

Communication

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*J. Am. Chem. Soc.*, **2004**, 126 (35), 10800-10801 • DOI: 10.1021/ja047410y • Publication Date (Web): 17 August 2004

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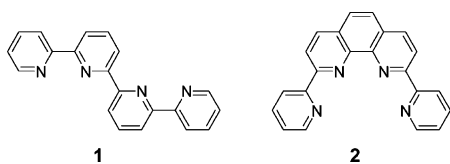
## 2,9-Di-(2'-pyridyl)-1,10-phenanthroline: A Tetradentate Ligand for Ru(II)

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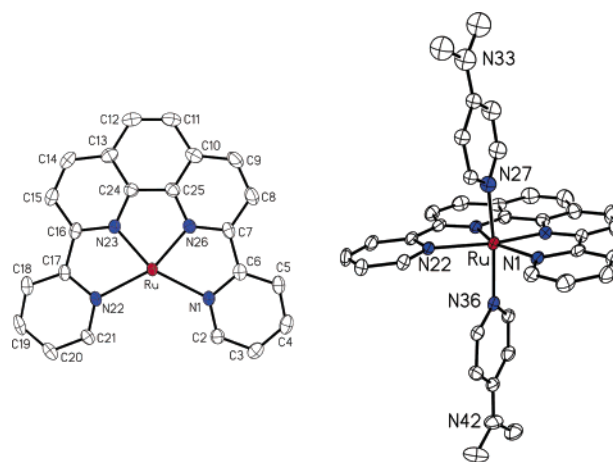
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Polypyridine derivatives of Ru(II) are the most widely studied of all transition metal complexes. Interest in these systems stems from the well-understood nature of their photophysical and electrochemical properties as well as their ease of synthesis, leading to the availability of a wide variety of substituted analogues.<sup>1</sup> Of the chelating polypyridines, 2,2'-bipyridine (bpy) is the bidentate prototype and 2,2':6',2''-terpyridine (tpy) is the tridentate. The next higher homologue, quaterpyridine (4), is well known but commonly acts as a bridging ligand with Ru(II), twisting about the central bond to adopt a helical conformation which binds two Ru(II) centers in a bidentate fashion.<sup>2,3</sup> We reasoned that restricting the central bond of this ligand by incorporating a phenanthroline subunit might prohibit bridging and induce mononuclear coordination. This Communication will describe the new tetradentate ligand 2,9-di-(2'-pyridyl)-1,10-phenanthroline (**2**) that promises to provide a novel family of well-behaved Ru(II) complexes.

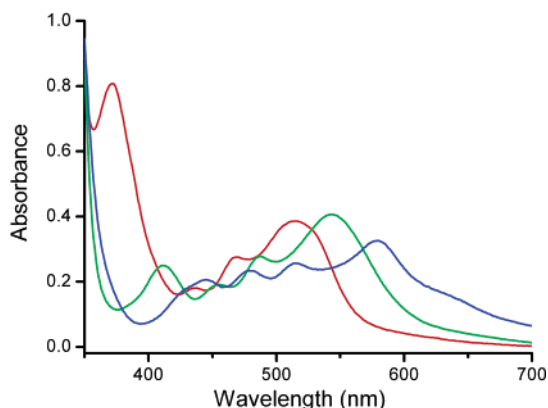


Ligand **2** was prepared in 62% yield by Pd(PPh<sub>3</sub>)<sub>4</sub>-catalyzed Stille coupling of 2,9-dichloro-1,10-phenanthroline<sup>4</sup> and 2-(tri-*n*-butylstannyl)pyridine.<sup>5</sup> The NMR spectrum of **2** exhibits 7 proton peaks and 11 <sup>13</sup>C signals,<sup>6</sup> indicating a symmetric structure. Treatment of **2** with RuCl<sub>3</sub> in refluxing absolute ethanol, followed by the introduction of 4-dimethylaminopyridine (4-NMe<sub>2</sub>py), 4-methylpyridine (4-Mepy), or 4-trifluoromethylpyridine (4-CF<sub>3</sub>py) gave a trans complex [Ru(2)(4-X-py)<sub>2</sub>]<sup>2+</sup> in yields of 95, 50, and 5%, respectively. The low yield for the 4-CF<sub>3</sub>py system is attributed to the much weaker coordinating ability of the pyridine such that [Ru(2)(4-CF<sub>3</sub>py)(Cl)]<sup>+</sup> is the major product (52%). All three complexes gave NMR spectra with the expected seven peaks for **2** as well as two 4H doublets for the pyridine protons. Particularly characteristic was the resonance of H6' on the distal pyridine rings of **2**, which was downfield shifted by 1.13–1.17 ppm. These protons lie in the molecular plane of **2** and are pushed close to one another, explaining the strong deshielding effect. The complexes were further characterized by MALDI-MS, IR, and elemental analyses. About 5% of [Ru(2)<sub>2</sub>]<sup>2+</sup> was also isolated from all three reactions and identified by its MALDI-MS and <sup>1</sup>H NMR (Supporting Information).

