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Highly Chemo- and Regioselective Reduction of Aromatic Nitro Compounds Catalyzed by Recyclable Copper(II) as well as Cobalt(II) Phthalocyanines

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Abstract: Copper/cobalt phthalocyanines were established for the first time as catalysts for the very efficient chemo- and regioselective reduction of aromatic nitro compounds to generate the corresponding amines. The selective reduction of nitro compounds was observed in the presence of a large range of functional groups such as aldehyde, keto, acid, amide, ester, halogen, lactone, nitrile and heterocyclic functional groups. Furthermore, the present method was found to be highly regioselective towards the reduction of aromatic dinitro compounds in a short time with high yields. In most of the cases the conversion and selectivity were >99% as monitored by GC-MS. The reduction mechanism was elucidated by UV-vis and electrospray ionization quadrupole time-of-flight tandem mass spectrometry.

Keywords: chemoselectivity; cobalt/copper phthalocyanines; hydrazine hydrate; nitro reduction; regioselectivity

Reduction of aromatic nitro compounds to the corresponding amines is an important chemical transformation in organic chemistry, mainly due to the fact that amines are important intermediates in the preparation of dyes, herbicides, pesticides, and pharmaceuticals.[1] Numerous methods have been developed to accomplish this transformation including catalytic hydrogenation,[2] sodium borohydride/catalyst,[3] hydrazine/catalyst,[4] and metals such as iron, tin, or zinc.[5] Over the last years, a variety of other catalytic systems such as $Mo(CO)_6$/DBU,[6] $Pd(OAc)_2$/PMHS,[7] Sm/I_2,[8] Sm/1,1′-dioctyl-4,4′-bipyridinium dibromide,[9] Sm/NH_4Cl,[10] Cu nanoparticles/$HCOONH_4$,[11] S_8/$NaHCO_3$,[12] HI[13] and silane/oxorhenium complexes[14a] have been reported. However, most of the synthetic methods lack the desired chemoselectivity over other functional groups that are often present in the substrates such as acid, aldehyde, ester, alkene, halide, benzyl, nitrile and, also, the desired regioselectivity in the reduction of dinitro compounds. In addition, the reduction of aromatic nitro compounds often stops at an intermediate stage, yielding hydroxylamines, hydrazines, and azoarenes. Due to the high importance of the selective reduction of aromatic nitro compounds, the search for alternative, efficient and highly chemo- and regioselective methods always remains an important task in organic synthesis.

Metal phthalocyanines (MPcs) (Figure 1) are traditionally used as dyes and pigments.[15] Their use has

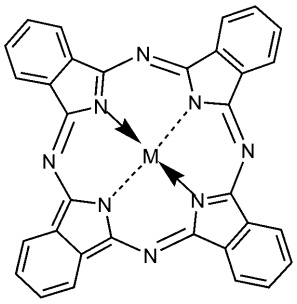


Figure 1. Structure of the metal phthalocyanines.

recently been extended to many high technological processes.[16] Furthermore, they are used as catalysts for photo or oxidative degradation of pollutants and as photosensitizers for photodynamic therapy.[17] Recently, cobalt phthalocyanine has been used for the oxidation of thiols[18] and for the selective reduction of the double bond in flavones.[19] But to the best of our knowledge the catalytic potential of MPcs for selective reduction of the nitro group in the presence of other reducible functionalities has not been reported.

Herein, we report the first copper (CuPc)- as well as cobalt phthalocyanine (CoPc)-catalyzed highly chemo- and regioselective reduction of aromatic nitro groups in the presence of hydrazine hydrate.

