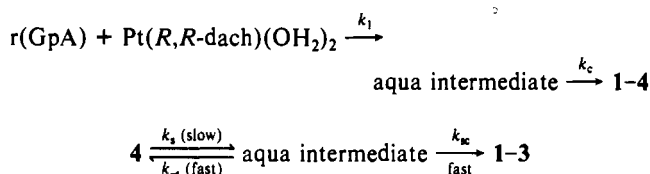


suppressed at low pH (supplementary material Figure S1). This is likely to be due to the fact that protonation at A-N1 of the aqua intermediate inhibits the formation of **2**. The competitions at A-N1 between platinum and proton are also expected to occur in the reaction forming **4** from the aqua intermediate, i.e.  $k_{-3}$ , and this is likely to lead a promotion of  $k_{\text{obs(s)}}$  observed at low pH.

The isomerization from **4** to **1–3** is enhanced in a presence of halogen ions. In the HPLC chromatogram, an intermediate peak, presumably Pt(*R,R*-dach)(X)(r(GpA)-N7(I)), X = Cl, Br, and I, has been observed. The observed rate constant for the conversion of **4** shows a linear dependence upon an excess of halogen ion concentration ( $[X] = 0.01\text{--}0.2\text{ M}$ ) and a nonzero intercept at  $[X] = 0$ . The data fit well in a two-term rate expression ( $k_{\text{obs}} = k_{\text{obs(s)}} + k_X[X]$ ), which is the well-known rate law for the substitution reactions of the square-planar platinum complex. The rate constants obtained from the intercepts were found to agree within experimental error with the rate constant obtained in an absence of halogen ions. The result also supports the solvolytic path in the isomerization reaction. The values<sup>14</sup> of  $k_X$  increases in the order  $\text{Cl}^- < \text{Br}^- < \text{I}^-$ .

In conclusion, the chelate formation reaction between [Pt(*R,R*-dach)]<sup>2+</sup> and r(GpA) proceeds according to the following reaction scheme (in the absence of halogen ions).



The reverse reaction (from **1–3** to **4**) was not observed. It is worth noting that the same reaction scheme has also been observed in the reaction between *cis*-[Pt(NH<sub>3</sub>)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>]<sup>2+</sup> and r(GpA) and d(GpA) and that the conversion reaction such as **4** → **1–3** could not be observed in the case of reaction between [Pt(*R,R*-dach)(OH<sub>2</sub>)<sub>2</sub>]<sup>2+</sup> and r(ApG) (unpublished observation).

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**Supplementary Material Available:** Table SI, giving kinetic data for the isomerization reaction, and Figure S1, showing the relative ratio of the final Pt adducts, **1–3**, as a function of pH (2 pages). Ordering information is given on any current masthead page.

(14)  $k_{\text{Cl}} = 6.7 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_{\text{Br}} = 4.0 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ , and  $k_1 = 8.1 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$  at 37 °C.

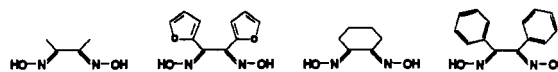
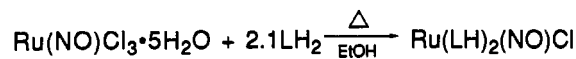
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### Preparation and Characterization of *trans*-Bis( $\alpha$ -dioximato)ruthenium Complexes

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The synthesis and characterization of transition-metal complexes that contain a ruthenium metal center coordinated to chelating nitrogen donor ligands have been subjects of considerable interest in our laboratory<sup>1–6</sup> and elsewhere.<sup>7–19</sup> In addition, the coordi-



LH<sub>2</sub> = DMGH<sub>2</sub>, DFGH<sub>2</sub>, NOXH<sub>2</sub>, DPGH<sub>2</sub>

**Figure 1.** Reaction scheme for the synthesis of *trans*-bis( $\alpha$ -dioximato)ruthenium complexes. DMGH<sub>2</sub> = dimethylglyoxime, DFGH<sub>2</sub> =  $\alpha$ -furil dioxime, NOXH<sub>2</sub> = 1,2-cyclohexanedione dioxime, and DPGH<sub>2</sub> = diphenylglyoxime.

