Ruthenium–Bipyridine Complex-Catalyzed Photo-Induced Reduction of Nitrobenzenes with Hydrazine

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The photo-induced reduction of nitrobenzenes with hydrazine hydrate was catalyzed by the ruthenium–bipyridine complex to give the corresponding anilines.

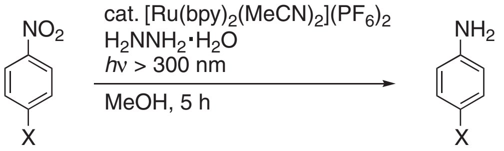
Photo-induced redox reactions have provided a variety of methods for synthetic reactions. An electron-transfer mechanism operates in these reactions. Ruthenium–bipyridine complexes are known as useful promoters to induce the redox reactions under photo-irradiation. The ruthenium–bipyridine complex has been reported to serve as an one-electron oxidant and reductant, which permits the construction of a catalytic redox system for the biomimetic reaction.[1] An efficient catalytic system with practical potential, however, should be developed from the viewpoint of synthetic methodology using ruthenium–bipyridine complexes. The reduction of nitrobenzenes to aniline derivatives is one of the important reductive transformations. The photochemical methods involve *N*-methylacridan–$HClO_4$, CdS–VCl_3–EtOH, and electrochemically generated nickel as a reduction system.[2] This reductive transformation has also been performed by a transition metal catalyzed reaction in both homogeneous and heterogeneous phases.[3] We herein report the photo-induced reduction of nitrobenzenes with hydrazine, catalyzed by the ruthenium–bipyridine complex.

Treatment of nitrobenzene with 10 molar equiv of $H_2NNH_2 \cdot H_2O$ in methanol in the presence of the ruthenium complex, $[Ru(bpy)_2(MeCN)_2](PF_6)_2$ (**3**), under photo-irradiation (Xe lamp, >300 nm, glass filter) gave aniline in 99% yield, as shown in Eq. 1 (X = H, Table 1, entry 1).[4] Without photo-irradiation and/or hydrazine, no reduction occurred (entries 2 and 3), indicating that the reduction is promoted by photo-excitation of the ruthenium complex. Hydrazine worked as a reductant. A similar function has been reported in Fe_2O_3–MgO-catalyzed reduction.[3b]

Table 1. GC Yields of Aniline in the Ru-Catalyzed Reduction of Nitrobenzene under Various Conditions[a)]

Entry	Conditions	GC yield of aniline/%
1	$h\nu$	99
2	dark, rt	0
3	dark, reflux	0
4	$h\nu$, without Ru complex	20

a) **3**, 0.06 mmol; hydrazine monohydrate, 1 mmol; solvent, MeOH; irradiation (>300 nm) for 5 h.



(1)

Methanol is a suitable solvent as shown in Table 2. Reduced efficiency was observed with CH_2Cl_2 (entry 2). Use of acetonitrile or THF drastically decreased the yield under similar conditions (entries 3 and 4). The other ruthenium–bipyridine complexes, $[Ru(bpy)_3]Cl_2$ and $[RuCl_2(tpa)]BF_4$ (tpa = tris[2-(pyridyl)methyl]amine), shown in Table 2 served as less efficient catalysts under similar conditions (entries 5 and 6). These findings suggest that acetonitrile of the ruthenium–bipyridine complex **3** can be considered to be an exchangeable ligand that will give a superior catalyst.

The present method using complex **3** as the catalyst was applicable to the reduction of various nitrobenzenes (Table 3). The nitrobenzenes bearing an electron-withdrawing or -donating group underwent the smooth reduction to give the corresponding aniline derivatives in high yields. The cyano and chloro groups were intact in this reaction.

A new absorption (b) appeared in UV–vis spectrum by treatment of **3** with $H_2NNH_2 \cdot H_2O$ under photo-irradiation (Fig. 1).

Table 2. Ru-Catalyzed Reduction of Nitrobenzene under Photo-Irradiation[a)]

Entry	Catalyst	Solvent	GC yield of aniline/%
1	**3**	MeOH	99
2	**3**	CH_2Cl_2	52
3	**3**	MeCN	12
4	**3**	THF	18
5	$[Ru(bpy)_3]Cl_2$	MeOH	82
6	$[RuCl_2(tpa)]BF_4$	MeOH	22

a) Ru catalyst, 0.06 mmol; hydrazine monohydrate, 1 mmol; irradiation (>300 nm) for 5 h.

Table 3. Ru-Catalyzed Reduction of Nitrobenzenes under Photo-Irradiation[a)]

Entry	**1** X	Catalyst	Isolated yield of **2** /%
1	H	**3**	92[b)]
2	H	$Ru(bpy)_3Cl_2$	64
3	Cl	**3**	82
4	Cl	$Ru(bpy)_3Cl_2$	8
5	CN	**3**	70
6	CN	$Ru(bpy)_3Cl_2$	17
7	OMe	**3**	88
8	OMe	$Ru(bpy)_3Cl_2$	56

a) Ru catalyst, 0.06 mmol; hydrazine monohydrate, 1 mmol; solvent, MeOH; irradiation (>300 nm) for 5 h. b) Isolated as acetanilide.

