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## Supramolecular Chemistry

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Edwin C. Constable<sup>a</sup>; Alexander M. W. Cargill Thompson<sup>a</sup>

<sup>a</sup> Institut für Anorganische Chemie, Universität Basel, Basel, CH, Switzerland

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COMMUNICATION

# Metallosupramolecular oligomers— Diruthenium complexes of a novel ligand incorporating N,N',N'' and N,N',C metal- binding domains

EDWIN C. CONSTABLE\* and ALEXANDER M.W. CARGILL THOMPSON

*Institut für Anorganische Chemie, Universität Basel, Spitalstrasse 51, CH 4056 Basel, Switzerland*

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The preparation of a dinucleating ligand containing N,N',N'' and N,N',C metal-binding domains is described. The diruthenium complex containing one metal in an N<sub>6</sub> and one in an N<sub>5</sub>C environment has been prepared and its properties are reported.

There is considerable current interest in the assembly of metallosupramolecules by the interaction of metal ions with multidentate ligands containing two or more metal-binding domains.<sup>1</sup> We have been concerned with the preparation of novel molecular architectures using metallosupramolecular principles.<sup>2</sup> Many coordination oligomers have been reported which make use of multinucleating ligands containing oligopyridine units, and the widespread interest in the photophysical and photochemical properties of ruthenium(II) and osmium(II) tris-2,2'-bipyridine complexes has promoted the design and synthesis of many multidomain species containing 2,2'-bipyridine (bpy) functionalities.<sup>3</sup> However, as we<sup>4,5</sup> and others<sup>6</sup> have discussed elsewhere, the inclusion of {M(bpy)<sub>3</sub>} centres results in coordination oligomers with numerous possible enantiomers and diastereomers. In contrast, the use of *pseudo*-octahedral {M(tpy)<sub>2</sub>} centres (tpy = 2,2':6',2''-terpyridine) in oligomers avoids the problems of isomerism if the tpy functionalities in the multinucleating ligands are linked "back-to-back" through the 4'-positions.

Unfortunately, unsubstituted {Ru(tpy)<sub>2</sub>}<sup>2+</sup> centres do not to exhibit room temperature luminescence,<sup>7</sup> and the dimers of the form [(tpy)Ru(L)Ru(tpy)]<sup>4+</sup> (L = "back-to-back" bis-tpy ligand) have shown little evidence of any

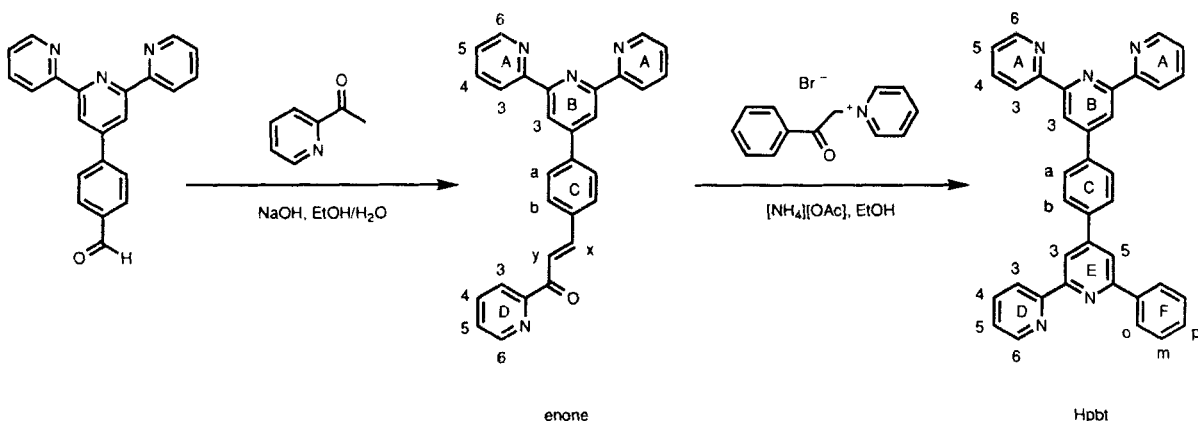
ground-state interaction between the metal centres. We have demonstrated that the introduction of electron-withdrawing substituents allows a tuning of the photophysical properties.<sup>7</sup> However, an alternative way to control the photophysical properties of such complexes is by the replacement of one ruthenium(II) site by an osmium(II) centre, and this results in oligomers in which electronic energy transfer is possible between the higher energy ruthenium {Ru(tpy)<sub>2</sub>} and the luminescent {Os(tpy)<sub>2</sub>} centres.<sup>8</sup>