nation chemistry of chelating  $\alpha$ -dioxime ligands has been extensively investigated with first-row transition metals,<sup>22–26</sup> where *trans*-bis( $\alpha$ -dioximato) transition-metal complexes have been utilized as analytical reagents,<sup>20,21,29</sup> models for biological systems such as vitamin B<sub>12</sub>,<sup>30–32</sup> dioxygen carriers,<sup>33,34</sup> and catalysts in chemical processes.<sup>35–38</sup> The only examples of *trans*-bis( $\alpha$ -di-

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oximate)ruthenium complexes for ruthenium have been reported by Wilkinson<sup>27</sup> and by Fukuchi.<sup>28</sup> Wilkinson studied the interaction of  $\text{Ru}^{\text{II}}(\text{PPh}_3)_3\text{Cl}_2$  with various dioxime ligands (dimethylglyoxime, 1,2-cyclohexanedione dioxime, diphenylglyoxime), but the resultant complexes could not be fully characterized due to poor solubility.<sup>27</sup> The ruthenium  $\alpha$ -dioximate complexes synthesized by Fukuchi utilized dimethylglyoxime or diphenylglyoxime, where a limited amount of physical characterization was reported.<sup>28</sup>

In order to further understand the area of bis( $\alpha$ -dioximate)ruthenium coordination chemistry, there is need for additional synthetic methodology and characterization of  $\alpha$ -dioxime complexes that contain ruthenium. In our continuing effort to synthesize and characterize ruthenium  $\alpha$ -dioximate complexes,<sup>39,40</sup> we wish to report the synthesis of a series of *trans*-bis( $\alpha$ -dioximate) complexes of ruthenium(II) that contain nitrosyl and chloride ligands and utilize various dioxime ligands (dimethylglyoxime, 1,2-cyclohexanedione dioxime, diphenylglyoxime), including the first example of a ruthenium complex containing  $\alpha$ -furyl dioxime (Figure 1). These complexes were fully characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, UV-visible, and infrared spectroscopies, cyclic voltammetry, and elemental analysis. <sup>13</sup>C NMR spectroscopy is a useful technique for elucidating structural orientation of the bis( $\alpha$ -dioximate) ligands,<sup>41-44</sup> but only a few studies have been conducted on transition-metal  $\alpha$ -dioximate complexes because of poor solubility.<sup>41-43,45</sup> The determination of <sup>13</sup>C NMR spectra of these complexes was possible due to the increased solubility obtained in utilizing a ruthenium system containing nitrosyl and chloride ligands.

### Experimental Section

**Materials.** The following chemicals were obtained commercially and used as received: ruthenium trichloride trihydrate (Johnson Matthey Inc.), dimethylglyoxime (DMGH<sub>2</sub>) (Lancaster Synthesis Ltd.), 1,2-cyclohexanedione dioxime (NOXH<sub>2</sub>) (Aldrich Chemical Co.), diphenylglyoxime (DPGH<sub>2</sub>) (Aldrich Chemical Co.), and  $\alpha$ -furyl dioxime monohydrate (DFGH<sub>2</sub>) (Spectrum Chemical Co.). All other solvents were of reagent grade and used as received. All syntheses were carried out under nitrogen unless otherwise stated.

**Measurements.** Elemental analyses were conducted by Atlantic Microlabs. Infrared spectra of Nujol mulls were measured with a Perkin-Elmer 710 B infrared spectrophotometer. Electronic absorption spectra were measured with a Milton Roy Spectronic 3000 array spectrophotometer equipped with a Hewlett-Packard 7470A plotter, and the <sup>1</sup>H NMR spectra were recorded with a JEOL FX90Q Fourier transform NMR spectrometer. <sup>13</sup>C NMR spectra were recorded with either a JEOL FX90Q or a Varian Gemini 300 Fourier transform NMR spectrometer. Chemical shifts are reported in parts per million relative to tetramethylsilane (TMS) for <sup>1</sup>H NMR experiments and relative to the deuterated solvent used for <sup>13</sup>C NMR experiments. Cyclic voltammetric experiments were carried out under a N<sub>2</sub> atmosphere by using methylene chloride as the solvent and tetra-*n*-butylammonium tetrafluoroborate as the supporting electrolyte, which was prepared by standard methods.<sup>46</sup> A platinum working electrode (Bioanalytical Systems), a platinum auxiliary electrode, and a saturated sodium chloride calomel reference electrode (SSCE) were used for all electrochemical experiments. Prior to use the platinum working electrode was polished for 30 s by utilizing a minimet polisher (Buehler Ltd.), 1- $\mu\text{m}$  diamond polishing compound (Buehler Ltd.), metadi fluid (Buehler Ltd.), and a 2<sup>7</sup>/<sub>8</sub>-in. polishing cloth (Buehler Ltd.), followed by sonication for 30 s in reagent grade methanol. Ferrocene was utilized as an internal standard for the measurement of  $\Delta E_p$  values. Cyclic voltammetry was conducted with an IBM EC/225

polarographic analyzer equipped with a Houston Instruments Model 100 recorder.

