

## Angle-Dependent Electronic Effects in 4,4'-Bipyridine-Bridged Ru<sub>3</sub> Triangle and Ru<sub>4</sub> Square Complexes

Louise A. Berben, Mary C. Faia, Nathan R. M. Crawford, and Jeffrey R. Long\*

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720, and the Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720

Received April 4, 2006

Use of 1,4,7,10-tetraazacyclododecane (cyclen) as a capping ligand and 4,4'-bipyridine (4,4'-bpy) as a bridging ligand enables assembly of redox-active Ru<sub>3</sub> triangle and Ru<sub>4</sub> square complexes. The former is produced by reacting [(cyclen)Ru(DMSO)Cl]Cl with 4,4'-bpy in a 3:1 ethanol:water mixture to precipitate [(cyclen)<sub>3</sub>Ru<sub>3</sub>(4,4'-bpy)<sub>3</sub>]Cl<sub>6</sub>·18H<sub>2</sub>O·THF (**4**), whereas the latter is generated as [(cyclen)<sub>4</sub>Ru<sub>4</sub>(4,4'-bpy)<sub>4</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>8</sub>·2CF<sub>3</sub>SO<sub>3</sub>H·5MeOH (**7**) by reacting (cyclen)Ru(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> with 4,4'-bpy in methanol. The crystal structure of **4**·11H<sub>2</sub>O reveals an equilateral triangle in which the 4,4'-bpy bridges are bowed outward, such that the pyridine rings are all forced to be perpendicular to the Ru<sub>3</sub> triangle. Consequently, adjacent pyridine rings are essentially coplanar, and the cyclic voltammogram of [(cyclen)<sub>3</sub>Ru<sub>3</sub>(4,4'-bpy)<sub>3</sub>]<sup>6+</sup> in acetonitrile displays three distinct one-electron oxidation events. Cyclic voltammetry measurements reveal redox processes centered at  $E_{1/2} = 0.207, 0.342, \text{ and } 0.434 \text{ V}$  versus Cp<sub>2</sub>Fe<sup>0/+</sup> that are assigned to 6+/7+, 7+/8+, and 8+/9+ couples of the [(cyclen)<sub>3</sub>Ru<sub>3</sub>(4,4'-bpy)<sub>3</sub>]<sup>n+</sup> triangle, respectively. In contrast, the structure of [(cyclen)<sub>4</sub>Ru<sub>4</sub>(4,4'-bpy)<sub>4</sub>]<sup>8+</sup> features a regular square geometry wherein the rings of the bridging 4,4'-bpy ligands are free to rotate, leading to just one four-electron oxidation couple centered at 0.430 V. Density functional theory calculations performed on [(cyclen)<sub>3</sub>Ru<sub>3</sub>(4,4'-bpy)<sub>3</sub>]<sup>6+</sup> reveal metal-based orbitals with contributions from the  $\pi$  system of the bridging 4,4'-bpy ligands, providing a likely pathway for electron transfer.

### Introduction

The directed assembly approach, in which ligand-capped transition-metal vertexes are combined with rigid organic linkers, has produced a remarkable array of molecular polygons and polyhedra.<sup>1</sup> These molecules have been targeted for potential applications in areas as diverse as selective guest encapsulation for chemical sensing,<sup>2</sup> reaction

catalysis,<sup>3</sup> photoinitiated guest-to-host and host-to-guest energy transfer,<sup>4</sup> and intermolecular electron transfer via both metal-to-metal<sup>5</sup> and ligand-to-ligand<sup>6</sup> exchange mechanisms. Our motivation for pursuing architectures of this type that incorporate conjugated linkers derives from a desire to engender electron delocalization between many metal centers and over long length scales. Ultimately, it is hoped that related systems may find applications as components in molecular electronics devices.<sup>7</sup>

The ability of pyrazine (pz) to facilitate strong electronic coupling between two metal centers was established several decades ago through studies of the mixed-valence Creutz–

\* To whom correspondence should be addressed. E-mail: jrlong@berkeley.edu.

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Taube ion, [(NH<sub>3</sub>)<sub>5</sub>Ru( $\mu$ -pz)Ru(NH<sub>3</sub>)<sub>5</sub>]<sup>5+</sup>.<sup>8</sup> Numerous analogues of this molecule, featuring substitutions of the bridging ligand,<sup>9</sup> metal centers,<sup>9</sup> and ancillary ligands,<sup>9</sup> have since permitted a systematic investigation into the factors that affect electronic coupling in mixed-valence systems.<sup>10</sup> The study of higher nuclearity complexes, however, has been much more limited, focusing mainly on linear chain motifs in which not all metal centers are equivalent.<sup>11</sup> In an effort to probe the nature of electron delocalization over more than two metal centers, we recently synthesized [(cyclen)<sub>4</sub>Ru<sub>4</sub>(pz)<sub>4</sub>]<sup>9+</sup> (cyclen = 1,4,7,10-tetraazacyclododecane), a “Creutz–Taube square” in which four equivalent ruthenium centers are bridged by pyrazine to yield an apparent class III mixed-valence complex.<sup>5</sup>

The related bridging ligand 4,4'-bipyridine (4,4'-bpy) provides a means by which electronic coupling might be varied through the rotational freedom about its central C–C bond. The inherent tendency for the two pyridyl rings to twist around this bond is evident in the gas-phase structure of 4,4'-bpy determined by electron diffraction, wherein the molecule exhibits a twist angle of  $\phi = 37.2^\circ$ .<sup>12</sup> It has been predicted<sup>13,14</sup> that if the two rings of a bridging 4,4'-bpy unit are forced to be coplanar, the exchange coupling between metal centers will increase substantially over the almost negligible coupling observed experimentally when the two rings are offset.<sup>9e,f</sup> Indeed, the twisting of the two rings of 4,4'-bpy with respect to each other within a molecule has been proposed as a

switching mechanism for turning on and off the flow of electron transfer in molecular electronic devices.<sup>13a</sup> To date, attempts to constrain adjacent aromatic rings in biphenyl and related bridging moieties to be perfectly coplanar have met with only partial success.<sup>15</sup> Efforts to utilize planar variants of 4,4'-bpy with conjugated linkers connecting the rings (e.g., diazapyrene, 3,8-phenanthroline, and 3,5,6,8-tetraazaphenanthroline) actually resulted in significantly reduced coupling, due to stabilization of an alternative  $\pi^*$  orbital pathway for electron delocalization.<sup>14a,16</sup>

A number of molecular squares have been constructed using 4,4'-bpy as a linker.<sup>17,18</sup> In the cases where these complexes have been crystallized, however, the pyridyl rings within each bridging unit are far from coplanar (typically,  $\phi = 25\text{--}37^\circ$ ).<sup>17c,i,18</sup> In addition, it has been suggested on the basis of solution NMR experiments that the square complex [(2,2'-bpy)<sub>4</sub>Pd<sub>4</sub>(4,4'-bpy)<sub>4</sub>]<sup>8+</sup> is actually in equilibrium with a 4,4'-bpy-bridged molecular triangle: [(2,2'-bpy)<sub>3</sub>Pd<sub>3</sub>(4,4'-bpy)<sub>3</sub>]<sup>6+</sup>.<sup>17e</sup> Although none have yet been isolated in pure form,<sup>19</sup> triangles of this type are of considerable interest, because the strain arising because of the discrepancy between the triangle corner angle of 60° and the preferred N–M–N

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angle of 90° can be anticipated to force all bridging pyridyl rings to be perpendicular to the plane of the triangle. Herein, we report the synthesis and characterization of a triangular complex, [(cyclen)<sub>3</sub>Ru<sub>3</sub>(4,4'-bpy)<sub>3</sub>]<sup>6+</sup>, which indeed exhibits coplanar pyridyl rings and enhanced electronic coupling relative to the square complex, [(cyclen)<sub>4</sub>Ru<sub>4</sub>(4,4'-bpy)<sub>4</sub>]<sup>8+</sup>.

