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Cyclometalated Ruthenium Chloro and Nitrosyl Complexes

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The novel cyclometalated Ru(III) complex, $[Ru(\eta^2\text{-phpy})(trpy)Cl][PF_6]\cdot$toluene **1**, and the $\{Ru\text{-}NO\}^6$ complex, $[Ru(\eta^2\text{-phpy})(trpy)NO][PF_6]_2$ **2**, where trpy is 2,2′: 6′,2″-terpyridine and phpy is 2-phenylpyridine, have been prepared and characterized by elemental analysis, IR, ^{1}H NMR, and electronic absorption spectroscopies, cyclic voltammetry, and crystallography. The crystal structure of **1** showed the chloride ion trans to the σ-bonding phenyl group of phpy and is an unusual example of a stable paramagnetic cyclometalated complex. The crystal structure of **2** shows the nitrosyl ligand trans to the σ-bonding phenyl group of phpy. The significant distortion of the normally linear Ru–NO bond angle (167.1(4)°) can be largely ascribed to the strong σ-donor properties of the phenyl group.

Introduction

Our research into mixed-valence complexes[1] has led us to cyclometalated complexes because of a desire to reduce the charge of the complex cation and dramatically perturb the stability of metal orbitals. One of the most commonly used ligands, which can form cyclometalated complexes, is 2-phenylpyridine (phpyH). Under suitable conditions, this ligand will deprotonate and will bind to a metal ion as a bidentate anion ligand (phpy⁻),
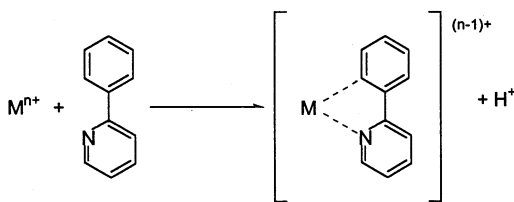
Cyclometalated complexes have gained great interest because of their photophysical and photochemical properties and their potential application to solar energy and sensor devices.[2] In the course of preparing cyclometalated precursor complexes to our mixed-valence systems, it became apparent that the chemistry of these cyclometalated complexes was sufficiently unique to warrant further investigation.

Cyclometalated complexes of ruthenium are usually six coordinate with ruthenium in the 2+ oxidation state, and they therefore obey the 18-electron rule.[3] Indeed, a literature search of ruthenium cyclometalated complexes revealed only

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one example of a cyclometalated mononuclear Ru(III) complex[4] and family of dinuclear complexes,[5] both incorporating the tridentate dianion ligand,
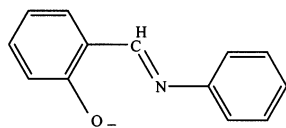
and its derivatives. For both studies,[4,5] the assigned oxidation state of ruthenium was supported by EPR spectroscopy and elemental analysis. In this study, we report the facile synthesis of a paramagnetic Ru(III) cyclometalated complex, [Ru(η^2-phpy)(trpy)Cl][PF$_6$]·toluene **1**, where trpy is 2,2′: 6′,2″-terpyridine, and the characterization of **1** by crystallography, elemental analysis, IR and UV−vis spectroscopies, and cyclic voltammetry.

Nitrosyl complexes have gained a deserved recognition as important models for nitrogen oxide regulation in biology.[6] Recent reviews[7] of the coordination chemistry of the nitrosyl ligand speak to the importance of this research, and so it was decided to attempt the synthesis of a nitrosyl complex using **1**. The result, [Ru(η^2-phpy)(trpy)NO][PF$_6$]$_2$ **2**, was prepared in nonaqueous solution and in high yields. Complex **2** was characterized by crystallography, elemental analysis, IR, ^{1}H NMR and UV−vis spectroscopies, and cyclic voltammetry. Spectroelectrochemical studies of **1** and **2** were also performed.