**Preparation of the Complexes. Ru(NO)Cl<sub>3</sub>·5H<sub>2</sub>O.** This complex was synthesized by modification of literature preparations.<sup>47-49</sup> A 2.50-g sample of  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  (9.6 mmol) was added to 10 mL of degassed 1 M HCl and the mixture heated to reflux, and then 1.97 g of  $\text{NaNO}_2$  (28.5 mmol) dissolved in 5 mL of  $\text{H}_2\text{O}$  was added dropwise over period of 30 min. The brown solution was heated at reflux for an additional 2.5 h. The existing dark red solution was taken to dryness under reduced pressure and the solid dissolved in 10 mL of ethanol. The red solution was filtered and reduced to dryness by rotary evaporation. This residue was dissolved in 5 mL of 6 M HCl and taken to dryness under reduced pressure. The brick red product was then dissolved in 2 mL of  $\text{H}_2\text{O}$  and reduced to dryness by rotary evaporation; this procedure was repeated an additional two times. The red residue was stored in a desiccator ( $\text{CaSO}_4$ ) for 12 h, yielding (2.6 g) 83% of the desired product. UV-vis max (6 M  $\text{HClO}_4$ ): 501 nm ( $\epsilon$  46), reported 480 nm ( $\epsilon$  49).<sup>49</sup> IR (Nujol mull): 1915  $\text{cm}^{-1}$  (NO), reported 1920  $\text{cm}^{-1}$ .<sup>49</sup>

***trans*-Ru(DMGH)<sub>2</sub>(NO)Cl (1).** A 0.500-g sample of  $\text{Ru}(\text{NO})\text{Cl}_3 \cdot 5\text{H}_2\text{O}$  (1.53 mmol) and 0.373 g of dimethylglyoxime (DMGH<sub>2</sub>) (3.21 mmol) were added to 50 mL of degassed ethanol, and the mixture was heated under reflux for 12 h. The resultant dark brown solution was cooled in an ice bath for 30 min and vacuum filtered. The dark orange solid was dissolved in 20 mL of a 50:50 mixture of methylene chloride and ethanol, and the solution was then rotary evaporated until precipitation was observed. The mixture was cooled in an ice bath for 2 h. Orange microcrystals were collected by vacuum filtration and washed with cold ethanol; yield (0.150 g) 25%. Anal. Calcd for  $\text{C}_8\text{H}_{14}\text{ClN}_2\text{O}_5\text{Ru}(\text{H}_2\text{O})$ : C, 23.16; H, 3.89. Found: C, 22.93; H, 3.63. UV-vis max ( $\text{CH}_2\text{Cl}_2$ ): 252 ( $\epsilon$  11 000), 341 nm (sh). IR (Nujol mull): 2650 and 1630 (O—H), 1900 ( $\text{N}=\text{O}$ ), 1530 (C=N), 1235 and 1085  $\text{cm}^{-1}$  (N—O). <sup>1</sup>H NMR ( $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  2.4 (s, 12), 13.5 (br s, 2). Proton-decoupled <sup>13</sup>C NMR ( $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  13.8 (s), 160.6 (s). Proton-coupled <sup>13</sup>C NMR ( $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  13.7 (q, <sup>1</sup> $J_{\text{C-H}}$  = 130 Hz), 160.4 (s).