## Experimental Section

**Preparation of Compounds.** With the exception of **1**, all compounds were synthesized under a dinitrogen atmosphere, using standard glovebox and Schlenk line techniques. The Ru(DMSO)<sub>4</sub>Cl<sub>2</sub> compound was prepared as described previously.<sup>20</sup> Methanol was distilled over Mg and degassed via three freeze–pump–thaw cycles prior to use. All other reagents were obtained from commercial vendors and used without further purification. The cyclen employed was purchased from Strem Chemical Co.

**[(cyclen)Ru(DMSO)Cl]Cl (1).** A suspension of Ru(DMSO)<sub>4</sub>Cl<sub>2</sub> (3.3 g, 6.9 mmol) and cyclen (1.2 g, 6.9 mmol) was heated at reflux in absolute EtOH (20 mL) for 2 h, during which time the reactants dissolved and a darker yellow precipitate formed. After being cooled to room temperature, the solid was collected by filtration, washed with benzene (5 mL) and ether (2 × 5 mL), and dried in air to yield 1.9 g (66%) of product. IR: ν<sub>NH</sub> 3163 (m), 3126 (s), ν<sub>CH</sub> 2938 (m), 2917 (m) ν<sub>other</sub> 1035 (s) cm<sup>-1</sup>. ES<sup>+</sup>–MS (MeCN): *m/z* 387 ([1 – Cl]<sup>+</sup>). Anal. Calcd for C<sub>10</sub>H<sub>26</sub>Cl<sub>2</sub>N<sub>4</sub>ORuS·0.5H<sub>2</sub>O: C, 27.84; H, 6.31; N, 12.99; S, 7.43. Found: C, 27.93; H, 6.65; N, 12.61; S, 7.80.

**[(cyclen)Ru(DMSO)(MeCN)](BF<sub>4</sub>)<sub>2</sub> (2).** A solution of **1** (500 mg, 1.3 mmol) and NaBF<sub>4</sub> (290 mg, 2.6 mmol) in 4 mL of acetonitrile was heated at reflux for 20 h. Upon removing the solvent in vacuo, we extracted the yellow residue into a minimal amount of MeNO<sub>2</sub> (ca. 3 mL) and filtered the resulting mixture to remove NaCl. Diffusion of ether vapor into the filtrate yielded 150 mg (23%) of product as yellow needle-shaped crystals suitable for X-ray analysis (see the Supporting Information, Figure S1). IR (solid, ATR): ν<sub>CH</sub> 2940 (m), 2884 (m), ν<sub>CN</sub> 2261 (w), ν<sub>BF<sub>4</sub>/SO</sub> 1017 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>12</sub>H<sub>30</sub>BF<sub>8</sub>N<sub>5</sub>ORuS: C, 25.90; H, 5.43; N, 12.59; S, 5.76. Found: C, 25.58; H, 5.23; N, 12.24; S, 5.28.

**(cyclen)Ru(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> (3).** Compound **1** (0.91 g, 2.2 mmol) was heated at 70 °C under reduced pressure (10 mmHg) for 16 h to remove any adsorbed water. The resulting solid was stirred and heated at 85 °C in neat CF<sub>3</sub>SO<sub>3</sub>CH<sub>3</sub> (4.5 g, 27 mmol) for 20 h to give a dark pink suspension, which was then filtered using a Hirsch funnel until all of the CH<sub>3</sub>CF<sub>3</sub>SO<sub>3</sub> had passed through. The remaining sticky solid was washed with ether (3 × 10 mL) and dried in vacuo to yield 1.6 g (98%) of product as a bright pink powder. IR (solid, ATR): ν<sub>NH</sub> 3197 (w), 3169 (w), ν<sub>CH</sub> 3022 (w), ν<sub>SO</sub> 1251 (m), 1226 (m), 1199 (s), 1171 (s) cm<sup>-1</sup>. μ<sub>eff</sub> = 1.65 μ<sub>B</sub> at 295 K. ES<sup>+</sup>–MS (MeCN): *m/z* 422 ([2 – H – 2CF<sub>3</sub>SO<sub>3</sub>]<sup>+</sup>). Anal. Calcd for C<sub>11</sub>H<sub>20</sub>F<sub>9</sub>N<sub>4</sub>O<sub>9</sub>RuS<sub>3</sub>: C, 18.34; H, 2.80; N, 17.78; S, 13.35. Found: C, 18.73; H, 2.86; N, 17.36; S, 13.71.

**[(cyclen)<sub>3</sub>Ru<sub>3</sub>(4,4'-bpy)<sub>3</sub>]Cl<sub>6</sub>·20H<sub>2</sub>O·THF (4).** A solution of **1** (1.8 g, 4.3 mmol) and 4,4'-bipyridine (0.67 g, 4.3 mmol) in a mixture of 18 mL of EtOH and 5 mL of water was stirred and heated at reflux under dinitrogen for 7 days. During this time, the solution turned red-purple in color and a precipitate of the same hue gradually formed. Upon cooling to room temperature, the solid was collected by filtration, washed with ether (2 × 10 mL), and dried in air. Diffusion of THF vapor into a concentrated aqueous

solution of the solid resulted in dark red, needle-shaped crystals of 4·11H<sub>2</sub>O suitable for X-ray analysis. The crystals were collected and dried in air to yield 0.91 g (32%) of product. UV–vis spectrum (H<sub>2</sub>O) λ<sub>max</sub> (ε<sub>M</sub>): 246 (53 000), 257 (sh, 46 000), 353 (6000), 431 (sh, 51 300), 466 (54 000), 509 (sh, 46 500) nm. IR: ν<sub>NH</sub> 3145 (m), ν<sub>CH</sub> 2923 (m), ν<sub>other</sub> 1487 (m), 1410 (m), 1059 (m), 1001 (m), 988 (m), 817 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR (D<sub>2</sub>O): δ 8.48 (d, J<sub>HH</sub> = 6.8 Hz, 12H; PyHα), 7.46 (d, J<sub>HH</sub> = 6.8 Hz, 12H; PyHβ), 5.48 (s, 6H; NH), 5.33 (s, 6H; NH), 3.75 (t, J<sub>HH</sub> = 6.8 Hz, 4H; THF), 3.28 (t, J<sub>HH</sub> = 8.8 Hz, 24H; CH<sub>2</sub>), 3.15 (t, J<sub>HH</sub> = 8.8 Hz, 24H; CH<sub>2</sub>), 1.88 (t, J<sub>HH</sub> = 6.8 Hz, 4H; THF). This compound is diamagnetic. Anal. Calcd for C<sub>58</sub>H<sub>132</sub>Cl<sub>6</sub>N<sub>18</sub>O<sub>21</sub>Ru<sub>3</sub>: C, 36.70; H, 7.01; N, 13.28. Found: C, 36.32; H, 6.60; N, 13.63. The water and THF content of this compound were confirmed by thermogravimetric analysis.