Experimental Section

Equipment. UV−vis spectroscopy was performed on a CARY 5 UV−vis−NIR spectrophotometer. IR spectra were taken with a BOMEM Michelson-100 FT-IR spectrophotometer (KBr disks). ^{1}H NMR data from acetonitrile-d_3 solutions were obtained by using a Bruker AMX-400 spectrometer. Cyclic voltammetry was performed using a BAS CV-27 voltammograph and plotted on a BAS XY recorder. The sample cell consisted of a double-walled glass crucible with an inner volume of ∼15 mL which was fitted with a Teflon lid incorporating a three-electrode system and argon bubbler. The cell temperature was maintained at (25.0 ± 0.1) °C by means of a HAAKE D8 recirculating bath. BAS 2013 Pt electrodes (1.6 mm diameter) were used as the working and counter electrodes. A silver wire functioned as a pseudo-reference electrode. Acetonitrile (MeCN) was dried over P$_2$O$_5$ and vacuum distilled. Tetrabutylammonium hexafluorophosphate (TBAH), purchased from Aldrich, was twice recrystallized from 1:1 ethanol/water and vacuum-dried at 110 °C. Ferrocene ($E° = 0.665$ V versus NHE) was used as an internal reference.[8] An OTTLE cell was used to perform the spectroelectrochemistry.[9] The cell had interior dimensions of

roughly 1 × 2 cm with a path length of 0.2 mm, was fitted with a silver/silver chloride reference electrode, and used ITO (indium− tin oxide) coated glass for the working and counter electrodes. Elemental analyses were performed by Canadian Microanalytical Services.

Materials. All reagents and solvents used were reagent grade or better. Nitrosonium tetrafluoroborate was purchased from Aldrich, and [Ru(trpy)Cl$_3$] was synthesized according to literature procedures.[10] ITO glass plates were purchased from Delta-Technologies.

Preparation of [Ru(η^2-phpy)(trpy)Cl][PF$_6$]·toluene, 1. [Ru-(trpy)Cl$_3$] (0.441 g, 1 mmol) and 2-phenylpyridine (0.155 g, 1 mmol) were dissolved in 20 mL of DMF and refluxed for 4 h, after which TlPF$_6$ (0.70 g, 2 mmol) was added and the solution refluxed for a further 1 h. The solution was cooled to −20 °C overnight and then filtered through Celite to remove the fine white TlCl precipitate. Diethyl ether (600 mL) was then added to the filtrate, precipitating the crude product, which was filtered off and then was purified by chromatography (grade III alumina, weakly acidic, 40 × 3 cm column). Elution with 1:2 acetonitrile/toluene yielded a purple band, which was not identified, followed by the green band of the target complex. The latter band was collected, evaporated to dryness, and then recrystallized by slow evaporation of a 3:1 acetonitrile/toluene solution of the complex. Yield: 0.39 g (51%). Anal. Calcd for [Ru(η^2-phpy)(trpy)Cl][PF$_6$]·toluene (C$_{33}$H$_{27}$N$_4$F$_6$PClRu): C, 52.08; H, 3.58; N, 7.36. Found: C, 51.88; H, 3.67; N, 7.53.

Preparation of [Ru(η^2- phpy)(trpy)NO][PF$_6$]$_2$, 2. A mixture of **1** (0.669 g, 1 mmol) and TlPF$_6$ (0.349 g, 1 mmol) was placed in 100 mL of acetonitrile and stirred at reflux for 1 h. The solution was chilled to −20 °C and filtered through Celite to remove the white TlCl precipitate. To the filtrate was then added nitrosonium tetrafluoroborate (0.14 g,1.2 mmol), and the resulting solution was stirred with slight heating (34−45 °C) for 5 h. The solution was evaporated, and the crude light brown solid recrystallized by the diffusion of diethyl ether into an acetonitrile solution of the complex. Yield: 0.65 g, (80%). Anal. Calcd for [Ru(η^2-phpy)(trpy)NO][PF$_6$]$_2$ (C$_{26}$H$_{19}$N$_5$OF$_{12}$P$_2$Ru): C, 38.63; H, 2.37; N, 8.66. Found: C, 38.90; H, 2.45; N, 8.82. IR ν(NO): 1858 cm^{-1}. ^{1}H NMR (400 MHz): 9.06 (1H, doublet), 8.75 (3H, multiplet), 8.60 (2H, doublet), 8.33 (4H, multiplet), 7.98 (3H, multiplet), 7.79 (1H, triplet), 7.57 (2H, triplet), 7.17 (1H, triplet), 6.88 (1H, triplet), 5.79 (1H, doublet) ppm.