A further method of inducing interactions between the metal centres in such dimers has been to replace the N<sub>6</sub> donor sets by N<sub>5</sub>C donor sets in which one of the tpy binding domains is replaced by a cyclometallating N<sub>2</sub>C analogue.<sup>9,10</sup> Significant metal-metal interactions are observed in such dimers, with mixed-valence ruthenium(II)-ruthenium(III) species being isolable. These effects depend on the presence of N<sub>5</sub>C donor sets, rather than on the exact location of the metallated ring within the donor set.<sup>10</sup>

In order to further investigate these effects, we have designed and synthesized a binucleating ligand Hpbt which contains a N<sub>3</sub> tpy donor set linked "back-to-back" with a potentially cyclometallating N<sub>2</sub>C 6-phenyl-2,2'-bipyridine functionality. This ligand (Scheme) is prepared<sup>11</sup> in 44% overall yield from 2,2':6',2''-terpyridine-4'-(benzene-4-carboxaldehyde)<sup>12</sup> by a two stage Kröhnke-type<sup>13</sup> methodology.

The reaction of Hpbt with two equivalents of [Ru(tpy)Cl<sub>3</sub>] at reflux in 5:1 MeOH-H<sub>2</sub>O with added *N*-ethylmorpholine affords a deep red solution from which [(tpy)Ru(pbt)Ru(tpy)][PF<sub>6</sub>]<sub>3</sub> is isolated as dark purple-brown powder (16%) following column chromatography

\*Corresponding author.

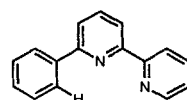


(Silica; MeCN, Saturated aqueous  $\text{KNO}_3$ ,  $\text{H}_2\text{O}$  (14:2:1)) and anion metathesis with  $[\text{NH}_4][\text{PF}_6]$ .<sup>14</sup>

The  $^1\text{H}$  NMR spectrum of a  $\text{CDCl}_3$  solution of the ligand Hpbt exhibits 16 resonances (Figure 1a). Assignments were made by comparison with the analogous "back-to-back" tpy ligand 1,4-bis(2,2':6',2''-terpyridinyl)benzene (btpy),<sup>5</sup> and with the potentially cyclometallating 2,2':6',2''-terpyridine analogue 6-phenyl-2,2'-bipyridine (Hpbpy).<sup>15</sup> The  $^1\text{H}$  NMR spectrum of a  $\text{CD}_3\text{CN}$  solution of the asymmetrical cyclometallated complex  $[(\text{tpy})\text{Ru}(\text{pbt})\text{Ru}(\text{tpy})][\text{PF}_6]_3$  is more complicated, and shows 29 resonances (Figure 1b). These were, however, readily assigned by comparison with spectra of the model complexes  $[(\text{tpy})\text{Ru}(\text{btpy})\text{Ru}(\text{tpy})][\text{PF}_6]_4$ <sup>5</sup> and  $[\text{Ru}(\text{pbpy})(\text{tpy})][\text{PF}_6]$ .<sup>16</sup> Of particular note are three resonances that appear upfield of the usual aromatic region at  $\delta$  6.82, 6.59 and 5.78. These resonances are ascribed to protons  $\text{H}^{4\text{F}}$ ,  $\text{H}^{5\text{F}}$ , and  $\text{H}^{6\text{F}}$ , respectively, on the cyclometallated phenyl ring,<sup>16</sup> and are characteristic of such a structure.