**[(cyclen)<sub>3</sub>Ru<sub>3</sub>(4,4'-bpy)<sub>3</sub>](BPh<sub>4</sub>)<sub>6</sub>·7H<sub>2</sub>O (5).** Addition of a solution of NaBPh<sub>4</sub> (400 mg, 1.2 mmol) in 5 mL of water to a solution of **4** (270 mg, 0.15 mmol) in 10 mL of water resulted in the immediate formation of a red precipitate. After being stirred for 1 h, the precipitate was collected by filtration and washed with water (3 × 5 mL) and ether (5 mL) to yield 470 mg (95%) of product. UV–vis spectrum (MeCN) λ<sub>max</sub> (ε<sub>M</sub>): 232 (sh, 138 000), 254 (sh, 79 500), 376 (7600), 454 (sh, 34300), 483 (45 000), 523 (sh, 28 000) nm. IR (solid, ATR): ν<sub>NH</sub> 3223 (w), ν<sub>CH</sub> 3054 (w), 2999 (w), ν<sub>Ph</sub> 734 (s), 705 (s) cm<sup>-1</sup>. This compound is diamagnetic. Anal. Calcd for C<sub>198</sub>H<sub>218</sub>B<sub>6</sub>N<sub>18</sub>O<sub>7</sub>Ru<sub>3</sub>: C, 71.41; H, 6.60; N, 7.57. Found: C, 71.48; H, 6.71; N, 7.85.

**[(cyclen)<sub>3</sub>Ru<sub>3</sub>(4,4'-bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>6</sub> (6) as a 1 mM solution in acetonitrile.** Compound **4** (7.1 mg, 4.0 μmol) and AgPF<sub>6</sub> (6.1 mg, 24 μmol) were added to 4 mL of acetonitrile. The mixture was allowed to stir for 12 h, during which time the solution turned red and a gray precipitate of AgCl formed. The reaction mixture was filtered, and the resulting red filtrate was employed in cyclic voltammetry measurements, after addition of Bu<sub>4</sub>NPF<sub>6</sub> (150 mg, to yield a 0.1 M solution) as the supporting electrolyte. Analysis of an identical reaction performed in CD<sub>3</sub>CN showed that the complex remained intact during the anion exchange. <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ 8.43 (d, J<sub>HH</sub> = 6.8 Hz, 12H; PyHα), 7.51 (d, J<sub>HH</sub> = 6.8 Hz, 12H; PyHβ), 4.77 (br, 6H; NH), 4.57 (s, 6H; NH), 3.20 (t, J<sub>HH</sub> = 8.8 Hz, 24H; CH<sub>2</sub>), 3.05 (t, J<sub>HH</sub> = 8.4 Hz, 24H; CH<sub>2</sub>). A 1 mM solution of [(cyclen)<sub>3</sub>Ru<sub>3</sub>(4,4'-bpy)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>6</sub> was prepared in a completely analogous fashion employing AgCF<sub>3</sub>SO<sub>3</sub>.

**[(cyclen)<sub>4</sub>Ru<sub>4</sub>(4,4'-bpy)<sub>4</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>8</sub>·2CF<sub>3</sub>SO<sub>3</sub>H·5MeOH (7).** A solution of **3** (800 mg, 1.1 mmol) and 4,4'-bpy (170 mg, 1.1 mmol) in methanol (10 mL) was stirred and heated under dinitrogen at 60 °C for 2 days to give a dark pink-red solution. Upon the solution being cooled to room temperature, diffusion of ether vapor into the reaction solution yielded 290 mg (11%) of product as dark red, needle-shaped crystals suitable for X-ray analysis. UV–vis spectrum (MeOH) λ<sub>max</sub> (ε<sub>M</sub>): 245 (55 300), 259 (sh, 37 700), 368 (19 800), 415 (sh, 27 900) 445 (41 800), 491 (sh, 32 600) nm. IR (solid, ATR): ν<sub>NH</sub> 3145 (m), ν<sub>CH</sub> 2923 (m), ν<sub>SO</sub> 1274 (m), 1254 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (MeCN): δ 8.42 (br, 16H; PyHα), 7.64 (br, 16H; PyHβ), 5.00 (br, 8H; NH), 4.54 (br, 8H; NH), 2.78 (64H; CH<sub>2</sub>). This compound is diamagnetic. Anal. Calcd for C<sub>87</sub>H<sub>134</sub>F<sub>30</sub>N<sub>24</sub>O<sub>35</sub>·Ru<sub>4</sub>S<sub>10</sub>: C, 31.33; H, 3.92; N, 10.08; S, 9.61. Found: C, 31.70; H, 4.06; N, 9.97; S, 9.51.

**X-ray Structure Determinations.** Single crystals of **2** and 4·11H<sub>2</sub>O were coated in Paratone-N oil, mounted on glass fibers, transferred to a Siemens SMART diffractometer, and cooled in a dinitrogen stream. Initial lattice parameters were obtained from a least-squares analysis of more than 30 centered reflections; these parameters were later refined against all data. A full hemisphere of data was collected for all compounds. Data were integrated and

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**Table 1.** Crystallographic Data<sup>a</sup> for [(cyclen)Ru(DMSO)(MeNO<sub>2</sub>)](BF<sub>4</sub>)<sub>2</sub> (**2**), [(cyclen)<sub>3</sub>Ru<sub>3</sub>(4,4'-bpy)<sub>3</sub>]Cl<sub>6</sub>·31H<sub>2</sub>O·THF (**4**·11H<sub>2</sub>O), and [(cyclen)<sub>4</sub>Ru<sub>4</sub>(4,4'-bpy)<sub>4</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>8</sub>·2CF<sub>3</sub>SO<sub>3</sub>H·5MeOH (**7**)

	<b>2</b>	<b>4</b> ·11H <sub>2</sub> O	<b>7</b>
formula	C <sub>12</sub> H <sub>29</sub> B <sub>2</sub> F <sub>8</sub> N <sub>5</sub> ORuS	C <sub>58</sub> H <sub>154</sub> Cl <sub>6</sub> N <sub>18</sub> O <sub>32</sub> Ru <sub>3</sub>	C <sub>87</sub> H <sub>134</sub> F <sub>30</sub> N <sub>24</sub> O <sub>35</sub> Ru <sub>4</sub> S <sub>10</sub>
fw	566.15	2131.99	3371.06
T (K)	158	122	172
space group	<i>Pc</i>	<i>P2m</i>	<i>C1</i>
Z	4	1	1
a (Å)	9.0164(10)	19.0160(13)	39.586(8)
b (Å)	19.309(2)		9.325(2)
c (Å)	12.3730(14)	8.9761(9)	24.118(13)
β (deg)	90.238(2)		121.958(13)
V (Å <sup>3</sup> )	2154.0(4)	2811.0(4)	7553(3)
d <sub>calcd</sub> (g/cm <sup>3</sup> )	1.746	1.259	1.482
cryst size (mm <sup>3</sup> )	0.30 × 0.30 × 0.15	0.42 × 0.12 × 0.05	0.14 × 0.06 × 0.02
R <sub>1</sub> (wR <sub>2</sub> ) <sup>b</sup> (%)	6.75 (17.54)	4.37 (10.83)	10.03 (23.21)
diff. peak, hole (e Å <sup>-1</sup> )	2.615, -1.917	0.824, -0.521	0.590, -0.391

<sup>a</sup> Obtained with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation for **2** and **4**·11H<sub>2</sub>O and with 0.77500 Å synchrotron radiation for **7**. <sup>b</sup> R<sub>1</sub> = Σ||F<sub>o</sub> - |F<sub>c</sub>||/Σ|F<sub>o</sub>|, wR<sub>2</sub> = {Σ[w(F<sub>o</sub><sup>2</sup> - F<sub>c</sub><sup>2</sup>)]/Σ[w(F<sub>o</sub><sup>2</sup>)]<sup>1/2</sup>.

corrected for Lorentz polarization effects using SAINT and were corrected for absorption effects using SADABS version 2.3.

Single-crystal diffraction data for **7** were collected using synchrotron radiation at the Advanced Light Source at Lawrence Berkeley National Laboratory. A crystal was coated in paratone-N oil and mounted on a Kaptan loop, transferred to a Bruker D8 controller, and cooled in a dinitrogen stream. Data were collected using a Bruker Platinum 200 with an APEX2 v1.0-27 detector. Initial lattice parameters were obtained from a least-squares analysis of more than 30 centered reflections; these parameters were later refined against all data. A full hemisphere of data was collected. Data were integrated using Bruker SAINT version 7.06 and corrected for Lorentz and polarization effects using SADABS.