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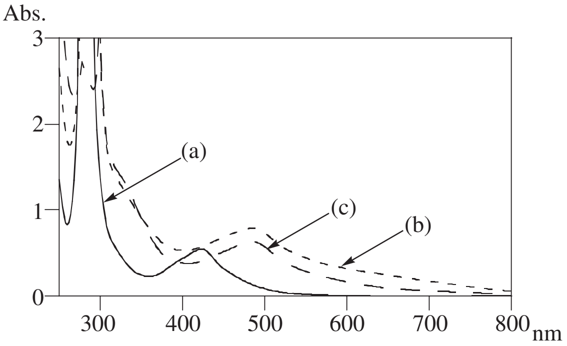
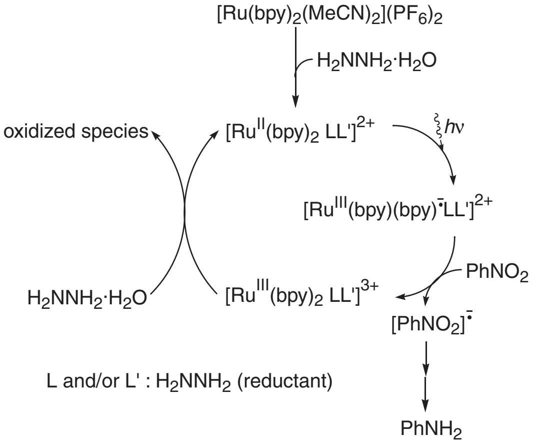


Fig. 1. UV–vis spectra in MeOH. (a) **3**; 5×10^{-5} M. (b) **3** + hydrazine (167 molar equiv). (c) Reaction mixture.



Scheme 1.

An active catalytic species is considered to be formed in the reaction system. The reaction mixture exhibited an absorption (c) similar to that observed in (b). Based on these spectral data, the species like a ruthenium–hydrazine complex is suggested to be involved in the one-electron reduction (Scheme 1). The hydrazine ligand might be oxidized to a diazene ligand in the redox reaction, as reported.[5] Trace amounts of azoxybenzene and azobenzene were detected by GC–MS, which also suggests the ruthenium-catalyzed one-electron reduction through a photo-induced metal to ligand electron transfer, followed by electron transfer from metal complex to nitrobenzene. Nitrosobenzene might be formed through proton and hydrogen transfer, as reported in this type of reduction.[3a,c]

In conclusion, the ruthenium–bipyridine complex catalyzed reduction with hydrazine under photo-irradiation has been achieved to provide a practical protocol for the reduction of nitrobenzenes. Further studies on the application of this method are now in progress.

References

1 a) O. Ishitani, S. Yanagida, S. Takamatsu, and C. Pac, *J. Org. Chem.*, **52**, 2790 (1987). b) J. T. Warren, W. Chen, D. H. Johnston, and C. Turro, *Inorg. Chem.*, **38**, 6187 (1999).

2 a) S. Fukuzumi and Y. Tokuda, *Bull. Chem. Soc. Jpn.*, **65**, 831 (1992). b) S. Maiorana, C. Baldoli, E. Licandro, L. Casiraghi, E. Magistris, A. Paio, S. Provera, and P. Seneci, *Tetrahedron Lett.*, **41**, 7271 (2000). c) A. Yasuhara, A. Kasano, and T. Sakamoto, *J. Org. Chem.*, **64**, 2301 (1999).

3 a) C. Yu, B. Liu, and L. Hu, *J. Org. Chem.*, **66**, 919 (2001). b) B. S. Kumbhar, J. Sanchez-Valente, and F. Figueras, *Tetrahedron Lett.*, **39**, 2573 (1998). c) P. M. G. Bavin, *Can. J. Chem.*, **36**, 238 (1958).

4 Typical procedure: $[Ru(bpy)_2(MeCN)_2](PF_6)_2$[6] (4.71 mg, 0.006 mmol) was placed in a 10 mL Pyrex glass tube with a stirring bar and a rubber cap. Nitrobenzene (10.2 μL, 0.1 mmol) and hydrazine monohydrate (48.5 μL, 1.0 mmol) in 1 mL of MeOH were added under argon atmosphere. After irradiation with Xe lamp for 5 h, the solvent was removed in vacuo. Then, acetic anhydride (48.7 μL, 0.5 mmol) in 1 mL of CH_2Cl_2 was added. The mixture was stirred for 30 min. The solvent was removed in vacuo. Acetanilide was isolated by thin-layer chromatography ($R_f = 0.50$, hexane/ethyl acetate = 2:3). Reduction of other substrates was similarly performed without acetylation.

5 G. Albertin, S. Antoniutti, A. Bacchi, M. Boato, and G. Pelizzi, *J. Chem. Soc., Dalton Trans.*, **17**, 3313 (2002).

6 G. M. Brown, R. W. Callahan, and T. J. Meyer, *Inorg. Chem.*, **14**, 1915 (1975).