of 4-nitrochalcone, the reduction of nitro as well as carbon–carbon double bond occurred in excellent yield (Table 8, entry 6j). High selectivity was observed for the reduction of nitro group in case of 7-nitro-3,4-benzocoumarin, however, product was obtained in moderate yield (Table 8, entry 6 k). Transesterified amino product was observed for the reduction of methyl-3-nitrobenzoate

Table 7 Screening of palladium catalysts for the reduction of nitro compounds[a]



Entry	Catalyst (mol %)	Conv.[%][b]	Sel.[%][b]
1	**Pd(II)Pc**	**98**	**>99**
2	$PdCl_2$	>99	86
3	$Pd(OAc)_2$	>99[c]	-
4	$Pd(OAc)_2$/A	>99	88
5	$Pd(OAc)_2$/B	>99	74
6	$Pd(OAc)_2$/C	>99[c]	84
7	$Pd(OAc)_2$/D	98	77
8	E	93[c]	9
9	F	97[c]	70
10	G	82[c]	25



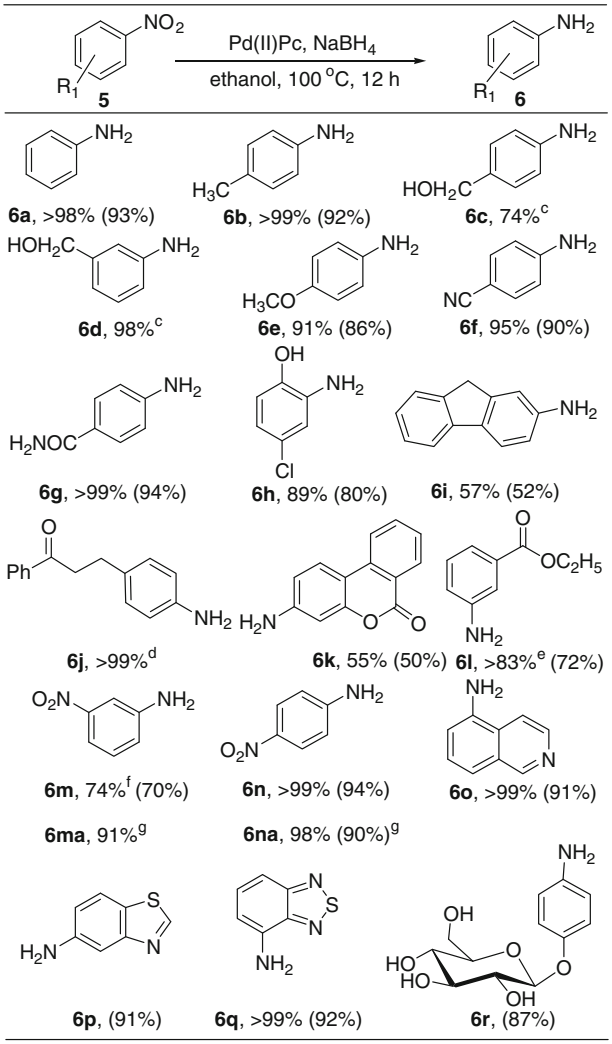
[a] Reaction condition: 4-nitrotoluene (1 mmol), $NaBH_4$ (2 mmol), catalyst (1 mol%), EtOH (5 mL), and 100 °C temperature for 12 h

[b] Determined by GC using *n*-hexadecane as internal standard; and also confirmed by GC–MS

[c] Intermediates were formed as other products

(Table 8, entry 6l). High regioselectivity was observed for the reduction of 1,3- and 1,4-dinitrobenzenes along with good to excellent yields (Table 8, entries 6m and 6n). In case of 1,3-dinitrobenzene 25 % of 1,3-diaminobenzene was also observed (Table 8, entry 6m). When reaction of dinitro compounds was carried out with doubled of the optimized amount of $NaBH_4$ (4 equiv.), the reduction of both nitro compounds was observed (Table 8, entries 6ma and 6na). Hence, present method can efficiently be utilized for the synthesis of diamines which are the precursors for the synthesis of various heterocyclic compounds. Present method

Table 8 Scope for the PdPc catalyzed reduction of nitro compounds[a,b]



[a] Reaction conditions: nitro compound (1 mmol), $NaBH_4$ (2 mmol), Pd(II)Pc (1 mol%), EtOH (5 mL), and 100 °C temperature for 12 h

[b] Determined by GC using *n*-hexadecane as internal standard; and also confirmed by GC–MS. Isolated yields given in parentheses

[c] Both aldehyde and nitro group were reduced

[d] Both carbon–carbon double bond in side chain and nitro group were reduced

[e] Transesterification of nitro reduced product was also occurred

[f] 25 % of diaminobenzene was observed

[g] Both nitro group were reduced using 4 equiv. of $NaBH_4$

was also applicable for the chemoselective reduction of heterocyclic nitro compounds such as 5-nitroisoquinoline, 5-nitrobenzothiazole and 4-nitrobenzothiadiazole in high yields (Table 8, entries 6o–6q). The reduction of 4-nitrobenzene-*β*-D-glucopyranoside afforded the corresponding amine in good yield (Table 8, entry 6r). The reduction of aliphatic nitro compounds was not observed under the present reaction conditions (Table S2, entries 1 and 2).