Space group assignments were made on the basis of systematic absences, *E* statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps and were refined against all data using the SHELXTL 5.0 software package. Thermal parameters for all non-hydrogen atoms were refined anisotropically, except in solvent molecules disordered over multiple partially occupied sites and carbon atoms in the cyclen rings of **7**. Hydrogen atoms in **2** and **4**·11H<sub>2</sub>O were assigned to ideal positions and refined using a riding model with an isotropic thermal parameter 1.2 times that of the attached carbon atom. The structure of **7** was solved in the nonstandard space group *C1* rather than *P1* because of the ease with which the twin law could be expressed. The twinned triclinic space group assignment was chosen over *C2/m* because of better refinement of the structure and a complete absence of disorder in the 4,4'-bpy rings in the twinned triclinic solution, which indicates that there is long-range order in the twisting of the rings (i.e., twinning) rather than disorder. The poor resolution of the structure (1.1 Å) is attributed to the extreme disorder associated with the triflate counteranions and methanol solvate molecules, both of which were accounted for using just oxygen atoms. Crystal and refinement parameters are summarized in Table 1.

**Other Physical Measurements.** Absorption spectra were measured with a Hewlett-Packard 8453 spectrophotometer. Infrared spectra were recorded on a Nicolet Avatar 360 FTIR spectrometer equipped with a horizontal attenuated total reflectance (ATR) accessory. Cyclic voltammetry and differential pulse voltammetry was performed in a 0.1 M acetonitrile solution of Bu<sub>4</sub>NPF<sub>6</sub> or Bu<sub>4</sub>NClO<sub>4</sub> using a Bioanalytical systems CV-50W voltammograph, a platinum disk working electrode, a platinum wire supporting electrode, and a silver wire reference electrode. Reported potentials are all referenced to the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) couple and

were determined using ferrocene as an internal standard. Magnetic susceptibility data were measured on a Quantum Design MPMS-XL SQUID magnetometer. Mass spectrometric measurements were performed on VG Quattro (Micromass) spectrometer equipped with an analytical electrospray ion source instrument. NMR spectra were measured with a Bruker AVB 400 MHz instrument.

**Electronic Structure Calculations.** Density functional theory (DFT) calculations were performed using the NWChem 4.5 quantum chemistry software package.<sup>21</sup> Geometries were taken from the crystal structure of **4**·11H<sub>2</sub>O and then optimized using the HCTH/407 functional.<sup>22</sup> Effective core potentials, including relativistic effects, were employed for Ru (LANL2DZ) together with the corresponding Gaussian basis sets;<sup>23</sup> the 6-31+G\* basis was employed for C and N. The Ahlrichs auxiliary basis sets were used for fitting the Coulomb potential.<sup>24</sup>

## Results and Discussion

**Syntheses.** The synthesis of the square complex [(cyclen)<sub>4</sub>Ru<sub>4</sub>(pz)<sub>4</sub>]<sup>9+</sup> had previously been accomplished by reacting [(cyclen)Ru(DMSO)Cl]Cl<sup>25</sup> (**1**) and pz in a 3:2 ethanol:water mixture and heating the solution at reflux for 12 h.<sup>5</sup> Attempts to synthesize [(cyclen)<sub>4</sub>Ru<sub>4</sub>(4,4'-bpy)<sub>4</sub>]<sup>n+</sup> in an analogous manner afforded an oily mixture of products that did not readily crystallize. Over the course of these experiments, it was noted that a precipitate formed during the reaction and that more precipitate was obtained if the amount of water in the solvent employed was decreased to a 3:1 ethanol:water mixture. In this way, an unexpected triangular complex was isolated in pure form as the red-purple solid [(cyclen)<sub>3</sub>Ru<sub>3</sub>(4,4'-bpy)<sub>3</sub>]Cl<sub>6</sub>·18H<sub>2</sub>O·THF (**4**). The oxidation of cyclen to imcyclen (1,4,7,10-tetraazacyclododeca-1-ene) during the

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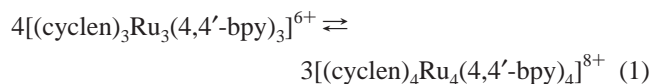
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reaction of cyclen ruthenium complexes with various pyridine ligands is sometimes observed.<sup>26</sup> To rule out the possibility that the cyclen ligands had been oxidized during this reaction, we performed HMQC and COSY NMR experiments (see Figures S2 and S3 in the Supporting Information). The absence of any correlations between the CH<sub>2</sub> proton signals at 3.28 and 3.15 ppm and proton signals in the range 5–9 ppm indicates that the N=CH moiety is not present in compound **4**.

Compound **4** is soluble in water and methanol. In the visible region, its absorption spectrum in water is dominated by an intense, broad band centered at 466 nm, with shoulders at 431 and 506 nm (see Figure S4 in the Supporting Information). The solvent dependence of this main feature supports its assignment as an MLCT transition, in which a 4d electron of Ru<sup>II</sup> is promoted into a  $\pi^*$  orbital of a 4,4'-bpy ligand.<sup>27</sup> The stability of the triangle in solution is supported by the diffuse reflectance spectrum of **4**, which matches that of the solution spectrum. In addition, the <sup>1</sup>H NMR spectrum of **4** dissolved in D<sub>2</sub>O displayed sharp resonances consistent with the presence of a triangular [(cyclen)<sub>3</sub>Ru<sub>3</sub>(4,4'-bpy)<sub>3</sub>]<sup>6+</sup> complex with *D*<sub>3h</sub> symmetry. After standing at room temperature for 24 h, the solution displayed the same sharp spectrum, indicating that no isomerization or decomposition of the triangular motif had occurred. In an effort to ascertain the thermodynamically favored 4,4'-bpy-bridged species, we heated a sample of **4** in D<sub>2</sub>O at 80 °C for 72 h. The major component (ca. 70%) of the resulting spectrum consisted of the original triangular complex. The remaining 30% of the spectrum consisted of a series of broad overlapping peaks, with approximately 10% matching those observed for the square complex in **7** and the remaining 20% presumably arising from decomposition of the molecule into mononuclear species. In general, partial decomposition of the triangular and square complexes at elevated temperatures thwarted attempts to probe the thermodynamics associated with the expected equilibrium between triangles and squares



To adjust the solubility of the triangular complex for electrochemical studies, we screened several different anions as potential replacements for the chloride anions. [(cyclen)<sub>3</sub>Ru<sub>3</sub>(4,4'-bpy)<sub>3</sub>](BPh<sub>4</sub>)<sub>6</sub>·7H<sub>2</sub>O (**5**) readily precipitates upon addition of NaBPh<sub>4</sub> to an aqueous solution of **4**. Additionally, in situ anion-exchange reactions were performed in acetonitrile to obtain solutions of the triangular complex. An appropriate amount of **4** in acetonitrile was stirred with 6

equiv of AgPF<sub>6</sub> for 12 h. Removal of the AgCl by filtration then resulted in an acetonitrile solution of [(cyclen)<sub>3</sub>Ru<sub>3</sub>(4,4'-bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>6</sub> (**6**) suitable for use in cyclic voltammetry measurements. <sup>1</sup>H NMR experiments performed on CD<sub>3</sub>CN solutions formed using identical reaction conditions indicated that the triangular geometry remains predominantly intact in acetonitrile; approximately 5% decomposition was apparent. Attempts were also made to synthesize a BF<sub>4</sub><sup>-</sup> salt of the triangular complex directly; however, reactions of [(cyclen)Ru(DMSO)(MeCN)](BF<sub>4</sub>)<sub>2</sub> (**2**) with 4,4'-bpy yielded only oily products that were not readily crystallized.