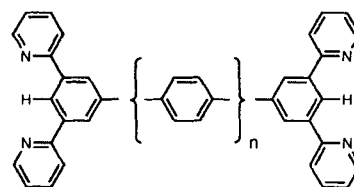
The non-cyclometallated complex  $[(\text{tpy})\text{Ru}(\text{N,N-Hpbt-N,N})\text{RuCl}(\text{tpy})][\text{PF}_6]_3$  could be prepared by a similar route to that used to obtain its cyclometallated counterpart, but using glacial acetic acid as the solvent. (We have discussed elsewhere the use of different solvents to determine the extent to which cyclometallation occurs in analogous mononuclear complexes<sup>16</sup>). The  $^1\text{H}$  NMR spectrum of a  $\text{CD}_3\text{CN}$  solution of this complex exhibits 28 resonances. Characteristic of this spectrum are one proton resonance shifted downfield to  $\delta$  10.24 and one resonance that is shifted upfield to  $\delta$  6.19, assigned to protons  $\text{H}^{6\text{D}}$  and  $\text{H}^{6\text{F}}$ , respectively. These two shifted resonances are typical of a non-metallated  $\text{N}_5\text{Cl}$  donor-set.<sup>16,17</sup>

The ligand Hpbt exhibits a molecular ion peak at  $m/z$  539 (539) in its electron impact mass spectrum. The cyclometallated complex  $[(\text{tpy})\text{Ru}(\text{pbt})\text{Ru}(\text{tpy})][\text{PF}_6]_3$  exhibits peaks at  $m/z$  1498 (1498), 1354 (1353) and 1206 (1208) in its positive ion fast atom bombardment mass spectrum<sup>18</sup> assigned to  $\{[(\text{tpy})\text{Ru}(\text{pbt})\text{Ru}(\text{tpy})][\text{PF}_6]_2\}^+$ ,  $\{[(\text{tpy})\text{Ru}(\text{pbt})\text{Ru}(\text{tpy})][\text{PF}_6]\}^+$  and  $\{[(\text{tpy})\text{Ru}(\text{pbt})-$