Initially, in order to assess the best reaction conditions, different catalysts, hydrogen sources, solvents and temperature were studied for the reduction of the test substrate, 4-nitrobenzonitrile. The progress of the reactions was monitored by TLC and GC-MS. Among the different catalysts, copper and cobalt phthalocyanines were found to be the most active catalysts at 70 °C (Table 1, entries 7 and 8), whereas no reaction was observed at room temperature. In order to confirm whether the corresponding metal salts from which the metal phthalocyanines were prepared could be able to reduce the nitro group or not, the reaction was carried out in the presence of copper sulphate, copper chloride and cobalt chloride. The reduction of the nitro compound in the presence of these metal divalent salts required significantly longer reaction times (12–13 h) and the amine was obtained in 12–15% yield (Table 1, entries 1, 2, 3 and 6). Also, when Cu_2O and CuI were used as catalyst no reaction was observed (Table 1, entries 4 and 5) which indicated the necessity of the divalent metal for the reduction of the nitro group. As expected, in the absence of catalyst reduction was not observed even after 13 h (Table 1, entry 9).When the CuPc- or CoPc-catalyzed reduction of nitrobenzene was performed, it showed >99% conversion (GC yield: 97 and 96.6% with CuPc and CoPc, respectively).

Furthermore, we investigated the role of different hydrogen sources on the CuPc- and CoPc-catalyzed reduction of 4-nitrobenzonitrile. The reaction with hydrazine hydrate was very fast, completely reducing the nitro compound in 2 h at 70 °C (Table 2, entry 3). However, the product was also observed in low yield with ammonium formate and potassium formate after 12 h.

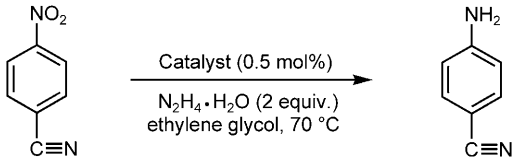
The reaction conditions were further optimized for the reduction of 4-nitrobenzonitrile through variation of the solvent. Changing the reaction solvent dramatically affected the reaction efficiency. Reduction in ethylene glycol gave the highest yield, whereas the yield was very low (15–25%) in methanol, ethanol, dichloromethane, tetrahydrofuran, dimethylformamide, toluene, acetonitrile and water. The deoxygenation of 4-nitrobenzonitrile in the absence of a solvent for a long period of time afforded the amine in 25% yield.

In addition, the amount of catalyst required for the completion of reaction was optimized by initially starting with 0.25 mol% of catalyst and gradually increasing the amount up to 1.50 mol%. It was observed that initially the yield increased with the amount of catalyst and a maximum yield was obtained with 0.50 mol% of catalyst. Both the yield and the rate of the reaction remain unaffected by further increases in the amount of catalyst.

After optimization of the reaction conditions, the scope of CuPc- and CoPc-catalyzed reduction of aromatic nitro compounds in the presence of hydrazine hydrate and ethylene glycol was explored. The results in Table 3 indicated the generality of this method and the efficiency of these new catalysts.

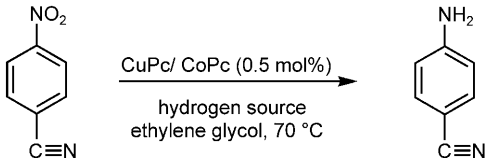
The reduction of 4-chloro-, 4-bromo-, 3-bromo-, and 4-iodonitrobenzenes was completed within 2 h,

Table 1. Evaluation of different catalysts for the reduction of 4-nitrobenzonitrile.



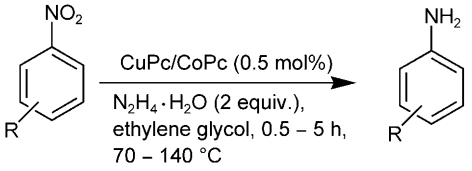
Entry	Catalyst	GC yield [%]
1	$CuSO_4$	10–12
2	$CuCl_2$	10–12
3	$CuSO_4 \cdot 5H_2O$	5–8
4	Cu_2O	no reaction
5	CuI	no reaction
6	$CoCl_2 \cdot 6H_2O$	12–15
7	copper phthalocyanine	99
8	cobalt phthalocyanine	98
9	without catalyst	no reaction

Table 2. Screening of different hydrogen sources for the reduction of 4-nitrobenzonitrile.



Entry	Hydrogen source	GC yield [%] with CuPc/CoPc
1	ammonium formate	45/39
2	potassium formate	34/32
3	hydrazine hydrate	99/98
4	ammonium chloride	no reaction
5	formic acid	no reaction
6	$NaBH_4$	no reaction
7	water	no reaction

Table 3. Reduction of aromatic nitro compounds to the corresponding aromatic amines.