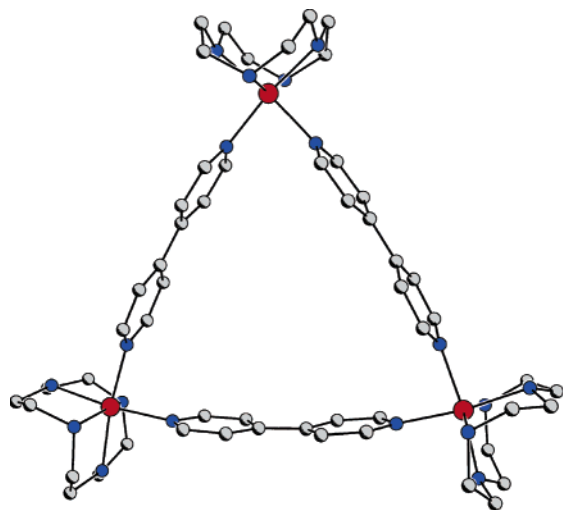
Synthesis of square-containing compound [(cyclen)<sub>4</sub>Ru<sub>4</sub>(4,4'-bpy)<sub>4</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>8</sub>·2CF<sub>3</sub>SO<sub>3</sub>H·5MeOH (**7**) was achieved by utilizing (cyclen)Ru(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> (**3**) in place of **1** in the reaction with 4,4'-bpy. The enhanced solubility of **3** over **1** prompted the use of methanol as the solvent rather than an ethanol:water mixture. The concentration of the reactants employed (0.1 M) was similar to that employed in the synthesis of triangle-containing compound **4** (0.2 M), and variation of these concentrations by  $\pm 0.05$  M did not alter the outcome of the reactions. It has been suggested previously that, at lower concentrations of reactants, entropy effects can begin to favor the formation of triangular species over squares.<sup>17e</sup> Although we observed no such trend, the verity of this contention is not ruled out here, because our successful syntheses included other variables, such as the counteranion and reaction solvent. Compound **7** is soluble in a variety of solvents, including water, methanol, ethanol, acetonitrile, THF, and DMF. The UV–vis spectrum of **7** in methanol is very similar to that of **4**, with only slight shifts in the absorption maxima (see Figure S5 in the Supporting Information). For the MLCT bands, these shifts do indicate, however, that the ruthenium 4d orbitals are better matched in energy with the  $\pi^*$  orbital of the 4,4'-bpy ligand in the triangular complex than in the square complex. <sup>1</sup>H NMR experiments performed on a CD<sub>3</sub>CN solution of **7** showed that the square complex was stable in solution at room temperature for at least 24 h. Measurements performed after heating the solution at 70 °C for 72 h revealed approximately 40% decomposition of the molecule, but gave no indication of triangle formation.

**Crystal Structures.** Crystallographic analysis of **4**·11H<sub>2</sub>O revealed the first structurally characterized 4,4'-bipyridine-bridged triangle, [(cyclen)<sub>3</sub>Ru<sub>3</sub>(4,4'-bpy)<sub>3</sub>]<sup>6+</sup> (see Figure 1 and Table 2). With idealized *D*<sub>3h</sub> point symmetry, the molecule features three cyclen-capped Ru<sup>II</sup> centers situated at the corners of an equilateral triangle with edge lengths of 11.264 Å. Each edge is spanned by a 4,4'-bpy ligand, with the Ru–N<sub>bpy</sub> distances of 2.106(5) Å lying in the midst of the 2.053–2.125 Å range reported for Ru<sup>II</sup>–N<sub>bpy</sub> bond distances.<sup>28</sup> The constraints imposed by the Ru···Ru···Ru angles of 60° associated with this triangular geometry are at odds with the rigidity of the 4,4'-bpy linkers, distorting the octahedral coordination environment of ruthenium to give N<sub>bpy</sub>–Ru–N<sub>bpy</sub> angles of 83.7(3)° and bowing the 4,4'-bpy ligands outward from the edges of the Ru<sub>3</sub> triangle. The resulting curvature forces the planes of the pyridine rings to be perpendicular to the plane of the Ru<sub>3</sub> triangle and affords

(25) Note that, previously, this compound was incorrectly assumed to be [(cyclen)RuCl<sub>2</sub>]Cl.<sup>5</sup>

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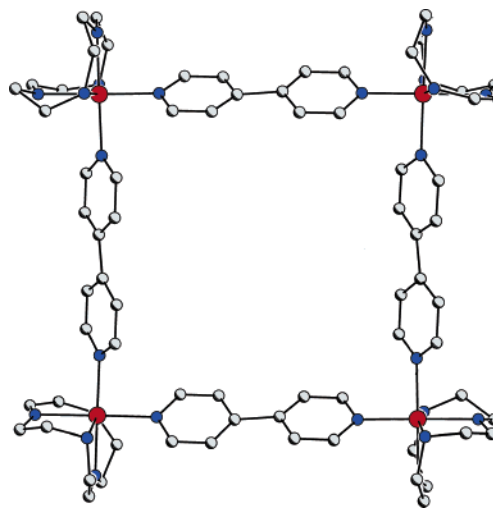
**Figure 1.** Structure of the triangular [(cyclen)<sub>3</sub>Ru<sub>3</sub>(4,4'-bpy)<sub>3</sub>]<sup>6+</sup> complex within 4·11H<sub>2</sub>O, as viewed parallel to the *a* axis of the crystal. Red, gray, and blue spheres represent Ru, C, and N atoms, respectively; H atoms are omitted for clarity. The complex resides on a site within the crystal.

**Table 2.** Selected Interatomic Distances (Å) and Angles (deg) for [(cyclen)<sub>3</sub>Ru<sub>3</sub>(4,4'-bpy)<sub>3</sub>]Cl<sub>6</sub>·31H<sub>2</sub>O·THF (4·11H<sub>2</sub>O) and [(cyclen)<sub>4</sub>Ru<sub>4</sub>(4,4'-bpy)<sub>4</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>8</sub>·2CF<sub>3</sub>SO<sub>3</sub>H·5MeOH (7)

	4·11H <sub>2</sub> O	7
Ru–N <sub>bpy</sub>	2.106(5)	2.106(7)–2.175(9)
Ru–N <sub>cyclen</sub>	2.13(3)	2.05(3)–2.32(4)
Ru···Ru	11.264	11.34
N <sub>bpy</sub> –Ru–N <sub>bpy</sub>	83.7(3)	89(2), 97(1)
N <sub>bpy</sub> –Ru–N <sub>cyclen</sub>	88.8(2), 99.13(10)	81(1)–90.1(6), 89.4(3)–106.9(9)
N <sub>cyclen</sub> –Ru–N <sub>cyclen</sub>	82.01(9), 98.6(4)	83(1)–92.8(7), 160(9)–178.2(9)
Ru···Ru···Ru	60	90
mean C–C–C–C ( $\phi$ )	0.25	1.0, 5.6

a C–C–C–C torsion angle ( $\phi$ ) of just 0.25° between adjacent pyridine rings. As observed for the molecular squares in [(cyclen)<sub>4</sub>Ru<sub>4</sub>(pz)<sub>4</sub>]Cl<sub>9</sub>·24H<sub>2</sub>O,<sup>5</sup> the triangular complexes stack in a perfectly eclipsed fashion via intermolecular N–H···Cl···H–N interactions, forming one-dimensional columns that run along the *a* axis of the crystal. Interestingly, the THF solvate molecules are located within the interior channels of the triangular columns.