***trans*-Ru(NOXH)<sub>2</sub>(NO)Cl (2).** A 0.500-g sample of  $\text{Ru}(\text{NO})\text{Cl}_3 \cdot 5\text{H}_2\text{O}$  (1.53 mmol) and 0.457 g of 1,2-cyclohexanedione dioxime (NOXH<sub>2</sub>) (3.21 mmol) were added to 50 mL of degassed ethanol, and the mixture was heated under reflux for 2 h. The resultant dark brown solution was cooled in an ice bath for 30 min and vacuum filtered. The orange solid obtained was dissolved in 20 mL of a 50:50 mixture of methylene chloride and ethanol. The existing solution was then rotary evaporated until precipitation was observed. The mixture was cooled in an ice bath for 2 h. Gold microcrystals were collected by vacuum filtration and washed with cold ethanol; yield (0.155 g) 23%. Anal. Calcd for  $\text{C}_{12}\text{H}_{18}\text{ClN}_3\text{O}_5\text{Ru}(\text{CH}_2\text{Cl}_2)$ : C, 29.25; H, 3.78. Found: C, 29.58; H, 3.95. UV-vis max ( $\text{CH}_2\text{Cl}_2$ ): 256 ( $\epsilon$  12 000), 352 nm (sh). IR (Nujol mull): 2675 and 1600 (O—H), 1890 ( $\text{N}=\text{O}$ ), 1520 (C=N), 1220 and 1050  $\text{cm}^{-1}$  (N—O). <sup>1</sup>H NMR ( $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  1.7 (s, 8), 2.8 (s, 8), 10.8 (br s, 2). Proton-decoupled <sup>13</sup>C NMR ( $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  20.0 (s), 26.2 (s), 160.4 (s). Proton-coupled <sup>13</sup>C NMR ( $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  23.3 (m, <sup>1</sup> $J_{\text{C-H}}$  = 145 Hz), 160.4 (s).

***trans*-Ru(DPGH)<sub>2</sub>(NO)Cl (3).** A 0.500-g sample of  $\text{Ru}(\text{NO})\text{Cl}_3 \cdot 5\text{H}_2\text{O}$  (1.53 mmol) and 0.770 g of diphenylglyoxime (DPGH<sub>2</sub>) (3.21 mmol) were added to 100 mL of degassed ethanol, and the mixture was heated under reflux for 15 h. The resultant dark red solution was cooled in an ice bath for 30 min and vacuum filtered. The red solid obtained was dissolved in 40 mL of a 50:50 mixture of methylene chloride and ethanol. The existing solution was then rotary evaporated until precipitation was observed. The mixture was cooled in an ice bath for 2 h. Dark orange microcrystals were collected by vacuum filtration and washed with cold ethanol; yield (0.263 g) 27%. Anal. Calcd for  $\text{C}_{28}\text{H}_{22}\text{ClN}_3\text{O}_5\text{Ru}$ : C, 52.13; H, 3.44. Found: C, 51.95; H, 3.42. UV-vis max ( $\text{CH}_2\text{Cl}_2$ ): 262 ( $\epsilon$  37 000), 322 nm (sh). IR (Nujol mull): 2550 and 1650 (O—H), 1880 ( $\text{N}=\text{O}$ ), 1505 (C=N), 1300 and 1100  $\text{cm}^{-1}$  (N—O). <sup>1</sup>H NMR ( $\text{CDCl}_3$ ):  $\delta$  7.3 (s, 20), 10.8 (s, 2). Proton-decoupled <sup>13</sup>C NMR ( $\text{CDCl}_3$ ) (Gemini 300):  $\delta$  128.2 (s), 128.6 (s), 129.9 (s), 130.2 (s), 156.1 (s). Proton-coupled <sup>13</sup>C NMR ( $\text{CDCl}_3$ ) (Gemini 300):  $\delta$  128.2 (dd, <sup>1</sup> $J_{\text{C-H}}$  = 163 Hz, <sup>3</sup> $J_{\text{C-H}}$  = 6 Hz), 128.5 (t, <sup>3</sup> $J_{\text{C-H}}$  = 7 Hz), 129.9 (dt, <sup>1</sup> $J_{\text{C-H}}$  = 164 Hz, <sup>3</sup> $J_{\text{C-H}}$  = 5 Hz), 130.2 (dt, <sup>1</sup> $J_{\text{C-H}}$  = 162 Hz, <sup>3</sup> $J_{\text{C-H}}$  = 7 Hz), 156.1 (s).