A single-crystal structure analysis of [Ru(2)(4-NMe<sub>2</sub>py)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>·C<sub>3</sub>H<sub>6</sub>O revealed that ligand **2** coordinates in a tetradentate fashion, forming a well-behaved Ru(2) plane (Figure 1).<sup>7</sup> The torsion angle of N1–N26–N23–N22 is only –0.2(2)°, and the ruthenium is located just 0.0024(3) Å away from this least-squares plane. The cation has C<sub>2v</sub> symmetry with the two auxiliary pyridines being approximately coplanar, bonding to ruthenium at a normal distance of about 2.10 Å. The tetradentate coordination is highly distorted



**Figure 1.** ORTEP drawings of the Ru(2) planar fragment (left) and the cation (right) for [Ru(2)(4-NMe<sub>2</sub>py)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>·(C<sub>3</sub>H<sub>6</sub>O).



**Figure 2.** Absorption spectra of [Ru(2)(4-X-py)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> in 5 × 10<sup>−5</sup> M CH<sub>2</sub>Cl<sub>2</sub>, where X = CF<sub>3</sub> (red), Me (green), and NMe<sub>2</sub> (blue).

but well organized. The exterior Ru–N bonds are longer, averaging 2.17 Å, while the interior Ru–N bonds measure only 1.94 Å. The central N23–Ru–N26 angle of 82.3° is not too distorted from the 90° ideal, while the adjacent N1–Ru–N26 and N22–Ru–N23 are compressed to 76.1° and the outer N1–Ru–N22 angle is expanded to 125.6°. The result is that N1 and N22 are separated by only 3.86 Å, while in a planar conformation of uncomplexed **2** a separation of 5.19 Å is calculated.<sup>8</sup> The complexes appear to be stable to the reaction conditions of refluxing aqueous ethanol and, in the presence of excess 4-X-pyridine, no other products were detected.

Variation of the 4-substituent on the axial pyridines of the complex exerts a strong effect on spectroscopic properties. Figure 2 shows the absorption spectra in the visible region, where four major bands are readily discernible and summarized along with the UV bands in Table 1. Typically these bands are assigned to a metal-to-ligand charge-transfer (MLCT) state involving a metal

**Table 1.** Electronic Absorption Data for [Ru(2)(4-X-py)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub><sup>a</sup>

X	$\lambda_{\max}(\log \epsilon)$
NMe <sub>2</sub>	225(4.46), 259(4.71), 281(4.87), 313(4.78), 445(3.61), 479(3.67), 514(3.71), 580(3.81)
Me	226(sh, 4.53), 241(4.64), 279(4.81), 315(4.66), 332(sh, 4.59), 411(3.70), 456(3.58), 487(3.74), 544(3.91)
CF <sub>3</sub>	224(4.47), 241(4.60), 277(4.77), 307(4.51), 338(4.56), 372(4.21), 437(3.56), 469(3.74), 516(3.89)

<sup>a</sup> Recorded in  $5 \times 10^{-5}$  M CH<sub>2</sub>Cl<sub>2</sub>; wavelength in nm and extinction coefficient in M<sup>-1</sup> cm<sup>-1</sup>.

**Table 2.** Cyclic Voltammetric Data for **2** and [Ru(2)(4-X-py)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub><sup>a</sup>

	$E_{1/2}^{\text{ox}}(\Delta E)$	$E_{1/2}^{\text{red}}(\Delta E)$	
<b>2</b>			-1.55 <sup>ir</sup>
X = NMe <sub>2</sub>	1.03(111)	-1.08(114)	-1.56 <sup>ir</sup>
X = Me	1.27(160)	-1.04(174)	-1.53 <sup>ir</sup>
X = CF <sub>3</sub>	1.36(189)	-0.97(169)	-1.39 <sup>ir</sup>

<sup>a</sup> Recorded in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M NBu<sub>4</sub>PF<sub>6</sub>;  $E_{1/2}$  in V vs SCE and  $\Delta E$  in mV; scan rate = 100 mV/s; irreversible process estimated by differential peaks.