Analysis of a single crystal of [(cyclen)<sub>4</sub>Ru<sub>4</sub>(4,4'-bpy)<sub>4</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>8</sub>·2CF<sub>3</sub>SO<sub>3</sub>H·5MeOH (7) using a synchrotron X-ray source yielded data enabling identification of the square complex depicted in Figure 2. Because of the high degree of disorder in the triflate counteranions and methanol solvate molecules and the extremely narrow width of the needle-shaped crystal, the diffraction data was of low resolution and large errors are associated with the distances and angles listed in Table 2. In this structure, four cyclen-capped Ru<sup>II</sup> centers are arranged in a nearly perfect square, with a mean edge distance of 11.34 Å. Note that, compared with those



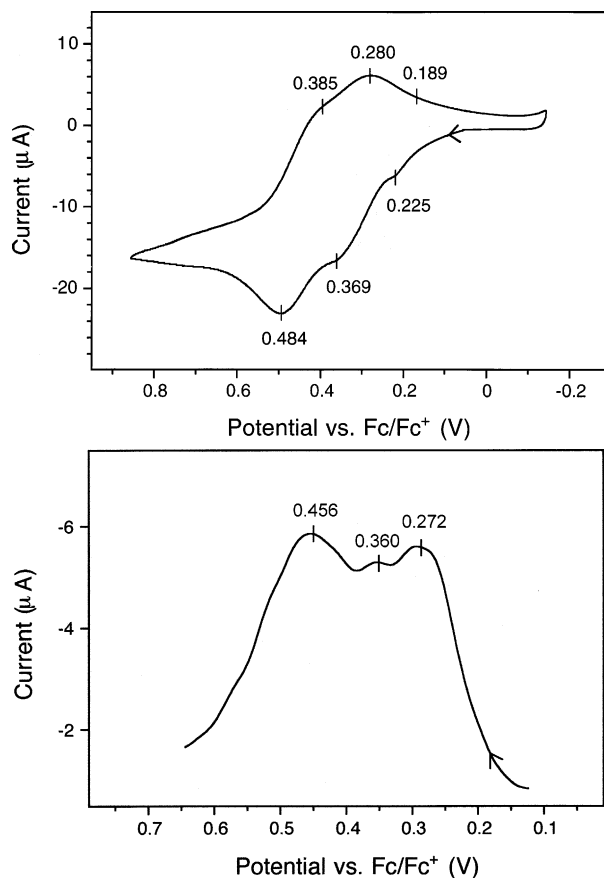
**Figure 2.** Structure of the square [(cyclen)<sub>4</sub>Ru<sub>4</sub>(4,4'-bpy)<sub>4</sub>]<sup>8+</sup> complex in 7, as viewed parallel to the *a* axis of the crystal. Red, gray, and blue spheres represent Ru, C, and N atoms, respectively; H atoms are omitted for clarity. The complex resides on an inversion center within the crystal.

in the triangular complex of 4·11H<sub>2</sub>O, these slightly longer Ru···Ru separations are consistent with linear rather than bowed 4,4'-bpy bridging ligands. On a related note, the mean N<sub>bpy</sub>–Ru–N<sub>bpy</sub> angle of 93(5)° in 7 is wider and closer to 90°. Of particular interest are the interpyridine ring twist angles, which are  $\phi = 1.0$  and 5.6° for opposing pairs of 4,4'-bpy ligands. Although these twist angles are greater than those found within the triangular complex, they are significantly lower than observed in the crystal structures of other 4,4'-bpy-bridged squares,<sup>17c,j</sup> including [(dppb)<sub>4</sub>Ru<sub>4</sub>Cl<sub>8</sub>(4,4'-bpy)<sub>4</sub>] ( $\phi = 10.9^\circ$  and 42.6°).<sup>18</sup> Very likely, the small twist angles are a result of the packing arrangement within the crystal, and are not retained upon dissolution. The [(cyclen)<sub>4</sub>Ru<sub>4</sub>(4,4'-bpy)<sub>4</sub>]<sup>8+</sup> squares in 7 are also stacked in a perfectly eclipsed fashion, forming one-dimensional columns along the *b* axis of the crystal. Surprisingly little electron density is evident within the interior channels of these square columns; however, this is potentially just a consequence of the poor resolution of the crystal structure.

**Electrochemistry.** Reversible electrochemical behavior was not observed for 4 in either water or methanol. In both cases, repeated cycling of the voltage resulted in the formation of fine precipitates, indicating that the products of the oxidation/reduction events are insoluble. Cyclic voltammetry experiments employing solutions of 5 in acetonitrile, DMF, and acetone were hindered by the intense peaks in the cyclic voltammogram corresponding to oxidation of the tetraphenylborate anions, which masked the ruthenium-based oxidation events. Fortunately, however, acetonitrile solutions of [(cyclen)<sub>3</sub>Ru<sub>3</sub>(4,4'-bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>6</sub> (6) and [(cyclen)<sub>3</sub>Ru<sub>3</sub>(4,4'-bpy)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>6</sub> were found to be suitable for electrochemical measurements. The results for measurements performed on compound 6 are described below; those for [(cyclen)<sub>3</sub>Ru<sub>3</sub>(4,4'-bpy)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>6</sub> were essentially identical.

As shown at the top of Figure 3, the cyclic voltammogram obtained for a 1 mM solution of 6 in acetonitrile displays one incompletely reversed and two fairly distinct redox processes centered at  $E_{1/2} = 0.207$  V ( $\Delta E_p = 36$  mV), 0.324

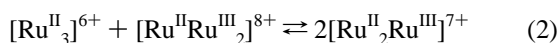
(28) Selected examples: (a) Szalda, D. J.; Fagalde, F.; Katz, N. E. *Acta Crystallogr., Sect. A* **1996**, *52*, 3013. (b) Coe, B. J.; Chamberlain, M. C.; Essex-Lopresti, J. P.; Gaines, S.; Jeffery, J. C.; Houbrechts, S.; Persoons, A. *Inorg. Chem.* **1997**, *36*, 3284. (c) Coe, B. J.; Harris, J. A.; Asselberghs, I.; Persoons, A.; Jeffery, J. C.; Rees, L. H.; Gelbrich, T.; Hursthouse, M. B. *Dalton Trans.* **1999**, 3617. (d) Heseck, D.; Hembury, G. A.; Drew, M. G. B.; Taniguchi, S.; Inoue, Y. *Inorg. Chem.* **2001**, *40*, 2478. (e) Bonnet, S.; Collin, J.-P.; Gruber, N.; Sauvage, J.-P.; Schofield, E. *Dalton Trans.* **2003**, 4654. (f) Coe, B. J.; Curati, N. R. M.; Grabowski, S. R.; Horton, P. N.; Hursthouse, M. B. *Acta Crystallogr., Sect. E* **2004**, *60*, m1562.



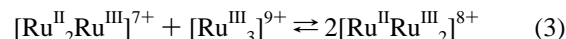
**Figure 3.** Cyclic voltammogram (upper) and differential pulse voltammogram (lower) of **6** in acetonitrile. The measurements were performed on a platinum electrode at scan rates of 100 and 20 mV/s, respectively, with 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> as the supporting electrolyte. Ferrocene (Fc) was employed as an internal standard.

V ( $\Delta E_p = 89$  mV), and 0.434 V ( $\Delta E_p = 99$  mV) versus Fc/Fc<sup>+</sup>. These events are reasonably assigned to the 6+/7+, 7+/8+, and 8+/9+ couples of the triangular complex, respectively. Consistent with the foregoing assignments, the differential pulse voltammogram for the same solution of **6** (shown at the bottom of Figure 3) displays three oxidation peaks of approximately equal magnitude at 0.272, 0.360, and 0.456 V versus Fc/Fc<sup>+</sup>. Addition of a stoichiometric amount of ferrocene to the solution confirmed that each peak corresponds to a one-electron oxidation event, and a simulation of the profile with three Gaussian peaks gave relative areas of 1.2:1.1:1.0 (see Figure S6 in the Supporting Information).

