

## Comparison of metal-metal electronic interactions in an isomeric pair of dinuclear ruthenium complexes with different bridging pathways: effective hole-transfer through a bis-phenolate bridge

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*Supplementary information: preparation and characterisation of ligands* INORG CHEM

**2,2'-bis(2-methoxyphenyl)-4,4'-bipyridine ( $\text{Me}_2\text{L}^1$ ).** This preparation is based on a published method.<sup>1</sup> To a stirred, ice-cold mixture of  $[\text{Ni}(\text{dppe})\text{Cl}_2]$  (0.05 g, 0.09 mmol) and 2,2'-dichloro-4,4'-bipyridine (0.21 g, 0.97 mmol) in dry THF under  $\text{N}_2$  was added a solution of the Grignard reagent 2-MeOC<sub>6</sub>H<sub>4</sub>MgBr [prepared from 2-bromoanisole (0.44 g, 2.34 mmol) and Mg turnings (0.056 g, 2.34 mmol) in THF]. The mixture was allowed to warm up to room temperature and was then stirred at this temperature for 16 h. The reaction was then quenched with aqueous NH<sub>4</sub>Cl, acidified with HCl, and the THF was removed *in vacuo*. The acidic aqueous solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> to remove organic impurities; this extract was discarded. The aqueous solution was then made weakly basic with NH<sub>3</sub>, and the product was extracted with several portions of CH<sub>2</sub>Cl<sub>2</sub> which were combined and dried over MgSO<sub>4</sub>. Removal of the solvent afforded  $\text{Me}_2\text{L}^1$  as a yellow oil (0.10 g, 27%).

EIMS:  $m/z$  368 ( $M^+$ ). <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>):  $\delta$  8.81 (2 H, dd,  $J$  = 5.3, 0.7 Hz; pyridyl H<sup>6</sup>), 8.11 (2 H, d,  $J$  = 1.6, 0.7 Hz; pyridyl H<sup>3</sup>), 7.82 (2 H, dd,  $J$  = 7.6, 2.0 Hz; phenyl), 7.48 (2 H, dd,  $J$  = 5.3, 1.6 Hz; pyridyl H<sup>5</sup>), 7.41 (2 H, td,  $J$  = 7.8, 1.6 Hz; phenyl), 7.11 (2 H, td,  $J$  = 7.4, 1.3 Hz; phenyl), 7.04 (2 H, d,  $J$  = 8.0 Hz; phenyl), 3.88 (6 H, s).

**3,3'-dibromo-4,4'-dimethoxybiphenyl.** A solution of 4,4'-dimethoxybiphenyl (2.50 g, 11.7 mmol) and bromine (1.35 cm<sup>3</sup>, 26.3 mmol) in acetic acid (60 cm<sup>3</sup>) was heated to reflux for 30 minutes and then cooled; the product 3,3'-dibromo-4,4'-dimethoxybiphenyl precipitated pure, and was filtered off and dried *in vacuo* (3.6 g, 82%). EIMS:  $m/z$  372 ( $M^+$ ), 357 ( $M^+ - \text{CH}_3$ ). <sup>1</sup>H

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.71 (2 H, d, *J* = 2.6 Hz; phenyl H<sup>2</sup>), 7.42 (2 H, dd, *J* = 8.4, 2.2 Hz; phenyl H<sup>6</sup>), 6.95 (2 H, d, *J* = 8.6 Hz; phenyl H<sup>5</sup>), 3.93 (6 H, s; Me). Found: C, 45.0; H, 3.3%. Required for C<sub>14</sub>H<sub>12</sub>O<sub>2</sub>Br<sub>2</sub>: C, 45.2; H, 3.3%.

**3,3'-bis(2-pyridyl)-4,4'-dimethoxybiphenyl (Me<sub>2</sub>L<sup>2</sup>).** This preparation is based on a published method.<sup>1</sup> To a stirred, ice-cold mixture of [Ni(dppe)Cl<sub>2</sub>] (1.03 g, 1.96 mmol) and 2-bromopyridine (3.09 g, 19.6 mmol) in dry thf (20 cm<sup>3</sup>) under N<sub>2</sub> was added a solution of the Grignard reagent {4-MeO-3-MgBr-C<sub>6</sub>H<sub>3</sub>}<sub>2</sub> [prepared from 3,3'-dibromo-4,4'-dimethoxybiphenyl (3.64 g, 9.79 mmol) and Mg turnings (0.48 g, 19.6 mmol) in thf]. The mixture was allowed to reach room temperature and was then stirred at this temperature for 16 h. The workup was identical to that described above for Me<sub>2</sub>L<sup>1</sup>, to give Me<sub>2</sub>L<sup>2</sup> as a yellow oil (1.25 g, 35%).