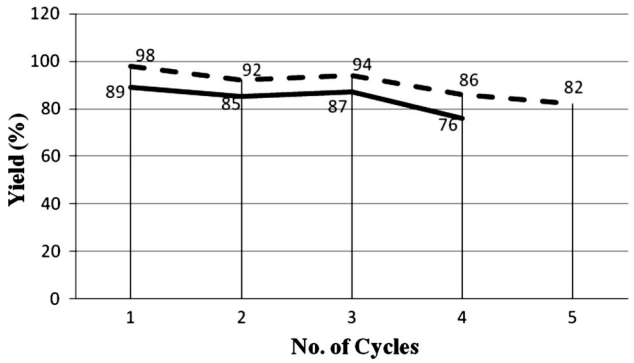
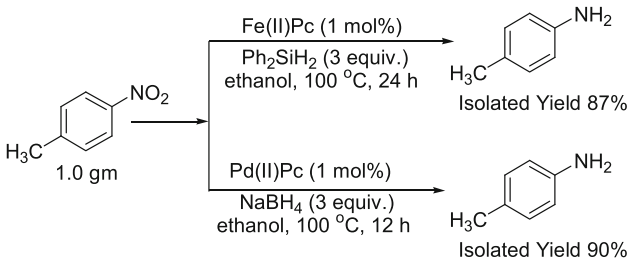


Fig. 1 Recycling of catalyst FePc (*dahsed line*) and PdPc (*hyphenated line*)



Scheme 1 FePc and PdPc catalyzed reduction of 4-nitrotoluene on gram scale

3.4 Recyclability of Catalysts

The recyclability of FePc and PdPc catalysts was evaluated by successive addition of 4-nitrotoluene and respective hydrogen sources (DPS or $NaBH_4$) and solvent to the residue (see supporting information). FePc was recycled up to four times, while, PdPc was recycled up to five times without any significant loss of activity (Fig. 1).

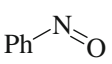
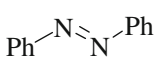
3.5 Gram Scale Reactions

Further, the two methods were successfully scaled-up to 1.0 g with 4-nitrotoluene (Scheme 1, FePc method; yield 87 % for 1.0 g *vs* 90 % for 1 mmol scale and PdPc method, yield 90 % for 1.0 g *vs* 92 % for 1 mmol scale). Although, 3 mmol of $NaBH_4$ was taken for 1.0 g scale reaction by PdPc catalyzed method.

3.6 Mechanistic Study

In order to get insight, which pathway (direct route and condensation route) [77] is going under present condition, reduction of the possible reaction intermediates i.e., nitrosobenzene (direct route intermediate) and azobenzene (condensation route intermediate), was carried out under the standard reaction condition for two methods. For FePc catalyzed method, nitrosobenzene provided aniline in 87 %

Table 9 Hydrogenation of probable reaction intermediates

Entry	Substrate				Time (h) FePc/PdPc	Yield of aniline[a] FePc/PdPc
1	1		6/4	87 %/92 %	6/4	87 %/92 %
2	2		12/8	18 %/59 %	12/8	18 %/59 %