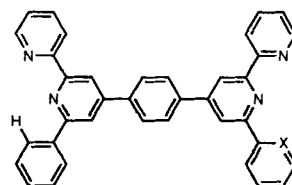


Hpbpy<sup>15, 16</sup>

The cyclometallating ligand 6-phenyl-2,2'-bipyridine



$n = 0, 1, 2$ <sup>9</sup>



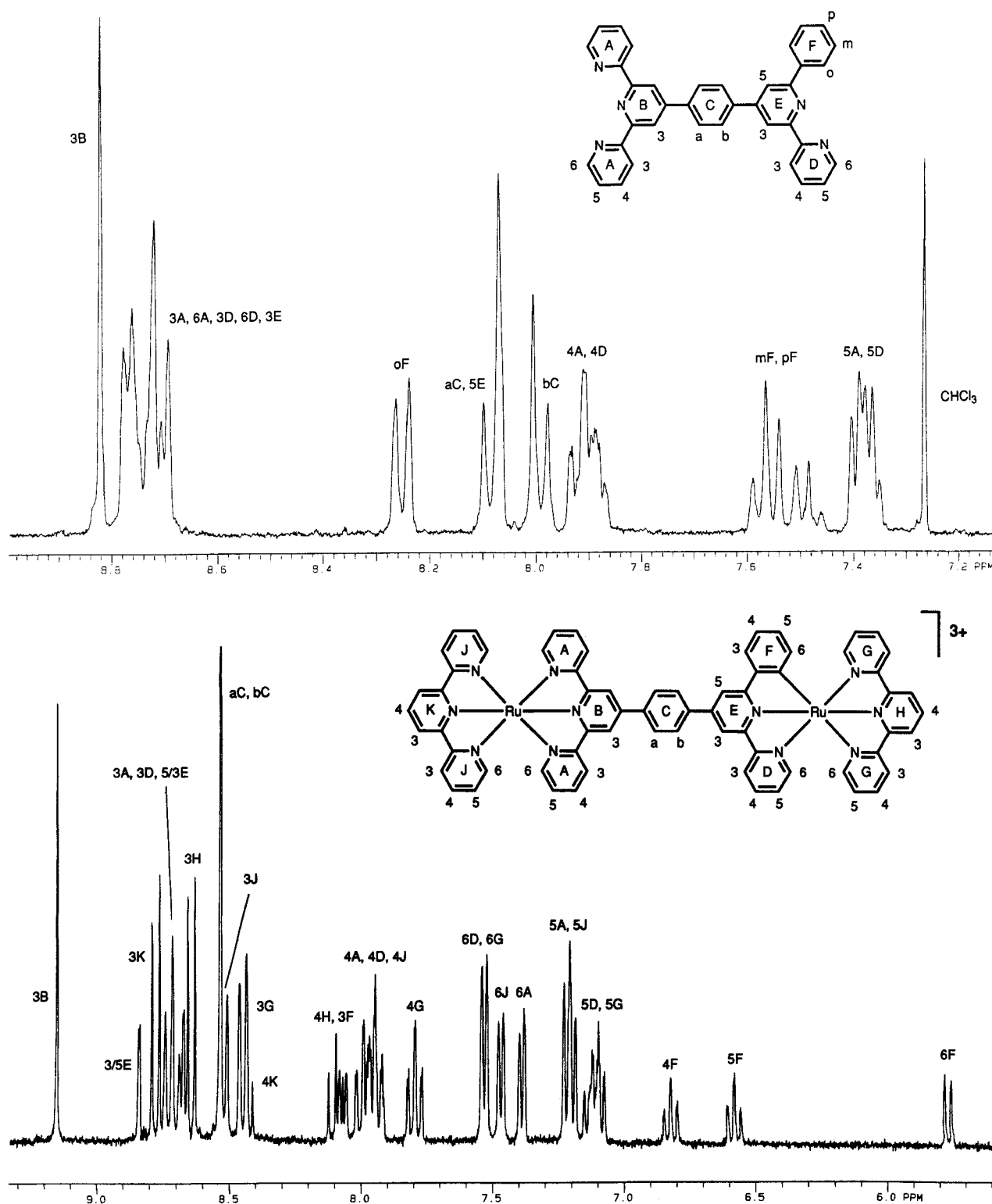
Hpbt X = N  
H<sub>2</sub>bpbpy X = CH

Cyclometallating bridging ligands

#### Scheme

$\text{Ru}(\text{tpy})\}^+$  fragments respectively. The non-metallated complex has peaks at  $m/z$  1534 (1534) and 1389 (1389), due to the loss of one and two  $\{\text{PF}_6\}$  counterions, respectively.

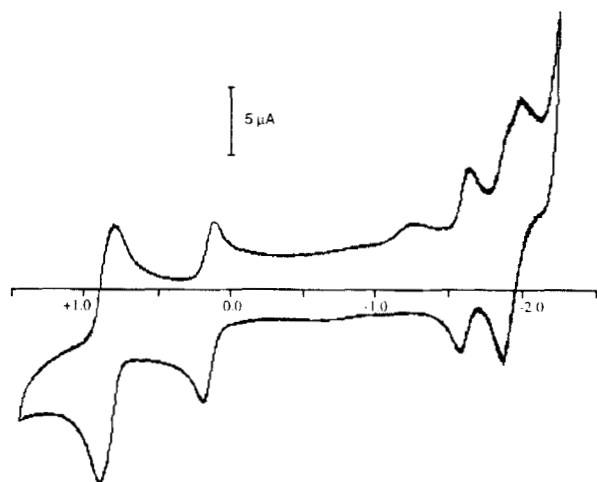
The cyclic voltammogram of an acetonitrile solution of  $[(\text{tpy})\text{Ru}(\text{pbt})\text{Ru}(\text{tpy})][\text{PF}_6]_3$  (Figure 2) exhibits two fully reversible metal-centred oxidative processes at +0.16 and +0.85 V (all potentials quoted with respect to internal ferrocene-ferrocenium couple). The process at



**Figure 1** 300 MHz  $^1\text{H}$  NMR spectra of a. HpbT ( $\text{CDCl}_3$  solution) and b. the cyclometallated complex  $[(\text{tpy})\text{Ru}(\text{pbt})\text{Ru}(\text{tpy})][\text{PF}_6]_3$  ( $\text{CD}_3\text{CN}$  solution).