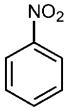
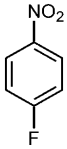
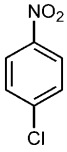
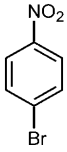
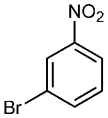
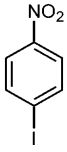
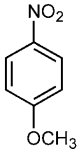
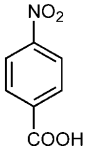
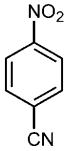
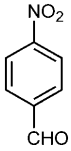
Entry	Aryl nitro compounds	*T* [°C]	*t* [h]	Yield[a] [%] with CuPc/CoPc
1		70	2	93/93
2		90	5	74/72
3		70	2	87/88
4		90	1	90/94
5		90	1	91/92
6		90	1	90/87
7		90	2	89/86
8		120	4	83/84
9		70	2	93/93
10		90	4	86/84[b]

Table 3. (Continued)

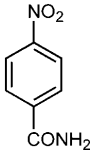
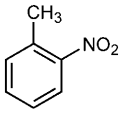
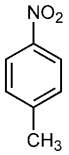
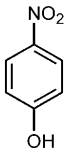
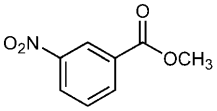
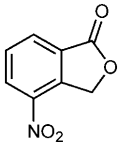
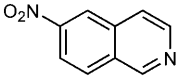
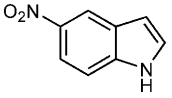
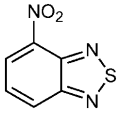
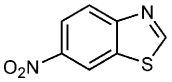
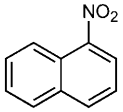
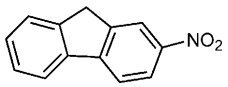
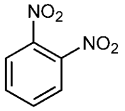
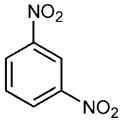
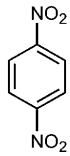
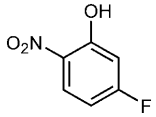
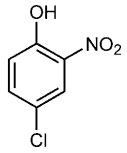
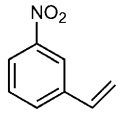
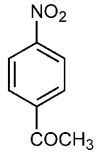
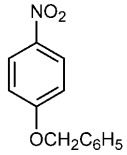
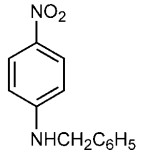
Entry	Aryl nitro compounds	*T* [°C]	*t* [h]	Yield[a] [%] with CuPc/CoPc
11		100	4	85/82
12		80	2	92/95
13		80	2	94/98
14		100	4	78/82
15		140	3	72/70[c]
16		70	3.5	90/85
17		90	1	94/93
18		90	2	91/84
19		100	2	81/84
20		100	2	93/88
21		80	2	85/87
22		90	2	97/94
23		70	2	85/81
24		70	1	92/94

Table 3. (Continued)

Entry	Aryl nitro compounds	T [°C]	t [h]	Yield[a] [%] with CuPc/CoPc
25		70	0.5	95/95
26		120	4.5	76/79
27		120	2	80/76
28		80	3	95/82[d]
29		70	5	79/85[e]
30		90	1.5	84/87
31		70	2	86/82

[a] The isolated yield is the average of three experiments in each case.
[b] Isolated as hydrazone derivatives.
[c] Characterization and yield as per GC-MS analysis.
[d] Total yield of amines with and without reduced double bond.
[e] 2 mL of 1 molar HCl was added after 2 h to the reaction mixture.