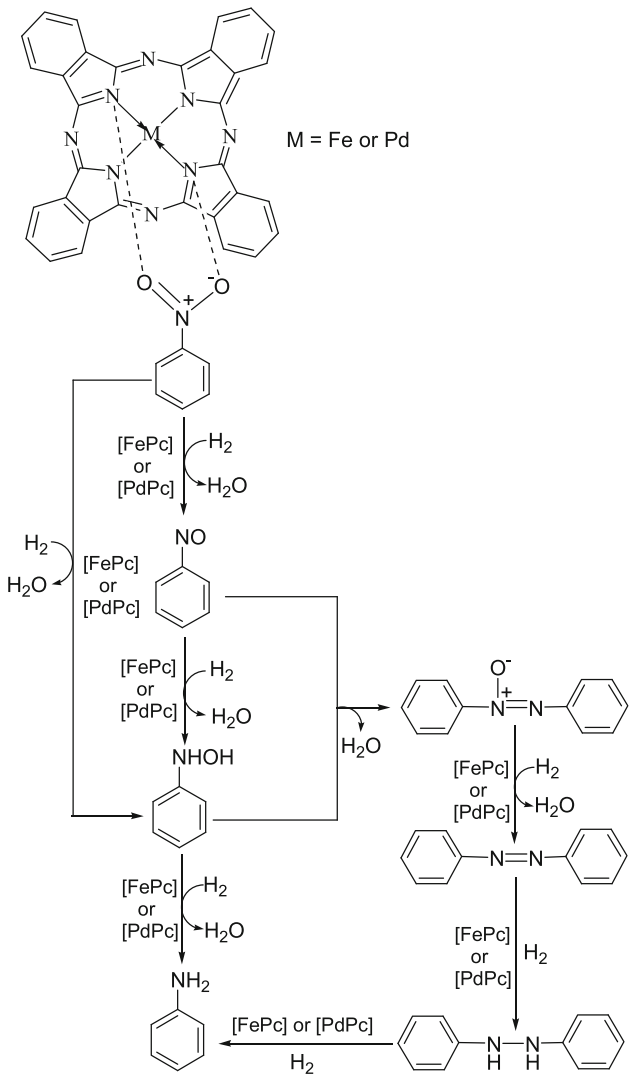
Reaction condition: substrate (1 mmol), Ph_2SiH_2 (3 mmol) or $NaBH_4$ (2 mmol), Fe(II)Pc or Pd(II)Pc (1 mol%), EtOH (5 mL), and 100 °C

[a] Yield determined by GC using *n*-hexadecane as internal standard

yield in 6 h, whereas, azobenzene yielded only 18 % aniline even after 12 h. The same reduction pattern was observed for PdPc catalyzed method for the same reactions (Table 9, entries 1 and 2). These results indicated the possibility of direct route.

Furthermore, the role of MPcs (FePc and PdPc) was also investigated. Transition metal complexes are well known to catalyzed generation of hydrogen from silanes/borohydrides and alcohols combination, leading to the formation of silyl ethers/borates as by-product [78–84]. Diphenyl silyl ethyl ether was observed in most of the FePc catalyzed reactions under present conditions.

Since, MPcs are known for the electron transport processes, based on these experimental observations and literature reports it can be postulated that FePc and PdPc helps in hydrogen generation from Ph_2SiH_2/ethanol with the formation of diphenyl silyl ethyl ether (Scheme S1a, see supporting information) and $NaBH_4$/ethanol with the evolution of sodium tetraethoxyborate (Scheme S1b, see supporting information), respectively. To prove this, the model reaction was carried out with some aprotic solvents (Table S3, entries 1–3, see supporting information). The inhibition of the reactions under aprotic solvent conditions proves the given hypothesis. Also, reaction proceeded with H_2 instead of using other hydrogen source, which implies the usage of hydrogen for the reduction (Table S4, see supporting information). These observations are also supported by the fact that reaction did not occur without catalysts (Table 1, entry 1). The partial electron transfer from the phthalocyanine macrocycle through two nitrogen atoms to the iron or palladium atom promoted the coordination of electron-deficient nitrogen atom and the electron enriched oxygen atom of the nitro group [85]. It was supported by the absence of nitro compound in mass spectra recorded after the five minutes of reaction time. When the nitro group is reduced to the electron-enriched amine group it tends to leave the MPcs (FePc or PdPc). This coordination of nitro compounds with MPcs is probably responsible for the chemo- and regio-selectivity of the present methods. Thus, the electronic character of MPcs possibly promotes the reduction of nitro compounds to the corresponding amines (Scheme 2).



Scheme 2 Plausible reaction mechanism

4 Conclusions

In conclusion, iron and palladium phthalocyanines has been established as the excellent catalysts for the chemo- and regio-selective reduction of functionalized nitro

compounds using Ph_2SiH_2 and $NaBH_4$ as reducing agents. Notably, the two methods are applicable to various aromatic and heteroaromatic nitro compounds tolerating a large number of functional groups such as halo, cyano, acetyl, amide, sulphonamide, hydroxyl, methoxy, ester, phenyl and carboxylic acid etc. Such functional group tolerance might omit the use of protecting groups for the synthesis of large complex molecules. Furthermore, present methods are highly regioselective for the reduction of dinitrobenzenes. The other remarkable advantages of the methods include recyclability of catalysts, no use of base or ligands like phosphines, gram scale applicability, high stability of catalysts, easy workup, high isolated yields and green solvent system.

Acknowledgments Authors are grateful to Director of the institute for providing necessary facilities. Financial support received from CSIR-India (fellowship to P. K. V) and DST under Fast Track Scheme (U. S.) is gratefully acknowledged.

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