EIMS: *m/z* 368 (M<sup>+</sup>). <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>):  $\delta$  8.71 (2 H, ddd, *J* = 4.6, 1.6, 1.0 Hz; pyridyl H<sup>6</sup>), 8.00 (2 H, d, *J* = 2.6 Hz; phenyl H<sup>2</sup>), 7.82 (2 H, dt, *J* = 7.9, 1.1 Hz; pyridyl H<sup>3</sup>), 7.71 (2 H, td, *J* = 7.6, 1.9 Hz; pyridyl H<sup>4</sup>), 7.65 (2 H, dd, *J* = 8.6, 2.4 Hz; phenyl H<sup>6</sup>), 7.21 (2 H, ddd, *J* = 7.6, 4.9, 1.3 Hz; pyridyl H<sup>5</sup>), 7.05 (2 H, d, *J* = 8.6 Hz, phenyl H<sup>5</sup>), 3.87 (6 H, s; Me).

**H<sub>2</sub>L<sup>1</sup>.** This preparation is based on a published method.<sup>2</sup> Pyridinium chloride was prepared by heating a mixture of pyridine (16 cm<sup>3</sup>) and concentrated HCl (17.6 cm<sup>3</sup>) under a stream of N<sub>2</sub> at 195 °C for 2h. After this time, Me<sub>2</sub>L<sup>1</sup> (0.10 g, 0.27 mmol) was added and the mixture was heated for a further 3h at 195 °C under N<sub>2</sub>. On cooling the mixture solidified; it was dissolved in water and neutralised with aqueous KOH, and then extracted with several portions of CH<sub>2</sub>Cl<sub>2</sub> which were combined and dried over MgSO<sub>4</sub>. The resultant solid was purified by column chromatography [silica, CH<sub>2</sub>Cl<sub>2</sub>/MeOH (99:1)] to give pure H<sub>2</sub>L<sup>1</sup> (0.060 g, 65%).

EIMS: *m/z* 340 (M<sup>+</sup>). <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>):  $\delta$  14.1 (2 H, br s; OH), 8.67 (2 H, d, *J* = 5.4 Hz; pyridyl H<sup>6</sup>), 8.15 (2 H, s; pyridyl H<sup>3</sup>), 7.92 (2 H, dd, *J* = 8.1, 2.0 Hz; phenyl), 7.51 (2 H, dd, *J* = 5.4, 1.6 Hz; pyridyl H<sup>5</sup>), 7.36 (2 H, td, *J* = 8.1, 1.7 Hz, phenyl), 7.07 (2 H, dd, *J* = 8.1, 1.7 Hz; phenyl), 6.95 (2 H, td, *J* = 8.1, 1.6 Hz; phenyl). Found: C, 77.2; H, 4.9; N, 7.8%. Required for C<sub>22</sub>H<sub>16</sub>O<sub>2</sub>N<sub>2</sub>: C, 77.6; H, 4.7; N, 8.2%.

**H<sub>2</sub>L<sup>2</sup>** was prepared from Me<sub>2</sub>L<sup>2</sup> using pyridinium chloride, exactly as described above for conversion of Me<sub>2</sub>L<sup>1</sup> to H<sub>2</sub>L<sup>1</sup>, in 40% yield.

EIMS: <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>):  $\delta$  14.4 (2 H, br s; OH), 8.54 (2 H, ddd, *J* = 5.1, 1.9, 1.0 Hz; pyridyl H<sup>6</sup>), 8.02 (2 H, d, *J* = 8.6 Hz; pyridyl H<sup>3</sup>), 7.97 (2 H, d, *J* = 2.3 Hz; phenyl H<sup>2</sup>), 7.87 (2 H, td, *J* = 7.9, 1.9; pyridyl H<sup>4</sup>), 7.53 (2 H, dd, *J* = 8.6, 2.3 Hz; phenyl H<sup>6</sup>), 7.27 (2 H, ddd, *J* = 7.3, 5.0, 1.0 Hz; pyridyl H<sup>5</sup>), 7.11 (2 H, dd, *J* = 8.5 Hz; phenyl H<sup>5</sup>). Found: C, 77.3; H, 4.6; N, 7.8%. Required for C<sub>22</sub>H<sub>16</sub>O<sub>2</sub>N<sub>2</sub>: C, 77.6; H, 4.7; N, 8.2%.

- (1) Holligan, B. M.; Jeffery, J. C.; Norgett, M. K.; Schatz. E.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1992**, 3345.
- (2) Dietrich-Buchecker, C.; Sauvage, J.-P. *Tetrahedron* **1990**, *46*, 503.