and the amines were isolated in high yields (Table 3, entries 3–6). The reduction of 4-fluoronitrobenzene required a longer time and the product was obtained in moderate yield as compared to the other nitro halides. (Table 3, entry 2). In general, dehalogenation of halogen-substituted aromatic nitro compounds takes place with the earlier reported methods such as hydrogenation[2c] or $Pd(OAc)_2$/PMHS[7] and S_8/mild base.[12] However, in the present study a selective reduction of the nitro halide was observed. A series of aromatic nitro substrates containing other functional groups such as methoxy, acid, nitrile, aldehyde, ester, amide, methyl, hydroxy, ketone, lactone and heterocycle was also successfully reduced, with >99% chemoselectivity and >99% conversion (Table 3, entries 7–22). In the case of *m*-nitrostyrene, a variation in the result was observed with the two catalysts. With CuPc >99% conversion but only 20% selectivity was observed whereas, in the case of CoPc, >85% conversion with 88% selectivity was observed (Table 3, entry 28). The selectivity and conversion were monitored by GC-MS analysis. One of the most exciting results in the present study was regioselective reduction of one nitro group in dinitrobenzene with good to excellent yields (Table 3, entries 23–25). Recently, the regioselective reduction of *o*-, *m*-, and *p*-dinitrobenzene has been carried out by using silane/oxorhenium complexes.[14a] However, the use of toxic silane as hydrogen source, costly metal complexes as catalyst, long reaction time (24–38 h) and low yield (58–76%) limit the scope of the method. Recently, a gold-based catalyst (Au/TiO_2) with CO and H_2O as the hydrogen source was successfully employed at room temperature to reduce the organic nitro compounds in shorter reaction times with high conversion and chemoselectivity.[14b] However, although Au nanoparticles supported on TiO_2 showed high activity, this involved the use of a costly metal. In the present study, regioselective reductions >99% of *o*-, *m*-, and *p*-dinitrobenzene occurred in a short time, producing the corresponding nitroanilines in high yields with >99% conversion (Table 3, entries 23–25). Also, hydrazine hydrate was used as hydrogen source which produces harmless by-products such as nitrogen gas and water. Many conventional procedures involving hydride reducing agents or hydrogenation failed to give such a high regioselectivity.[2b]

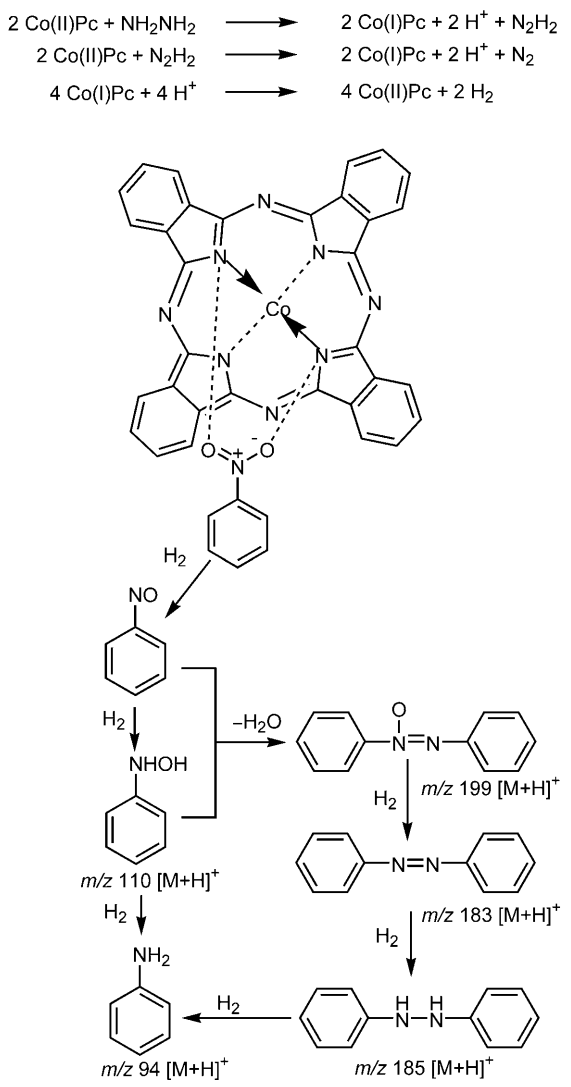
The most important finding of present method is the tolerance of acid, aldehyde and amide groups which failed in most of the earlier used catalytic systems.[5b,11] All these products were isolated in good yield (Table 3, entry 8, 10 and 11). In all the cases the conversion and selectivity were >99% as monitored by GC-MS.

In addition to this, the reduction of a more complex trisubstituted benzene was also carried out. The reduction of 5-fluoro-2-nitrophenol under the present reaction conditions afforded the corresponding amine in 76–79% yield after 4.5 h (Table 3, entry 26). Also, the reduction of 4-chloro-2-nitrophenol was complete in 2 h with 76–80% yield (Table 3, entry 27).