Crystallography. Crystals of **1** were grown by the slow evaporation of a 3:1 acetonitrile/toluene solution of the complex. Diffusing diethyl ether into an acetonitrile solution of the complex grew crystals of **2**. For both complexes, the data were collected on a 1K Siemens Smart CCD using Mo Kα radiation ($\lambda = 0.71073$ Å) at 203(2) K using an ω-scan technique and corrected for absorptions using equivalent reflections.[11] No symmetry higher than triclinic was observed, and solution in the centric space group option yielded chemically reasonable and computationally stable results of refinement. The structure was solved by direct methods and refined with full-matrix least-squares procedures. For **1**, two half-occupied molecules of toluene were found cocrystallized near the inversion center in the asymmetric unit. These were refined with phenyl groups idealized as rigid, flat hexagons. In addition, the PF$_6$ counterion in **1** was restrained to have similar cis F···F interatomic separations. Anisotropic refinement was performed on all non-hydrogen atoms. All hydrogen atoms were calculated.

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**Table 1.** Crystal Data and Structure Refinement for Complexes **1** and **2**

	1	**2**
formula	$C_{33}H_{27}F_6ClN_4PRu$	$C_{26}H_{19}F_{12}N_5OP_2Ru$
fw	761.08	808.47
space group	$P\bar{1}$	$P\bar{1}$
cryst syst	triclinic	triclinic
Z'	2	
D_c, g/cm^3	1.636	1.864
a, Å	11.165(3)	8.9387(8)
b, Å	11.335(3)	10.4325(9)
c, Å	13.447(4)	16.7004(15)
α, deg	68.768(2)	77.6950(10)
β, deg	78.303(3)	88.7732(2)
γ, deg	80.274(3)	71.3870(10)
V, Å^3	1544.7(8)	1440.2(2)
temp, K	203(2)	203(2)
GOF on F^2	1.038	1.063
R1^a	0.0518	0.0509
wR2^b	0.1075	0.1494

^{a} R1 = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} wR2 = $(\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$.

Scattering factors are contained in the SHELXTL 5.1 program library.

Results and Discussion

The synthetic strategy to prepare complex **1** was based on a modification of the procedure used to prepare [Ru(bpy)$_2$-(η^2-phpy)]$^+$.[12] The latter complex was prepared by the reaction of stoichiometric amounts of [Ru(bpy)$_2$Cl$_2$], phenylpyridine, and silver(I) tetrafluoroborate in refluxing dichloromethane, without the addition of base to deprotonate 2-phenylpyridine. In this study, a similar reaction between the Ru(III) complex, [Ru(trpy)Cl$_3$], 2-phenylpyridine, and thallium hexafluorophosphate in refluxing dimethylformamide (eq 1), gave **1** in 51% final yield. Refluxing dimeth-

$$[Ru(trpy)Cl_3] + 2TlPF_6 + Hphpy \rightarrow$$
$$[Ru(phpy)(trpy)Cl]^+ + 2TlCl\downarrow + 2PF_6^- + H^+ \quad (1)$$
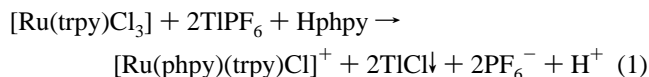
ylformamide was thought necessary to overcome the greater inertness of Ru(III) toward substitution reactions. Elemental analysis of **1** was entirely consistent with its proposed stoichiometry, and attempts to determine its ^{1}H NMR spectrum showed that the complex was paramagnetic, supporting a Ru(III) oxidation state. An unambiguous determination of the stoichiometry of **1** was made by crystallography.