The separation between the first two redox couples in the cyclic voltammogram of **6** suggests an approximate comproportionation constant of  $K_c = 10^{2.0}$  associated with the following equilibrium.

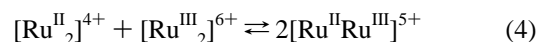


The second pair of redox couples is marginally closer in energy, implying a slightly lesser degree of stability for the  $[\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}_2]^{8+}$  mixed-valence complex. Thus, consistent with the greater average oxidation state of +2.67 for ruthenium centers, the estimated comproportionation constant is slightly lower for the following equilibrium, with  $K_c = 10^{1.9}$ .



Unfortunately, the electrochemical regions of stability are probably too narrow to permit facile isolation of either of the mixed-valence triangular complexes,  $[(\text{cyclen})_3\text{Ru}_3(4,4'\text{-bpy})_3]^{7+}$  or  $[(\text{cyclen})_3\text{Ru}_3(4,4'\text{-bpy})_3]^{8+}$ . These results are striking, however, given that 4,4'-bpy-bridged Ru<sub>2</sub> complexes are generally found to exhibit essentially no electronic coupling.<sup>29,30</sup> The lack of coupling in such dinuclear complexes can be attributed to the rapid rotation in solution of the pyridine rings of 4,4'-bpy ligand with respect to each other.<sup>13,14,16,29,31</sup> In contrast, the ring rotations are severely restricted by the bowing of the 4,4'-bpy ligands in the triangular  $[(\text{cyclen})_3\text{Ru}_3(4,4'\text{-bpy})_3]^{n+}$  complexes, resulting in enhanced electronic coupling.

It could perhaps be argued that the enhanced wave separation in the triangular molecule is simply due to charge repulsion effects, rather than true electronic coupling through the bridging ligands. It has been established that such electrostatic interactions are proportional to the products of the charges on the metal ions.<sup>32</sup> Taking the example of  $[(\text{NH}_3)_5\text{Ru}(\mu\text{-}4,4'\text{-bpy})\text{Ru}(\text{NH}_3)_5]^{5+}$ , the relevant equilibrium is



The relative repulsion factors are then  $(2 \times 2) + (3 \times 3) = 13$  on the left, versus  $2 \times (2 \times 3) = 12$  on the right. Hence, the mixed-valence state is more stable electrostatically by 1 part in 13. Applying the same method, the stabilization of the two mixed-valence states of an Ru<sub>3</sub> triangle can be calculated as follows. Reaction 2 above describes the equilibrium associated with the first  $K_c$  value, which leads to relative repulsion factors of  $[3 \times (2 \times 2)] + [2 \times (2 \times 3) + (3 \times 3)] = 33$  on the left, versus  $2 \times [(2 \times 2) + 2 \times (2 \times 3)] = 32$  on the right. The first mixed-valence state for the triangle is therefore stabilized electrostatically by only 1 part in 33. Reaction 3 describes the equilibrium associated with the second  $K_c$  value, which leads to relative repulsion factors of  $[(2 \times 2) + 2 \times (2 \times 3)] + [3 \times (3 \times 3)] = 43$  on the left, versus  $2 \times [2 \times (2 \times 3) + (3 \times 3)] = 42$  on the right. The second mixed-valence state for the triangle is therefore stabilized electrostatically by even less, only 1 part in 43. Thus, the increase in the number of Ru–Ru interactions, plus the stepwise nature of the oxidation of the total molecule, actually leads to less electrostatic stabilization for the mixed-valence states of the Ru<sub>3</sub> triangle than for a similarly bridged Ru<sub>2</sub> species.

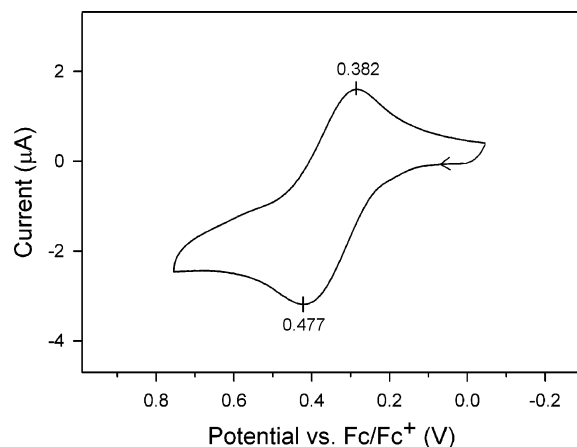
The electrochemistry of the square complex  $[(\text{cyclen})_4\text{Ru}_4(4,4'\text{-bpy})_4]^{8+}$  provides further evidence that the electronic communication observed in the triangular complex is de-

(29) (a) Powers, M. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 1785. (b) Sutton, J. E.; Sutton, P. M.; Taube, H. *Inorg. Chem.* **1979**, *18*, 1017.

(30) Sutton, J. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 3125.

(31) (a) Fleischer, E. B.; Lavalley, D. K. *J. Am. Chem. Soc.* **1972**, *94*, 2599. (b) Tom, G. M.; Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1974**, *96*, 7827. (c) Callahan, R. W.; Brown, G. M.; Meyer, T. J. *Inorg. Chem.* **1975**, *14*, 1443. (d) Powers, M. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 1289.

(32) Richardson, D. E.; Taube, H. *Coord. Chem. Rev.* **1984**, *60*, 107.



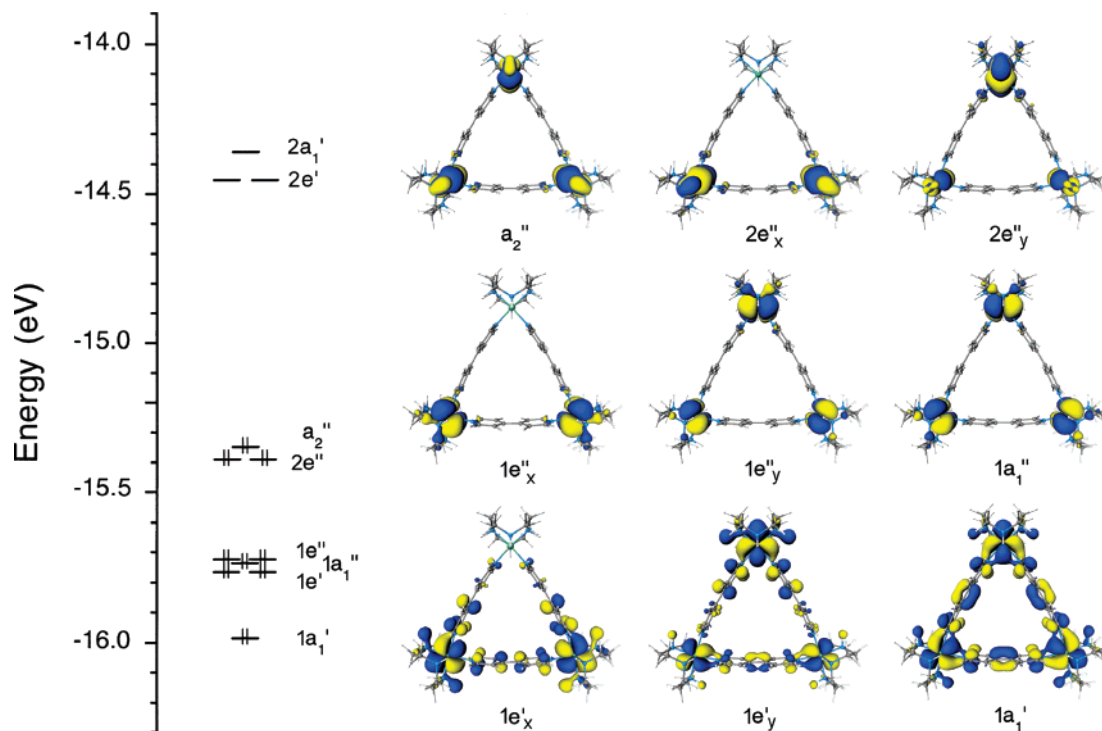
**Figure 4.** Cyclic voltammogram of **7** in acetonitrile. The measurement was performed on a platinum electrode at a scan rate of 1000 mV/s with 0.1 M (Bu<sub>4</sub>N)ClO<sub>4</sub> as the supporting electrolyte. At significantly slower scan rates, the oxidation was irreversible. Ferrocene (Fc) was employed as an internal standard.

