# Reduction of Coordinated Acetonitrile to Ethylamine in a Ruthenium Complex by *p*-Phenylenediamine or Hydroquinone

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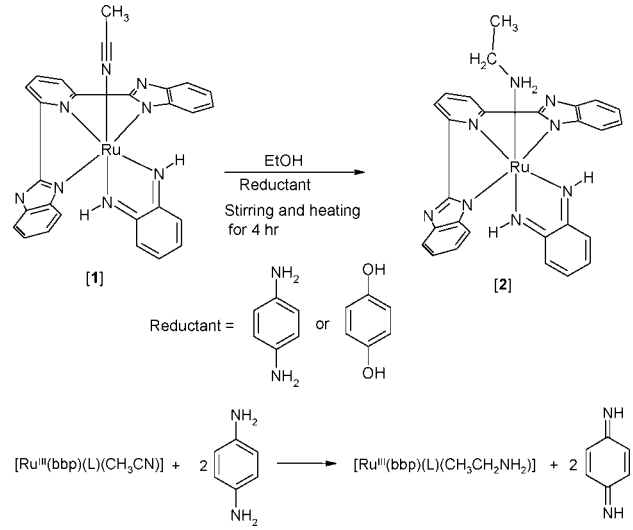
*Summary: A ruthenium complex, [Ru$^{II}$(bbp)(L)(CH$_3$CN)] (**1**) [bbp = 2,6-bis(benzimidazol-2-yl)pyridine; L = o-phenylenediamine], has been synthesized and characterized by various spectroscopic and analytical techniques as well as by a single-crystal structure. The coordinated acetonitrile is found to be reduced to ethylamine in the presence of p-phenylenediamine or hydroquinone. The reduced product, complex **2**, has been characterized by spectroscopic studies and single-crystal structure.*

The reductions of the coordinated acetonitrile ($-N_\alpha{\equiv}C_\beta-CH_3$) to acetimidoyl [$\eta^2$-N(H)=C$-$CH$_3$; bonded through $N_\alpha$ and $C_\beta$], ethylidenimido [$\eta^2$-N=CH$-$CH$_3$],[1] aza-vinylidenyl [$-$N=CH$-$CH$_3$],[2] imino [$-$NH=CH$-$CH$_3$],[2,3] ethylimido [$\equiv$N$-$CH$_2-$CH$_3$],[4] ethylamido [$-$NH$-$CH$_2-$CH$_3$],[2] and aza-allylic [$\eta^3$-CH$_2-$CH$-$NH$_2$][5] ligands are well documented in the literature. In all cases, the reductions are carried out either by hydrogen[6] or by hydride[7] sources (e.g., NaH, NaBH$_4$, LiAlH$_4$, LiHBEt$_3$).[8] There is also precedence for the protonation of acetonitrile complexes by HCl or HBF$_4\cdot$Et$_2$O. This protonation leads to the oxidation of an electron-rich metal center to form ethylimido[9] or imino complexes.[5] In some cases, hydride formation also takes place.[10] Meyer et al. have reported an example of reversible 2e$^-$/2H$^+$ reduction of coordinated acetonitrile to the corresponding imine in Os$^{III}$-sulfilimido complexes.[11]

We report here a unique reduction of coordinated acetonitrile to ethylamine in [Ru$^{III}$(bbp)(L)(CH$_3$CN)] (**1**) [bbp = 2,6-bis(benzimidazol-2-yl)pyridine; L = *o*-phenylenediamine] in the presence of *p*-phenylenediamine or hydroquinone (Scheme 1).

**Scheme 1**




Complex **1** has been prepared by refluxing an ethanolic solution of [Ru(bbp)Cl$_3$] in the presence of an equivalent amount of *o*-phenylenediamine followed by chromatographic separation with an acetonitrile/dichloromethane solvent mixture. The neutral, nonconducting complex shows the ($m$ + 1) molecular ion peak at 558.743 in the positive ion ESI mass spectrum. Further characterization of the complex has been done by the single-crystal X-ray structure (Figure 1). The crystal structure reveals that the bbp ligand is bonded to the metal in dianionic form and the ancillary ligand, *o*-phenylenediamine, is present in neutral iminoquinone form. The bond distances are comparable with those of the reported quinone form of the *o*-phenylenediamine ligand [Ru1$-$N7, 1.967(5); Ru1$-$N6, 1.980(5); N6$-$C20, 1.323(8); N7$-$C25, 1.326(7); C21$-$C22, 1.310(11); C22$-$C23, 1.414(11); C23$-$C24, 1.350(10); C24$-$C25, 1.425(9); C25$-$C20, 1.450(8) Å].[12] As the complex is neutral and nonconducting, it is evident that the ruthenium is in +II oxidation state. $^1$H NMR study shows the expected number of