For **1**, crystal structure data can be found in Table 1 and an ORTEP is shown in Figure 1 together with selected bond lengths and bond angles. The crystal structure shows terpyridine, phenylpyridine, and chloride ligands coordinated to a Ru(III) ion in which the σ-bonded phenyl group of phenylpyridine is trans to the chloride ligand. Ru–nitrogen and Ru–carbon bond lengths of **1** are significantly shorter than those of complex **2** (discussed below), whose metal ion oxidation state is formally Ru(II). The contracted coordination sphere of **1** compared to **2** is therefore a consequence of the oxidation state of the central metal ion.
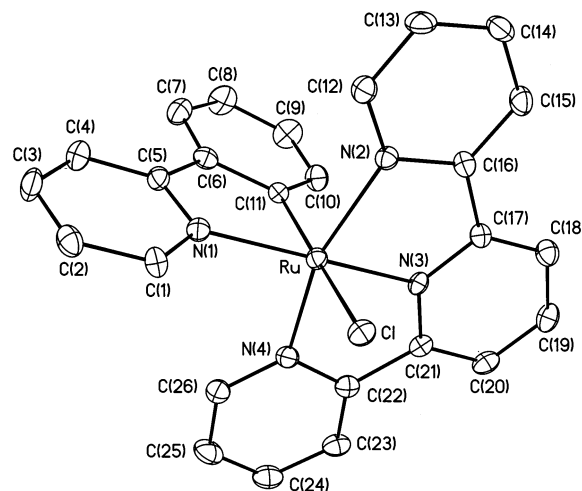
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Figure 1. ORTEP drawing of [Ru(η^2-phpy)(trpy)Cl]PF$_6$·toluene **1**. The counterion and solvent of crystallization have been omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Ru–N(3), 1.971(4); Ru–N(4), 2.060(4); Ru–N(2), 2.076(3); Ru–C(11), 2.024(4); Ru–N(1), 2.091-(4); Ru–Cl, 2.4431(13); N(3)–Ru–C(11), 95.43(16); N(3)–Ru–N(4), 79.70(15); C(11)–Ru–N(4), 90.93(15); N(3)–Ru–N(2), 79.05(14); C(11)–Ru–N(2), 86.23(15); N(4)–Ru–N(2), 158.19(15); N(3)–Ru–N(1), 174.54-(14); C(11)–Ru–N(1), 79.77(16); N(4)–Ru–N(1), 97.68(14); N(2)–Ru–N(1), 103.07(14); N(3)–Ru–Cl, 90.64(10); C(11)–Ru–Cl, 171.43(13); N(4)–Ru–Cl, 96.11(10); N(2)–Ru–Cl, 89.00(10); N(1)–Ru–Cl, 94.41-(10).

Cyclic voltammetry was performed on an acetonitrile solution of **1** with 0.1 M TBAH supporting electrolyte. Three couples were observed at +0.46, −1.32, and −1.61 V vs NHE that we assigned to the Ru(III/II) reduction couple and two terpyridine reduction couples, respectively. Terpyridine's π^* orbitals are expected to be more stable compared to anionic phenylpyridine and should be reduced first.[1b] The cyclic voltammogram of the Ru(III/II) couple possessed equivalent anodic and cathodic waves whose separation (60 mV) was independent of scan rate (100−450 mV/s). Figure 2 shows the spectroelectrochemistry associated with this Ru-(III/II) couple. In Figure 2, complex **1** shows low-energy bands in the visible region that, due to their intensity, are likely phenyl to Ru(III) ligand-to-metal charge transfer transitions, $p\pi \rightarrow d\pi$. Upon reduction to Ru(II) (Figure 2), these bands are replaced by a number of $d\pi \rightarrow p\pi^*$ metal-to-ligand charge transfer transitions derived from the π^* orbitals of terpyridine. Regeneration of **1** occurred with greater than 95% recovery of the original spectrum.