pendent on the alignment of the 4,4'-bpy rings. As shown in Figure 4, very different behavior is apparent in the cyclic voltammogram obtained for a 1 mM solution of **7** in acetonitrile. At slow scan rates, one broad, irreversible oxidation wave is observed; however, as the scan rate is increased, the reverse wave becomes increasingly distinct. At 1000 mV/s, a reversible four-electron redox couple centered at 0.430 V ( $\Delta E_p = 120$  mV) versus Fc/Fc<sup>+</sup> is obtained, corresponding to formation of the 12+ ion state of the square complex.<sup>33</sup> Upon comparison with the reversible one-electron couple for the internal standard of ferrocene, which displays a peak-to-peak separation of  $\Delta E_p = 70$  mV, the significance of the breadth of the couple becomes evident. The broadening is consistent with a series of closely

overlapping, unresolved one-electron couples rather than a single four-electron redox couple. More directly, the differential pulse voltammogram confirms the four-electron nature of the overlapping redox couples (see Figure S7 in the Supporting Information). The addition of a stoichiometric amount of ferrocene to the solution and simulation of the profiles of the differential pulse voltammogram with Gaussian peaks gave relative areas of 3.8:1.0 for the broad, square-based couple versus the Fc/Fc<sup>+</sup> couple.

The cyclic voltammogram of [(dppb)<sub>4</sub>Ru<sub>4</sub>Cl<sub>8</sub>(4,4'-bpy)<sub>4</sub>] in dichloromethane also reveals no evidence of electronic coupling, exhibiting a single four-electron redox couple at  $E_{1/2} = 0.55$  V versus Ag/AgCl.<sup>18</sup> Similarly, just one redox couple was observed in the cyclic voltammograms of dinuclear 4,4'-bpy-bridged complexes, namely, at  $E_{1/2} = 1.36$  V ( $\Delta E_p = 90$  mV) versus a sodium chloride calomel electrode for [(2,2'-bpy)<sub>2</sub>(py)Ru( $\mu$ -4,4'-bpy)Ru(py)(2,2'-bpy)<sub>2</sub>]<sup>4+</sup> in acetonitrile solution<sup>29</sup> and 0.369 V ( $\Delta E_p = 111$  mV) versus NHE for [(NH<sub>3</sub>)<sub>2</sub>Ru( $\mu$ -4,4'-bpy)Ru(NH<sub>3</sub>)<sub>5</sub>]<sup>4+</sup> in a 0.1 M aqueous HCl solution.<sup>30</sup> It should be noted that, in all of the aforementioned cases, only the peak-to-peak separation of the redox couples signals a series of overlapping one-electron waves rather than one multielectron wave. These previous results serve to highlight the unusual degree of coupling attained within the triangular [(cyclen)<sub>3</sub>Ru<sub>3</sub>(4,4'-bpy)<sub>3</sub>]<sup>n+</sup> species, for which the redox couples are separated enough to be distinctly resolved and allow estimation of comproportionation constants.

**Electronic Structure Calculations.** DFT calculations were performed on [(cyclen)<sub>3</sub>Ru<sub>3</sub>(4,4'-bpy)<sub>3</sub>]<sup>6+</sup> in order to probe the nature of the orbitals implicated in the electron-transfer events. Figure 5 shows the energy levels and some



**Figure 5.** Frontier energy level scheme and depictions of the highest occupied molecular orbitals for the triangular complex [(cyclen)<sub>3</sub>Ru<sub>3</sub>(4,4'-bpy)<sub>3</sub>]<sup>6+</sup>, as calculated using DFT.



orbital depictions for the frontier orbitals of the closed-shell, triangular complex. Below the HOMO–LUMO gap of 1.06 eV, the nine highest occupied orbitals lie within an energy spread of 0.60 eV and arise from combinations of the  $t_{2g}$  orbitals of the three Ru<sup>II</sup> centers. The six filled orbitals highest in energy,  $1a_1''$ ,  $1e''$ ,  $2e''$ , and  $a_2''$ , are almost entirely ruthenium-based, with no 4,4'-bpy character. In contrast, the two orbitals below these,  $1a_1'$  and  $1e'$ , exhibit significant orbital contributions from the bridging 4,4'-bpy ligands, which provide a  $\pi$  orbital system connecting the ruthenium  $\pi$ -type orbitals. These then represent the orbitals most likely responsible for electron exchange upon oxidation of the molecule. Indeed, consistent with the 0.154 V region of stability observed by cyclic voltammetry, the results of DFT calculations performed on the one-electron oxidized triangle,  $[(\text{cyclen})_3\text{Ru}_3(4,4'\text{-bpy})_3]^{7+}$ , show that the same nine highest occupied orbitals lie within a narrower energy spread of just 0.25 eV. Presumably, the unpaired electron is able to move between these levels, the average energy spacing being merely 0.041 eV, and electron transfer is facilitated via involvement of the  $1a_1'$  and/or  $1e'$  orbitals.

(33) After a single voltage loop in the cyclic voltammetry experiment for **7** employing  $\text{Bu}_4\text{NClO}_4$  as the electrolyte was scanned, subsequent loops revealed a second, less intense redox couple at higher potential, which was presumably due to some decomposition product. Experiments performed using  $\text{Bu}_4\text{NPF}_6$  as the supporting electrolyte revealed two completely irreversible oxidation waves at the same potentials as those observed in  $\text{Bu}_4\text{NClO}_4$  electrolyte solution. We conclude that the square complex is somewhat unstable in acetonitrile, but that rapidly scanning the voltage with  $\text{Bu}_4\text{NClO}_4$  as the electrolyte has enabled us to see the series of four overlapping, one-electron reversible waves associated with the intact complex before decomposition occurs.

## Outlook

The foregoing results suggest that electronic coupling can be achieved through bridging 4,4'-bpy ligands by utilizing a triangular geometry that constrains the pyridyl rings to be coplanar. With the use of appropriate blocking ligands, this effect can perhaps be extended to larger supramolecular cage constructs, such as a  $\text{Ru}_4(\mu\text{-}4,4'\text{-bpy})_6$  tetrahedron. These, together with related pyrazine-bridged cage complexes, are of particular interest for potential guest-specific sensing applications. Future research will focus on the elaboration of such species, as well as related modular, linear systems of possible utility as redox-active components in molecular electronic devices.<sup>7</sup>

**Acknowledgment.** This research was supported by a DOE LDRD grant obtained through Lawrence Berkeley National Laboratory and NSF Grant ECS-0210426. Single-crystal synchrotron measurements performed at the Advanced Light Source were funded in part by DOE Grant DE-AC03-76SF00098. We thank Dr. A. G. Oliver for experimental assistance, and Prof. M. Fujita, Dr. F. J. Hollander, and Dr. A. G. Oliver for helpful discussions.

**Supporting Information Available:** A depiction of the structure of **2**, HMQC and COSY NMR spectra for **4**, UV–visible spectra of compounds **4** and **7**, a plot of the differential pulse voltammogram for **7**, and a complete version of ref 21 (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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