***trans*-Ru(DFGH)<sub>2</sub>(NO)Cl (4).** This complex was prepared as described for **2**, where a 0.500-g sample of  $\text{Ru}(\text{NO})\text{Cl}_3 \cdot 5\text{H}_2\text{O}$  (1.53 mmol) and 0.765 g of  $\alpha$ -furyl dioxime monohydrate (DFGH<sub>2</sub>) (3.21 mmol) were added to 50 mL of degassed ethanol and the mixture was heated under

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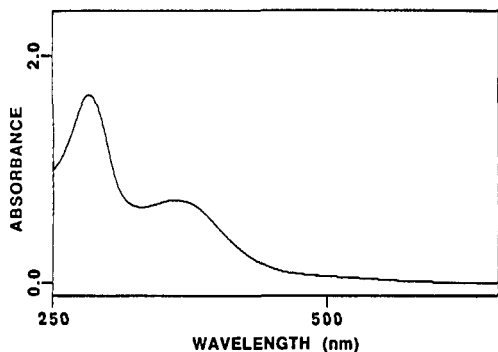


Figure 2. UV-visible spectrum of Ru(DFGH)<sub>2</sub>(NO)Cl ( $3.8 \times 10^{-5}$  M) in methylene chloride.

reflux for 1.5 h. The product was purified as for **2**. The product was collected by vacuum filtration as purple microcrystals, which were washed with cold ethanol; yield (0.105 g) 11%. Anal. Calcd for C<sub>20</sub>H<sub>14</sub>ClN<sub>3</sub>O<sub>9</sub>Ru: C, 39.71; H, 2.33. Found: C, 39.60; H, 2.37. UV-vis max (CH<sub>2</sub>Cl<sub>2</sub>): 283 ( $\epsilon$  43 000), 362 (19 000). IR (Nujol mull): 2550 and 1630 (O—H), 1870 (N=O), 1560 (C=N), 1300 and 1105 cm<sup>-1</sup> (N—O). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  6.6 (m, 4), 7.5 (m, 8), 10.0 (s, 2). Proton-decoupled <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  112.0 (s), 118.7 (s), 141.8 (s), 143.9 (s), 145.2 (s). Proton-coupled <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  112.0 (d, <sup>1</sup>J<sub>C-H</sub> = 178 Hz), 118.7 (d, <sup>1</sup>J<sub>C-H</sub> = 182 Hz), 141.6 (s), 144.0 (d, <sup>1</sup>J<sub>C-H</sub> = 205 Hz), 145.2 (s).

## Results and Discussion

**Synthesis.** This paper describes the synthesis of four ruthenium complexes containing  $\alpha$ -dioxime ligands, including the first reported ruthenium complex containing  $\alpha$ -furyl dioxime. The complexes *trans*-Ru(DMGH)<sub>2</sub>(NO)Cl, *trans*-Ru(NOXH)<sub>2</sub>(NO)Cl, *trans*-Ru(DPGH)<sub>2</sub>(NO)Cl, and *trans*-Ru(DFGH)<sub>2</sub>(NO)Cl were obtained from the reaction of Ru(NO)Cl<sub>3</sub>·5H<sub>2</sub>O with 2.1 mol equiv of the desired  $\alpha$ -dioxime in refluxing ethanol for a period of 1.5–15 h (Figure 1). Analytically pure products were obtained by recrystallization from a 50:50 mixture of methylene chloride and ethanol. The use of Ru(NO)Cl<sub>3</sub>·5H<sub>2</sub>O provided a useful source of ruthenium and yielded *trans*-bis( $\alpha$ -dioximate) complexes that are soluble in common organic solvents, therefore allowing these complexes to be fully characterized. In addition, we utilized a chloride-containing starting material instead of the analogous iodide material, because it was reported by Fukuchi that the chloride-containing starting material produces *trans*-bis( $\alpha$ -dioximate)ruthenium complexes without contamination from the *cis* isomers.<sup>28</sup> Notably, attempts to prepare ruthenium  $\alpha$ -dioximate complexes utilizing ruthenium starting materials such as Ru<sup>III</sup>Cl<sub>3</sub>·3H<sub>2</sub>O, Ru<sup>II</sup>(DMSO)<sub>4</sub>Cl<sub>2</sub>, K<sub>2</sub>[Ru<sup>III</sup>Cl<sub>5</sub>(H<sub>2</sub>O)], and Ru<sub>2</sub>(OAc)<sub>4</sub>Cl, which have been employed for the synthesis of ruthenium complexes containing polydentate ligands including monooxime and  $\alpha$ -dioxime ligands,<sup>7–12,17,39,40</sup> failed to yield the desired ruthenium complexes.