Ruthenium nitrosyl complexes have been previously prepared[13–15] by the acid decomposition of the corresponding nitro complex in aqueous solution,

$$Ru^{II} - NO_2 + 2H^+ \rightarrow \{Ru(NO)\}^6 + H_2O \quad (2)$$

To prepare **2** in nonaqueous solution, nitrosonium tetrafluoroborate was added to an acetonitrile solution of the complex (eqs 3−5). Nitrosonium oxide is a powerful oxidant (1.52

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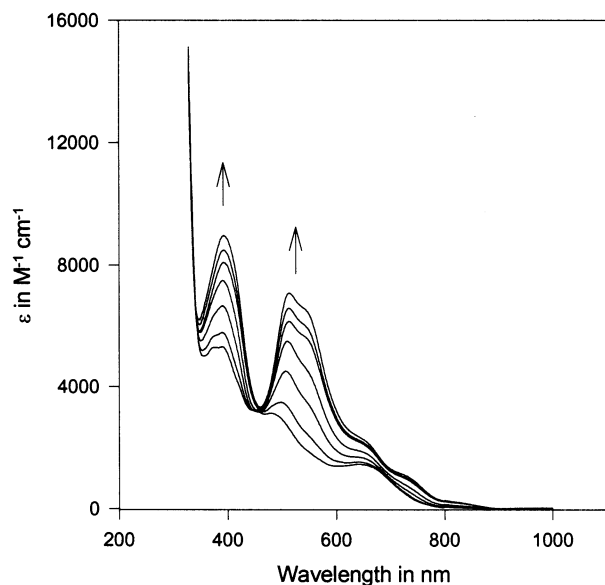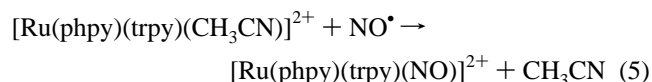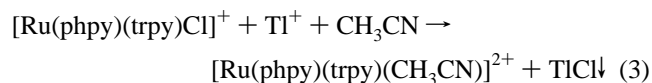(15) Dovletoglou, A.; Adeyemi, S. A.; Meyer, T. J. *Inorg. Chem.* **1996**, *35*, 4120−4127.

Figure 2. Spectroelectrochemical reduction of **1**, 0.1 M TBAH electrolyte in acetonitrile. Potential change from +0.6 to −0.3 V vs silver/silver chloride reference electrode.

V vs NHE),[16] and it seems probable, on the basis of the yield of **2** (80%), that the concentration of reducing impurities in acetonitrile generated sufficient nitrogen oxide to nearly quantitatively react with the Ru(III)−solvato complex.

$$[Ru(phpy)(trpy)Cl]^+ + Tl^+ + CH_3CN \rightarrow$$

$$[Ru(phpy)(trpy)(CH_3CN)]^{2+} + TlCl\downarrow \quad (3)$$

$$NO^+ + e^- \rightarrow NO^\bullet \quad (4)$$

$$[Ru(phpy)(trpy)(CH_3CN)]^{2+} + NO^\bullet \rightarrow$$

$$[Ru(phpy)(trpy)(NO)]^{2+} + CH_3CN \quad (5)$$

Another possible route to **2** is the ligand substitution reaction of the Ru(II) solvato complex with NO^+, but this seems less likely as it would require that the ruthenium(III) solvato complex be reduced before NO^+.[17]

For **2**'s ^{1}H NMR spectrum (see Experimental Section), only 10 chemical shifts out of the expected 14 were observed, but, as indicated by integration, this was clearly due to the overlap of chemical shifts. The elemental analysis is in agreement with the proposed stoichiometry, which, because there are six π electrons between metal and the nitrosyl ligand, identifies **2** as a $\{Ru(NO)\}^6$ system.[18] For the majority of ruthenium nitrosyl complexes, the nitrosyl ligand is formally NO^+ and its coordination to the metal ion is linear.[13−15,19] However, crystal structures of iron and ruthenium porphyrin $\{M-NO\}^6$ systems, in which a phenyl group was trans to a nitrosyl ligand, showed a bent coordination