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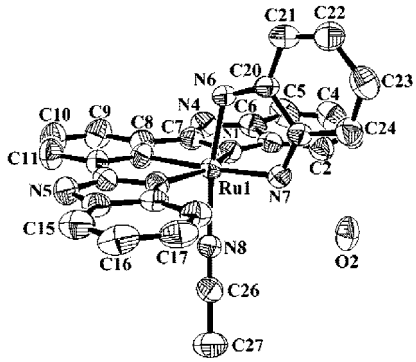
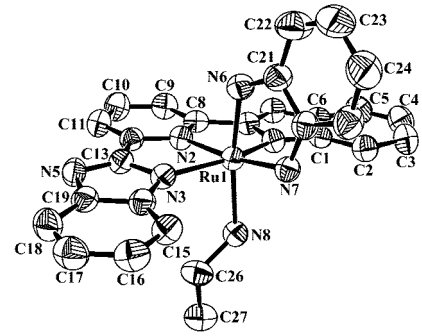



**1**




**2**

**Figure 1.** ORTEP diagram of complexes **1** and **2** (H atoms are removed for clarity).

aromatic protons with a sharp singlet at $\delta \approx 2.04$ ppm corresponding to three protons from coordinated acetonitrile (Supporting Information).[13]

Complex **1**, on refluxing with three equivalent of *p*-phenylenediamine in ethanol solvent for 4 h, afforded a dark colored solution. The solvent was then dried and removed and the dark-colored solid mass, on chromatographic purification using silica gel column, yielded complex **2** (yield ~70%) (Scheme 1). In the positive ion ESI mass spectrum, the molecular ion peak appears at 562.74, which indicates the reduction of coordinated acetonitrile to ethylamine.

This complex, as expected, is neutral, nonconducting, and diamagnetic. The formulation of **2** is further confirmed by its single-crystal structure (Figure 1). In complex **2**, the Ru−amine(N8) bond has been found to be elongated to 2.173(4) Å in comparison to the Ru−nitrile bond {2.059(5) Å} in complex **1** (Supporting Information).

The reduction of the coordinated acetonitrile to ethylamine is also confirmed by the $^1$H NMR studies. The $^1$H NMR spectra of complexes **1** and **2** in $(CD_3)_2SO$ show the calculated number of fifteen aromatic protons overlapping between 6.7 and 8.2 ppm (Supporting Information); eleven from the bbp ligand and four from iminoquinone moiety. In both complexes, the NH-protons from the iminoquinone moiety appear at ~11.7 ppm, which is appreciably shifted downfield because of coordination to the metal center. These NH-protons, as expected, disappeared on $D_2O$ exchange.[14] In complex **1**, the three methyl protons of the coordinated acetonitrile appear as a sharp singlet at 2.04 ppm, whereas, in complex **2**, the $CH_3$ and $CH_2$ protons of the coordinated ethyl amine appear at 1.5 ppm as a triplet and 2.4 ppm as a multiplet, respectively.

The reduction of the acetonitrile to ethylamine is evidently a $4e^-/4H^+$ process; hence, it results in the oxidation of two equivalent of *p*-phenylenediamine to the corresponding aminoquinone (in the case of hydroquinone, to the corresponding quinone) (quantitatively determined by isolated product analysis).

In contrast, Meyer et al. have recently reported that $[(trpy)(Cl)(NSAr)Os^{III}-N{\equiv}CCH_3]$ in $2e^-/2H^+$ reduction gives $[(trpy)(Cl)(NSAr)Os^{III}-N(H){=}CHCH_3]$ [trpy = 2,2′:6,2″-terpyridine; Ar = $C_6H_5$, 4-$MeC_6H_4$, 3,5-$Me_2C_6H_3$].[11] This $[(trpy)(Cl)(NSC_6H_3Me_2)Os^{III}-N(H){=}CHCH_3]$ complex can reduce various substrates such as PhCHO, $CH_3CN$, and 1,4-quinone and comes back to the parent acetonitrile-coordinated complex. Venanzi et al. reported the conversion of acetonitrile to ethylamine in $[(triars)Ru(NCMe)_3]^{2+}$ with $NaBH_4$ in methanolic solution.[15] It is proposed that the ruthenium center first polarizes the nitrile and activates the $\beta$-carbon toward hydride attack followed by the addition of proton to the nitrogen, and this finally results in the amine.[16] However, it is not clear whether the hydrides are introduced directly to the $\beta$-carbon or through a 1,3-metal hydride shift from the ruthenium to the $\beta$-carbon. The azavinylidene and imine complexes are the proposed intermediates for this conversion.[17]

Thus, the present work demonstrates a unique example of reduction of coordinated acetonitrile to ethylamine by the nonclassical reducing agent *p*-phenylenediamine (or hydroquinone). This results in the oxidation of the reductant to the corresponding iminoquinone (or quinone) derivatives. The starting complex and the reduced product are characterized by microanalysis, UV−visible spectra, $^1$H NMR, mass spectroscopy, and finally crystal structure analysis. The oxidation products are determined quantitatively by GC-MS as well as isolated yield analysis.

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**Supporting Information Available:** Syntheis of the complexes, crystallographic data, cif files for complexes **1** and **2**, and spectroscopic characterization of the complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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