**Electronic Spectroscopy.** All the *trans*-bis( $\alpha$ -dioximate)ruthenium(II) complexes display two absorbances in the range 250–750 nm. For all of the complexes, the absorbance at the shorter wavelength is assigned to intraligand ( $\alpha$ -dioxime)  $\pi \rightarrow \pi^*$  transitions, by analogy to reported results for cobalt(III) and rhodium(III)  $\alpha$ -dioximate complexes.<sup>50–52</sup> In addition, the absorbance at the longer wavelength is assigned to charge-transfer bands associated with the central ruthenium atom and the chelate rings of the coordinated  $\alpha$ -dioximes (Figure 2). The assignment of this absorbance is consistent with those reported for analogous cobalt(III) complexes.<sup>53</sup> All UV-visible experiments were con-

Table I.  $E_{1/2}$  Potentials and  $\Delta E_p$  and  $i_{pc}/i_{pa}$  Values for Ru(LH)<sub>2</sub>(NO)Cl Complexes in CH<sub>2</sub>Cl<sub>2</sub><sup>a</sup>

L <sup>b</sup>	$E_{1/2}$ , V vs SSCE	$\Delta E_p$ , mV	$i_{pc}/i_{pa}$
DMG	-0.13	110	1.0
	-1.02 <sup>c</sup>		
	+1.55 <sup>d</sup>		
NOX	+0.01	110	1.0
	-0.93 <sup>c</sup>		
	+1.63 <sup>d</sup>		
DPG	-0.12	80	1.0
	-1.02 <sup>c</sup>		
DFG	+1.28	80	0.8
	-0.05		
	-0.93 <sup>c</sup>		
	+1.26 <sup>d</sup>		

<sup>a</sup>  $E_{1/2} = (E_{pa} + E_{pc})/2$ ;  $\Delta E_p$  = peak separation;  $i_{pc}/i_{pa}$  = peak current ratio. Conditions: 0.2 M *n*-Bu<sub>4</sub>NBF<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub>; Pt working electrode; SSCE reference electrode; scan rate = 100 mV/s. <sup>b</sup> DMG = dimethylglyoxime; NOX = 1,2-cyclohexanedione dioxime; DPG = diphenylglyoxime; DFG =  $\alpha$ -furyl dioxime. <sup>c</sup> Cyclic voltammogram was irreversible; report is  $E_p$  for the cathodic wave. <sup>d</sup> Cyclic voltammogram was irreversible; reported is  $E_p$  for the anodic wave.

ducted at three concentrations in order to verify that the absorbances reported obeyed Beer's law.

**Cyclic Voltammetry.** The results for all the voltammetric experiments are presented in Table I. All the ( $\alpha$ -dioximate)ruthenium complexes display one reversible couple ( $i_{pc}/i_{pa} = 1.0$ ) corresponding to the [Ru(LH)<sub>2</sub>(NO)Cl]<sup>0/-</sup> couple accessed upon scanning negatively from +0.2 V, in the range of +0.01 to -0.13 V (Figure 3, supplementary material). Also displayed upon scanning negatively is an irreversible wave corresponding to the reduction of [Ru(LH)<sub>2</sub>(NO)Cl]<sup>-</sup> with a cathodic peak potential in the range of -0.93 to -1.02 V. Upon being scanned positively from +0.2 V, the complexes containing dimethylglyoxime, 1,2-cyclohexanedione dioxime, and  $\alpha$ -furyl dioxime display an irreversible wave corresponding to the oxidation of [Ru(LH)<sub>2</sub>(NO)Cl] with an anodic peak potential in the range of +1.26 to +1.63 V. Notably, the complex [Ru(DPGH)<sub>2</sub>(NO)Cl] displays a partially reversible couple ( $i_{pc}/i_{pa} = 0.8$ ) at +1.28 V corresponding to the [Ru(LH)<sub>2</sub>(NO)Cl]<sup>+0</sup> couple (Figure 4, supplementary material). All the reversible and partially reversible couples have peak separations ( $\Delta E_p$ ) equal to the  $\Delta E_p$  values measured for the internal standard (ferrocene) and also display linear relationships between the square root of the scan rates ( $v^{1/2}$ ) and the peak current.<sup>46</sup>

**<sup>1</sup>H NMR Spectroscopy.** The <sup>1</sup>H NMR spectra provide data concerning the  $\alpha$ -dioxime ligand utilized and serve as means of verifying the presence of intramolecular hydrogen bonding. The protons associated with the intramolecular hydrogen bonding appear as singlets in the range 10.0–13.5 ppm, which is consistent with the results reported for other *trans*-bis( $\alpha$ -dioximate) complexes.<sup>45,51,59</sup>

**<sup>13</sup>C NMR Spectroscopy.** Proton-decoupled <sup>13</sup>C NMR spectroscopy is very useful for distinguishing between *cis* and *trans* conformations of bis( $\alpha$ -dioximate) transition-metal complexes and therefore was conducted on all Ru(LH)<sub>2</sub>(NO)Cl complexes synthesized. Proton-coupled <sup>13</sup>C NMR experiments were also conducted in order to further verify the complexation of *trans*  $\alpha$ -dioxime ligands and as an aid in the assignment of the various carbon atoms present.