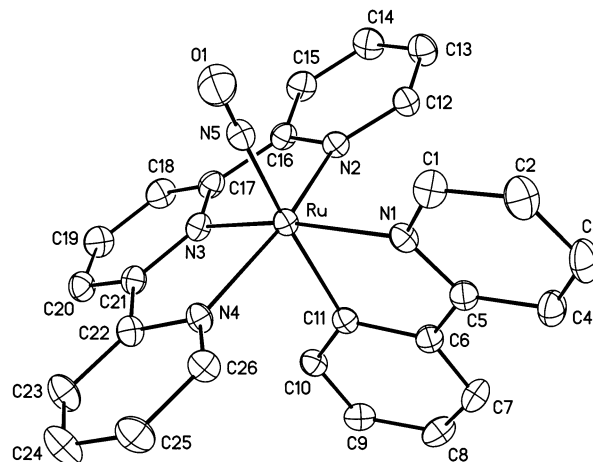(16) Rathore, R.; Lindeman, S. V.; Kochi, J. K. *J. Am. Chem. Soc.* **1997**, *119*, 9393−9404. $NO^{+/0}$ = 1.28 V vs SCE.

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Figure 3. ORTEP drawing of $[Ru(\eta^2\text{-phpy})(trpy)NO][PF_6]_2$ **2**. The counterions have been omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Ru−N(1), 2.111(4); Ru−N(4), 2.108(3); Ru−N(2), 2.101(3); Ru−N(3), 1.991(4); Ru−C(11), 2.096(4); Ru−N(5), 1.826(4); N(5)−O(1), 1.139(5); N(5)−Ru−C(11), 170.30(16); N(5)−Ru−N(3), 100.79-(15); N(3)−Ru−C(11), 88.31(15); N(5)−Ru−N(2), 97.13(15); N(3)−Ru−N(2), 79.60(14); C(11)−Ru−N(2), 87.76(14); N(5)−Ru−N(4), 91.59(15); N(3)−Ru−N(4), 79.12(14); C(11)−Ru−N(4), 86.78(14); N(5)−Ru−N(1), 92.62(15); N(2)−Ru−N(4), 158.17(14); C(11)−Ru−N(1), 78.41(15); N(2)−Ru−N(1), 97.35(13); N(4)−Ru−N(1), 102.21(13); O(1)−N(5)−Ru, 167.1-(4).

mode of the nitrosyl ligand.[19] As the phenyl group of the phpy ligand is also expected to be trans to the nitrosyl in **2**, it was therefore of interest to determine the crystal structure of **2**.

Crystal structure data for **2** can be found in Table 1, and an ORTEP drawing is shown in Figure 3, together with selected bond lengths and bond angles. The crystal structure shows that the phenyl group is trans to the nitrosyl ligand. The Ru−nitrosyl bond length (Ru−N(5)) is 1.826(4) Å and is significantly shorter than the other Ru−N bonds. In addition, the NO bond length of 1.139(5) Å shows the triple-bond character of the nitrosyl ligand. These facts are consistent with a π acceptor NO^+ ligand. On the other hand, the Ru−NO bond angle (O(1)−N(5)−Ru) is 167.1(4)° and outside the normal range of linear ruthenium nitrosyl bonds (170−180°).[19] As mentioned above, crystal structures of ruthenium and iron octaethylporphyrinato dianion $\{M(NO)\}^6$ complexes in which the nitrosyl ligand is trans to a strong σ-donating phenyl ligand showed unexpected metal−nitrosyl bending (154.9(3)° and 157.4(2)°, respectively).[19] Density functional based calculations reproduced these structural distortions, and the authors suggest that a bent metal−nitrosyl bond is intrinsic to species of the type [(por)M(NO)X] where X is a strong σ donor ligand and por is a porphyrin.[19] While the same degree of bending is not seen in **2** despite having a phenyl ligand trans to the nitrosyl, this is probably related to the charge and electron-donating ability of the auxiliary ligands. Porphyrins are dianion tetradentate ligands and are expected to donate significantly greater electron density to the metal ion compared to the four neutral pyridine moieties in **2**.