d-orbital and the  $\pi^*$ -orbital of a ligand. The long-wavelength bands are consistent with MLCT to the more electronegative ligand **2**. The energies of these bands are influenced by the axial ligands, where electron-donating substituents ( $\lambda_{\max} = 580$  nm for NMe<sub>2</sub>) destabilize the d-level relative to electron-withdrawing substituents ( $\lambda_{\max} = 516$  nm for CF<sub>3</sub>). All four bands correlate well with Hammett  $\sigma_p$  constants.<sup>9</sup>

On the basis of AM-1 calculations, the LUMO and thereafter higher energy orbitals for ligand **2** are estimated at -1.50, -1.02, -0.80, and -0.07 eV, while the LUMO for 4-NMe<sub>2</sub>py, 4-Mepy, and 4-CF<sub>3</sub>py are estimated at -0.00, -0.11, and -0.51 eV, respectively. While we argue that low-energy MLCT is due mainly to  $d\pi(\text{Ru})\text{-to-}\pi^*(\mathbf{2})$ , the higher energy bands at 445, 411, and 372 nm likely involve the participation of the auxiliary pyridines, which become most important in the case of 4-CF<sub>3</sub>py, the best  $\pi$ -acceptor. The Hammett correlation further supports these assignments.

Cyclic voltammetric measurements in dichloromethane displayed two one-electron, ligand-centered reductions as well as one metal-centered oxidation, and the data are summarized in Table 2. Oxidation involves the removal of an electron from a metal d-orbital, while reduction involves the addition of an electron to the more electron-accepting ligand. Thus, we observe a decrease in oxidation potential as the auxiliary 4-NMe<sub>2</sub>py donates electron density to ruthenium, raising the HOMO ( $d\pi$ ) of the metal. Reduction of the 4-NMe<sub>2</sub>py and 4-Mepy complexes clearly involves the ligand **2**, where only small differences are observed as compared to reduction of the free ligand itself. The 4-CF<sub>3</sub>py system exerts a strong electron-withdrawing effect and thus causes a small increase in the reduction potential for this system.

The complexes are not emissive at room temperature and 77 K. This observation is most likely explained by a weak ligand field associated with the highly distorted coordination geometry. These distortions cause a lowering of the d-d-states, which provides an alternate pathway for depopulation of the excited state. A similar argument has been set forth to explain the lack of room-temperature luminescence for the less distorted [Ru(tpy)<sub>2</sub>]<sup>2+</sup>.<sup>10</sup>

In summary, unlike quaterpyridine **1**, ligand **2** binds to a ruthenium primarily as a tetradentate ligand, generating a planar Ru(**2**) subunit which may be a useful building block for supramolecular assembly, as demonstrated by the preparation of several *trans*-bis-pyridine adducts. Further work will involve variations on the central phenanthroline or the distal pyridine moieties to enlarge this family of novel tetradentate ligands.

**Acknowledgment.** We thank the Robert A. Welch Foundation (E-621) and the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy (Contract No. DE-FG03-02ER15334), for financial support of this work. We also thank Dr. James Korp for assistance with the X-ray analysis.

**Supporting Information Available:** Synthetic details including the reported byproducts, <sup>1</sup>H NMR and IR spectra, expanded Figure 1, and sample CV (PDF); X-ray crystallographic data (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (6) <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  9.12 (d,  $J = 8.1$  Hz, 2H), 8.91 (d,  $J = 8.4$  Hz, 2H), 8.79 (dd,  $J = 4.5, 1.8$  Hz, 2H), 8.43 (d,  $J = 8.7$  Hz, 2H), 8.03 (dt,  $J = 8.1, 1.8$  Hz, 2H), 7.88 (s, 2H), 7.44 (m, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  156.2, 155.9, 149.1, 145.7, 137.1, 137.0, 129.1, 126.7, 124.2, 122.2, 120.6.
- (7) Crystal data for [Ru(2)(4-NMe<sub>2</sub>py)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>·(C<sub>3</sub>H<sub>8</sub>O):  $T = 223(2)$  K, triclinic,  $P1$ ,  $Z = 2$ ,  $a = 8.6475(5)$  Å,  $b = 11.3708(7)$  Å,  $c = 22.7506(14)$  Å,  $\alpha = 102.309(1)^\circ$ ,  $\beta = 93.762(1)^\circ$ ,  $\gamma = 96.210(1)^\circ$ ,  $V = 2163.7(2)$  Å<sup>3</sup>,  $R1 = 0.0398$ ,  $wR2 = 0.0996$ , GOF on  $F^2 = 1.071$ .
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JA047410Y