The recyclability of the catalyst was evaluated by using 4-nitrobenzonitrile as test substrate. After completion of reaction the product was extracted with ethyl acetate and the remaining residue was used as such after drying over a rotary evaporator. Successive reactions were carried out by sequential addition of fresh substrate and hydrazine hydrate to the crude re-

mains after extracting the product. The catalytic activity of CuPc/CoPc did not decrease in up to four cycles. However, the reduction of the substrate was not complete in the fifth cycle.

A mechanistic study was carried out by using nitrobenzene as substrate with the help of ESI-QTOF-MS/MS. The reaction was monitored by taking mass spectra at different time intervals of 10, 20, 30, 40, 60, 120 min. The detection of hydroxylamine and azoxybenzene as intermediates (Scheme 1) in the mass spectra suggested both types of classical mechanisms for the nitro reduction. Furthermore, to confirm which pathway is prominent, the reduction of the intermediates nitrosobenzene and azobenzene under the present reaction condition was carried out. It was observed that nitrsobenzene gave aniline with a yield of 71% in 30 min while, the reduction of azobenzene was not completed even after five hours and aniline was obtained only in 20% yield. These results clearly suggested that the azobenzene route is disfavoured and the nitrsobenzene route is favoured.



Scheme 1. Probable mechanism for nitro reduction and observed masses of intermediates in ESI-MS.

It is well known that the surface electronic state has an important effect on the catalytic activity of a material. Since, metal phthalocyanines have been proved to be involved in electron-transfer mechanisms; it has been proposed that the nitro group coordinates with CuPc/CoPc due to a charge transfer process. The coordination of the nitro group to phthalocyanine was further assisted by the fact that the nitro compound was not detected in ESI-MS recorded after 10 min. In CuPc/CoPc, partial electron transfer from the phthalocyanine macrocycle through N-1 and N-2 to the copper/cobalt atom promotes coordination of the electron-deficient nitrogen atom and the electron-enriched oxygen atom of the nitro group.[20] When the nitro group is reduced to the electron-enriched amine group it tends to leave the CuPc/CoPc. Thus, the electronic character of CuPc/CoPc possibly promotes the reduction of nitro compounds to the corresponding amines. On the other hand the catalytic decomposition of hydrazine hydrate in contact with CuPc/CoPc also plays a crucial role in the reduction.

However, the decomposition of hydrazine hydrate is not known, it has been proposed that the electron-transfer mechanism between CuPc/CoPc and hydrazine hydrate leads to the generation of hydrogen. This was confirmed with the help of UV-vis spectrophotometry. When hydrazine hydrate was added to a CoPc solution in ethylene glycol a red shift in the Q band from 642 to 708 nm was observed (Figure 2) specifying the formation of Co(I)Pc.[21] This is due to the tendency of the metal phthalocyanine to take up an electron reversibly in the d_{Z^2} orbital of the central metal.[22] A specific change in colour was also observed when hydrazine hydrate was added in the reaction mixture, supporting the involvement of Co(I)Pc in the reduction process.[19] The same observation was made when THF was used as solvent for UV analysis, where the red shift of the Q band from 670 to 714 nm was observed due to the transformation of Co(II)Pc to Co(I)Pc. Moreover, the steady decrease in the band at 714 nm and the appearance of the original band at 670 nm suggested the regeneration of Co(II)Pc. The above observation indicated that the conversion of Co(II)Pc to Co(I)Pc and *vice-versa* leads to the generation of hydrogen from hydrazine hydrate. The mechanism of the reduction reaction is proposed in Scheme 1.