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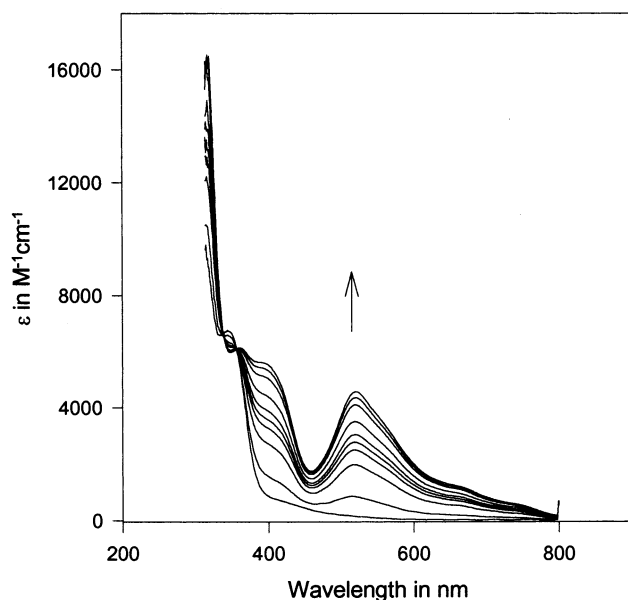
Figure 4. Irreversible spectroelectrochemical reduction of **2**, 0.1 M TBAH electrolyte in acetonitrile. Potential change from +0.6 to −0.6 V vs silver/silver chloride reference electrode.

Cyclic voltammetry was performed on an acetonitrile solution of **2** with 0.1 M TBAH supporting electrolyte. In contrast to **1**, the voltammogram of **2** showed significant irreversibility of the reduction couples. A couple at −0.03 V vs NHE was assigned to the {Ru(NO)}$^{6/7}$ reduction and based on previous studies[14,15] is likely nitrosyl localized. This couple's cyclic voltammogram showed the cathodic wave to be considerably larger than the anodic wave, suggesting that a rearrangement or chemical reaction follows reduction. The electronic absorption spectra associated with this irreversible reduction are seen in Figure 4. Two new absorptions centered at 415 and 481 nm are likely dπ* metal-to-ligand charge transfer transitions of Ru(II) to the π* orbitals of terpyridine (by analogy compare Figure 4 to the reduction of **1**, Figure 2). The oxidation of this reduction product did not reproduce the original spectrum of **2**, and so a new complex has formed. If this oxidized complex was reduced, the same absorption spectrum seen upon reduction of **2** was obtained (Figure 4). A recent study of the final degradation products of ruthenium nitrosyl complexes of the general formula *cis*-[Ru(bpy)$_2$X(NO)]$^{n+}$ {Ru(NO)}^{7} in acetonitrile showed a significant dependence of products upon the nature of the ligand X.[17] For the complex, *cis*-[Ru(bpy)$_2$Cl(NO)]$^+$ only two products were identified: the starting material *cis*-[Ru(bpy)$_2$Cl(NO)]$^{2+}$ and the solvolysis product, *cis*-[Ru-(bpy)$_2$Cl(CH$_3$CN)]$^+$. By analogy to this result, we suggest that the final absorption spectrum of the reduction product of **2** in Figure 4 is likely [Ru(η^2-phpy)(trpy)(CH$_3$CN)]$^+$ (eq 6). The oxidation of this complex (eq 7) was reversible.

$$[Ru(phpy)(trpy)(NO)]^{2+} + e^- \rightarrow$$
$$[Ru(phpy)(trpy)(CH_3CN)]^+ + NO^{\bullet} \quad (6)$$