The proton-decoupled <sup>13</sup>C NMR spectrum of Ru(NOXH)<sub>2</sub>(NO)Cl displays three singlets at 20.0, 26.2, and 160.4 ppm. The two upfield singlets are assigned to the methylene carbon atoms associated with the 1,2-cyclohexanedione dioxime ligands, while the remaining downfield singlet is assigned to the imine carbon atoms. The proton-coupled <sup>13</sup>C NMR spectrum of Ru-

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(NOXH)<sub>2</sub>(NO)Cl displays a singlet at 160.4 ppm corresponding to the imine carbon atoms and a four-line multiplet centered at 23.3 ppm ( $^1J_{C-H} = 145$  Hz). The four-line multiplet is formed from the overlapping of two closely spaced triplets, since the C-H coupling constant is equal to the peak separation of the two methylene carbon atoms. All the above data demonstrate that the two  $\alpha$ -dioxime ligands present are equivalent and therefore suggest that the two  $\alpha$ -dioxime are trans to each other.

The proton-decoupled <sup>13</sup>C NMR spectrum of Ru(DPGH)<sub>2</sub>(NO)Cl displays four closely spaced singlets in the range 128.2–130.2 ppm and a singlet at 156.1 ppm. The singlet at 156.1 ppm is assigned to the imine carbon atoms (vide infra). The two singlets at 128.6 and 130.2 ppm are assigned to either the quaternary phenyl carbon atom or the para phenyl carbon atom, and the singlets at 128.2 and 129.9 ppm are assigned to either the meta or ortho phenyl carbon atoms. This assignment is suggested since the singlets at 128.6 and 130.2 are less than half the height of the other two singlets (Figure 5, supplementary material). In the proton-coupled <sup>13</sup>C NMR spectrum of Ru(DPGH)<sub>2</sub>(NO)Cl, three of the four singlets of the above proton-decoupled <sup>13</sup>C NMR spectrum in the range 128.2–130.2 ppm appear as doublets with C-H coupling constants in the range 162–164 Hz. The fourth phenyl carbon atom does not display C-H coupling and appears as a singlet at 128.5 ppm. Thus, the three doublets are assigned to the protonated phenyl carbon atoms (para, ortho, meta), while the singlet is assigned to the quaternary phenyl carbon atoms. In

addition to displaying one-bond C-H coupling, all the carbon atoms associated with the phenyl rings display long-range C-H coupling ( $J_{C-H}$ ) with coupling constants of 5–7 Hz (Figure 5, supplementary material). The presence of long-range coupling is consistent with that displayed for monohalobenzenes,<sup>60</sup> and from the nature of the long-range coupling the phenyl carbon atom resonances can be assigned. The resonance at 128.2 ppm is assigned to the meta phenyl carbon atoms, while the resonances at 128.5, 129.9, and 130.2 ppm are assigned to the quaternary, ortho, and para phenyl carbon atoms, respectively. Finally, the singlet at 156.1 ppm does not display C-H coupling, thus the assignment of this resonance to the imine carbon atoms.

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**Supplementary Material Available:** Cyclic voltammograms of Ru(DPGH)<sub>2</sub>(NO)Cl upon scanning negatively from +0.2 V (Figure 3) and of Ru(DPGH)<sub>2</sub>(NO)Cl upon scanning positively from +0.2 V (Figure 4), a <sup>13</sup>C NMR spectrum of Ru(DPGH)<sub>2</sub>(NO)Cl (Figure 5), a <sup>1</sup>H NMR spectrum of Ru(DFGH)<sub>2</sub>(NO)Cl (Figure 6), and an infrared spectrum of Ru(DMGH)<sub>2</sub>(NO)Cl (Figure 7) (5 pages). Ordering information is given on any current masthead page.

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