In conclusion, copper/cobalt phthalocyanines were for the first time established as catalysts for a very efficient regio- and chemoselective reduction of aromatic nitro compounds to generate the corresponding amines. The present process is highly chemoselective, tolerating a large range of functional groups such as aldehyde, acid, amide, ester, halo, lactone, nitrile and

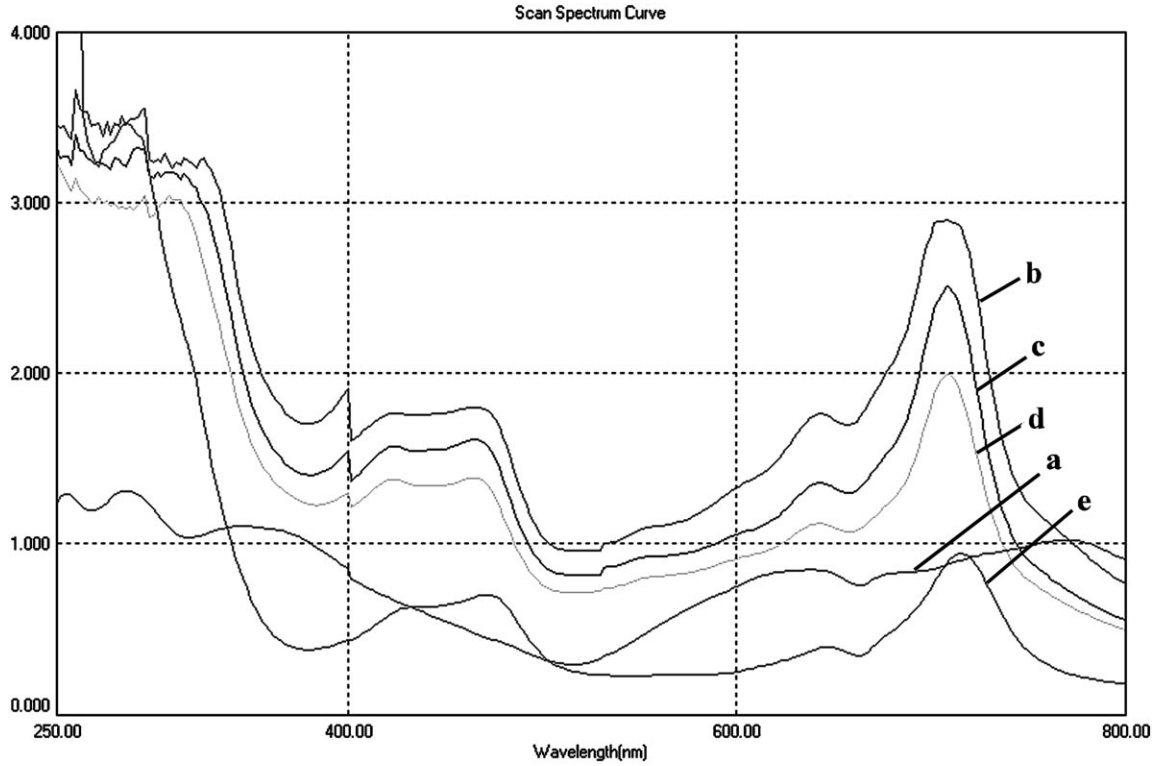


Figure 2. UV-vis spectra of CoPc in ethylene glycol: (**a**) original, (**b**) on addtion of N_2H_4, (**c–e**) at intervals of 2 min.

heterocyclic functional groups. Furthermore, the present method was found to be highly regioselective towards the reduction of aromatic compounds in a short time with high yields. Other remarkable advantages of this methodology include high isolated yields, clean reactions, easy work-up procedure and reusability of the catalyst. Also, copper/cobalt phthalocyanine exhibits an unusual physical and chemical stability.

Experimental Section

General Procedure for the Reduction of Aromatic Nitro Compounds

To a mixture of nitro compound (0.67 mmol) and catalyst (0.5 mol%) in ethylene glycol (5 mL) hydrazine hydrate (2 equiv.) was added. The reaction solution was stirred at a temperature of 70–140 °C and the progress of the reaction was monitored by TLC (silica gel; hexane/ethyl acetate) and GC-MS. After completion, the reaction mixture was cooled to ambient temperature and extracted with ethyl acetate (3 × 5 mL). The combined ethyl acetate fractions were washed with water and dried under reduced pressure by using a rotatory evaporator. After washing with water, the crude product was purified by column chromatography (silica 230–400; *n*-hexane/ethyl acetate mixture) to afford the amine product. In the case of water-soluble products the ethyl acetate extract was directly subjected to chromatographic purification.

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