$$[Ru(phpy)(trpy)(CH_3CN)]^+ \rightleftharpoons$$
$$[Ru(phpy)(trpy)(CH_3CN)]^{2+} + e^- \quad (7)$$
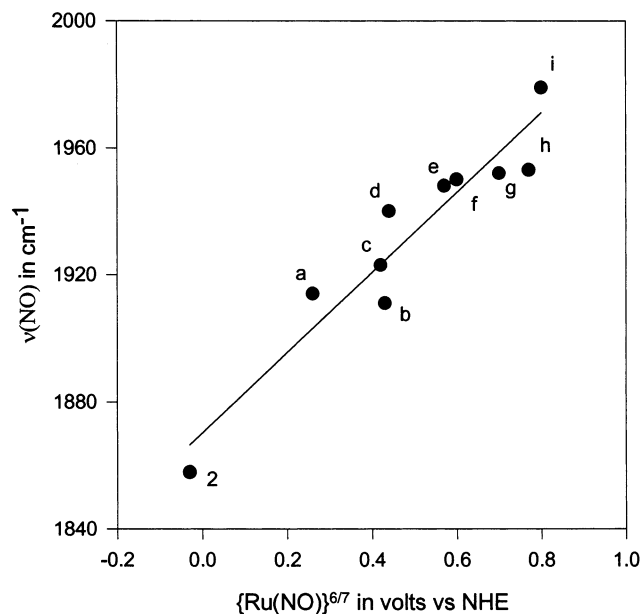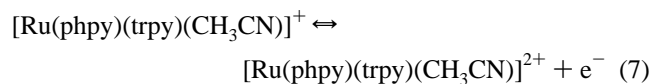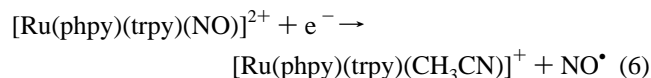
Figure 5. Plot of {Ru(NO)}$^{6/7}$ couples in acetonitrile versus ν(NO). Data points: **2**, [Ru(η^2-phpy)(trpy)(NO)]$^{2+}$, and from refs 13−15, (a) *cis*-[Ru-(trpy)(acetylacetonate)NO]$^{2+}$ in CH$_2$Cl$_2$, (b) *trans*-[Ru(bpy)$_2$(NO)Cl]$^{2+}$, (c) *cis*-[Ru(bpy)$_2$(NO)N$_3$]$^{2+}$, (d) *cis*-[Ru(bpy)$_2$(NO)Cl]$^{2+}$, (e) *cis*-[Ru(bpy)$_2$-(NO)NO$_2$]$^{2+}$, (f) *cis*-[Ru(bpy)$_2$(NO)NH$_3$]$^{3+}$, (g) [Ru(trpy)(bpy)NO]$^{3+}$, (h) *cis*-[Ru(bpy)$_2$(NO)pyridine]$^{3+}$, (i) *cis*-[Ru(bpy)$_2$(NO)(CH$_3$CN)]$^{3+}$. Best fit linear equation: ν(NO) = 126{Ru(NO)}$^{6/7}$ + 1870, R^2 = 0.91.

Linear plots of the {Ru(NO)}$^{6/7}$ couple versus ν(NO) have appeared in the literature[14,15] with the rationalization that if the initial reduction of a nitrosyl complex is associated with the NO$^{+/0}$ couple, it should be very sensitive to the energy of the lowest unoccupied molecular orbital (LUMO) of NO$^+$, which will vary depending on the ability of the metal ion to π-donate to the π acceptor NO$^+$. Figure 5 shows this plot together with a data point derived from **2** and the linear least-squares best-fit equation of all the data. Inclusion of **2** has almost doubled the range of the linear correlation in Figure 5, but there is still a need for further data to establish this relationship throughout the entire range.

Conclusions

Two novel cyclometalated ruthenium complexes have been synthesized and structurally characterized. Complex **1** represents an unusual example of a paramagnetic organometallic complex possessing a Ru(III) central ion. This complex showed good reversibility upon reduction as evidenced by spectroelectrochemical studies. The crystal structure of the {Ru(NO)}^{6} complex, **2**, showed a σ-donating phenyl group trans to the nitrosyl ligand and significant deviation of the Ru−NO bond angle (167.1(4)°) from linearity. This degree of bending is not as much as that seen for ruthenium and iron octaethylporphyrinato dianion {M(NO)}^{6} complexes in which the nitrosyl ligand is trans to a strong σ-donating phenyl ligand (M−NO angle = 154.9(3)° and 157.4(2)°, respectively) and is likely a consequence of the greater electron density donated by the porphyrin ligand to ruthenium. Complex **2** is suggested to be an intermediate case between linear and bent coordination modes for ruthenium nitrosyl complexes.

Supporting Information Available: Two X-ray crystallographic files, in CIF format, for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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