+0.16 V is assigned to the ruthenium(II)/ruthenium(III) process at the cyclometallated  $N_3C$  site, by analogy with the mononuclear complex  $[\text{Ru}(\text{tpy})(\text{pbpy})][\text{PF}_6]$  (+0.12 V).<sup>16</sup> The process at +0.85 V is assigned to the rutheni-

um(II)/ruthenium(III) process at the  $\{\text{Ru}(\text{tpy})_2\}$  centre (*c.f.* a potential of +0.93 V for the simultaneous oxidation of both ruthenium(II) centres in the dinuclear complex  $[(\text{tpy})\text{Ru}(\text{btpy})\text{Ru}(\text{tpy})][\text{PF}_6]_4$ ).<sup>5</sup> One reversible



**Figure 2** Cyclic voltammogram of the cyclometallated complex [(tpy)Ru(pbt)Ru(tpy)][PF<sub>6</sub>]<sub>3</sub> (V. vs internal Fc/Fc<sup>+</sup>) MeCN solution, 0.1 M [nBu<sub>4</sub>N][PF<sub>6</sub>] supporting electrolyte.

ligand-centred reductive process is observed at  $-1.60$  V, with several coincident processes occurring around  $-1.92$  V. The cyclic voltammogram of the non-metallated complex [(tpy)Ru(*N,N',N''*-pbt-*N''',N''''*)RuCl(tpy)][PF<sub>6</sub>]<sub>3</sub> exhibits two reversible oxidation processes at  $+0.41$  and  $+0.88$  V, as well as various reductive processes. The process at  $+0.41$  V is ascribed to the *N*<sub>5</sub>Cl centre by comparison with the mononuclear analogue [Ru(tpy)(Hpbpy)Cl][PF<sub>6</sub>]<sub>3</sub><sup>16</sup> which exhibits such a peak at  $+0.44$  V. The process at  $+0.88$  V is again due to the {Ru(tpy)<sub>2</sub>} centre.<sup>5</sup>

We are currently investigating the photophysical and photochemical properties of these dimers, as well as developing synthetic strategies for incorporating the ligand Hpbtp into longer chain coordination oligomers. We are also studying the complexes of the bis-cyclometallating analogue of Hpbtp, 1,4-benzene-bis(4-(6-phenyl-2,2'-bipyridine)) (H<sub>2</sub>bpbpy), and of the triscyclometallating "starburst" ligand 1,3,5-benzene-tris(4-(6-phenyl-2,2'-bipyridine)).

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- 11 **enone**: Aqueous NaOH (80 ml, 1 M) was added to a stirred solution of 2,2':6',2''-terpyridine-4'-(benzene-4-carboxaldehyde)<sup>12</sup> (480 mg, 1.42 mmol) and 2-acetylpyridine (0.16 cm<sup>3</sup>, 1.42 mmol) in ethanol (250 cm<sup>3</sup>) at 0°C. After stirring at 0°C for 2 hours, water (200 cm<sup>3</sup>) was added, and the resulting off-white precipitate was collected by filtration, washed with water, and dried *in vacuo*. The enone was obtained as a pale coloured powder (510 mg, 81%). [MP: decomposes above 95°C; EIMS: *m/z* 440 (440) M<sup>+</sup>; IR:  $\nu_{\text{C=O}}$  1671 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  8.79 (d, 1H, H<sup>6D</sup>), 8.78 (s, 2H, H<sup>3B</sup>), 8.75 (d, 2H, H<sup>6A</sup>), 8.69 (d, 2H, H<sup>3A</sup>), 8.39 (d, 1H, H<sup>N5</sup>),  $J_{\text{C5,6}}$  = 15.9 Hz), 8.21 (d, 1H, H<sup>3D</sup>), 7.97 (m, 8H, H<sup>aC, bC, y/x, 4A, 4D</sup>), 7.42 (dd, 1H, H<sup>5D</sup>), 7.38 (dd, 2H, H<sup>5A</sup>)].  
**Hpbtp**: The above enone (300 mg, 0.68 mmol), phenacetylpyridinium bromide (260 mg, 0.94 mmol) and ammonium acetate (1.5g, excess) were heated at reflux in ethanol (10 cm<sup>3</sup>) for 16 hours. The reaction mixture was then cooled, and the resulting yellow precipitate (200 mg, 54%) collected by filtration, washed well with methanol, and dried *in vacuo*. [MP: >270°C; EIMS: *m/z* 539 (539) M<sup>+</sup>; IR:  $\nu$  1600 m, 1583 s, 1568 m, 1542 m, 1466 m, 1418 m, 1388 m cm<sup>-1</sup>; Analysis found (sample recrystallised from toluene): C 83.6, H 5.3, N 9.6. (Calculated for C<sub>37</sub>H<sub>25</sub>N<sub>5</sub>2C<sub>7</sub>H<sub>8</sub>: C 84.6, H 5.7, N 9.7%); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  8.82 (s, 2H, H<sup>3B</sup>), 8.74 (m, 7H, H<sup>3A, 6A, 3D, 6D, 3E</sup>), 8.25 (d, 2H, H<sup>6F</sup>), 8.08 (m, 3H, H<sup>aC, 5E</sup>), 7.99 (d, 2H, H<sup>bC</sup>), 7.90 (m, 3H, H<sup>4A, 4D</sup>), 7.52 (m, 3H, H<sup>6E, 6F</sup>), 7.38 (m, 3H, H<sup>5A, 5D</sup>)].
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- 14 **Cyclometallated [(tpy)Ru(pbt)Ru(tpy)][PF<sub>6</sub>]<sub>3</sub>**: The ligand Hpbtp (30 mg, 0.056 mmol) was heated at reflux for 16 hours with [Ru(tpy)Cl<sub>3</sub>] (54 mg, 0.123 mmol) in 5:1 MeOH-H<sub>2</sub>O (12 cm<sup>3</sup>) to which *N*-ethylmorpholine (4 drops) had been added. The resulting deep red solution was reduced in volume, and chromatographed directly on a silica column, using MeCN, Saturated aqueous KNO<sub>3</sub>, H<sub>2</sub>O (14:2:1) as the eluent system. The fast moving purple band was collected as fractions, which were compared by t.l.c. (same eluent system) prior to combination. Excess [NH<sub>4</sub>][PF<sub>6</sub>] was added and the solution was reduced in volume to induce precipitation. Recrystallisation from aqueous acetonitrile afforded [(tpy)Ru(pbt)Ru(tpy)][PF<sub>6</sub>]<sub>3</sub> as a dark purple-brown powder (15 mg, 16%). [+FABMS: *m/z* 1498 (1498) {[(tpy)Ru(pbt)Ru(tpy)][PF<sub>6</sub>]<sub>2</sub>}<sup>+</sup>, 1354 (1353) {[(tpy)Ru(pbt)Ru(tpy)][PF<sub>6</sub>]<sub>3</sub>}<sup>+</sup>, and 1206 (1208) {[(tpy)Ru(pbt)Ru(tpy)]<sup>+</sup>; Analysis found: C

48.3, H 3.3, N 8.7. (Calculated for  $\text{RuC}_{67}\text{H}_{46}\text{N}_{11}\text{P}_3\text{F}_{18}$ : C 49.0, H 2.8, N 9.4%).

**Non-metallated [(tpy)Ru(N,N,N-Hpbt-N,N)RuCl(tpy)][PF<sub>6</sub>]<sub>3</sub>;** An identical method was used to that for [(tpy)Ru(pbt)Ru(tpy)][PF<sub>6</sub>]<sub>3</sub> above, except that glacial acetic acid (10 cm<sup>3</sup>) was used as the solvent instead of aqueous methanol. After column chromatography and work-up, [(tpy)Ru(N,N,N-Hpbt-N,N)RuCl(tpy)][PF<sub>6</sub>]<sub>3</sub> was obtained as a dark purple-brown powder (9 mg, 10%). [+FABMS: *m/z* 1534 (1534) {[(tpy)Ru(Hpbt)RuCl(tpy)][PF<sub>6</sub>]<sub>2</sub>}<sup>+</sup>, 1389 (1389) {[(tpy)Ru(Hpbt)RuCl(tpy)][PF<sub>6</sub>]<sub>2</sub>}<sup>+</sup>; Analysis found: C 48.2, H 3.2, N 8.3.

(Calculated for  $\text{RuC}_{67}\text{H}_{47}\text{N}_{11}\text{ClP}_3\text{F}_{18}$ : C 47.9, H 2.8, N 9.2%).

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- 18 4-Nitrobenzyl alcohol matrix; expected values (<sup>102</sup>Ru, <sup>35</sup>Cl) given in parentheses; isotopomer distributions were as expected.