

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 (Me₂L¹). This preparation is based on a published method.¹ To a stirred, ice-cold mixture of [Ni(dppe)Cl₂] (0.05 g, 0.09 mmol) and 2,2'-dichloro-4,4'-bipyridine (0.21 g, 0.97 mmol) in dry thf under N₂ was added a solution of the Grignard reagent 2-MeOC₆H₄MgBr [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 NH₄Cl, acidified with HCl, and the thf was removed *in vacuo*. The acidic aqueous solution was extracted with CH₂Cl₂ to remove organic impurities; this extract was discarded. The aqueous solution was then made weakly basic with NH₃, and the product was extracted with several portions of CH₂Cl₂ which were combined and dried over MgSO₄. Removal of the solvent afforded Me₂L¹ as a yellow oil (0.10 g, 27%).

EIMS: *m/z* 368 (*M*⁺). ¹H NMR (270 MHz, CDCl₃): δ 8.81 (2 H, dd, *J* = 5.3, 0.7 Hz; pyridyl H⁶), 8.11 (2 H, d, *J* = 1.6, 0.7 Hz; pyridyl H³), 7.82 (2 H, dd, *J* = 7.6, 2.0 Hz; phenyl), 7.48 (2 H, dd, *J* = 5.3, 1.6 Hz; pyridyl H⁵), 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 cm³, 26.3 mmol) in acetic acid (60 cm³) 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*⁺ - CH₃). ¹H

NMR (300 MHz, CDCl_3): δ 7.71 (2 H, d, $J = 2.6$ Hz; phenyl H^2), 7.42 (2 H, dd, $J = 8.4, 2.2$ Hz; phenyl H^6), 6.95 (2 H, d, $J = 8.6$ Hz; phenyl H^5), 3.93 (6 H, s; Me). Found: C, 45.0; H, 3.3%. Required for $\text{C}_{14}\text{H}_{12}\text{O}_2\text{Br}_2$: C, 45.2; H, 3.3%.

3,3'-bis(2-pyridyl)-4,4'-dimethoxybiphenyl (Me_2L^2). This preparation is based on a published method.¹ To a stirred, ice-cold mixture of $[\text{Ni}(\text{dppe})\text{Cl}_2]$ (1.03 g, 1.96 mmol) and 2-bromopyridine (3.09 g, 19.6 mmol) in dry thf (20 cm^3) under N_2 was added a solution of the Grignard reagent $\{4\text{-MeO-3-MgBr-C}_6\text{H}_3\}_2$ [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_2L^1 , to give Me_2L^2 as a yellow oil (1.25 g, 35%).

EIMS: m/z 368 (M^+). ^1H NMR (270 MHz, CDCl_3): δ 8.71 (2 H, ddd, $J = 4.6, 1.6, 1.0$ Hz; pyridyl H^6), 8.00 (2 H, d, $J = 2.6$ Hz; phenyl H^2), 7.82 (2 H, dt, $J = 7.9, 1.1$ Hz; pyridyl H^3), 7.71 (2 H, td, $J = 7.6, 1.9$ Hz; pyridyl H^4), 7.65 (2 H, dd, $J = 8.6, 2.4$ Hz; phenyl H^6), 7.21 (2 H, ddd, $J = 7.6, 4.9, 1.3$ Hz; pyridyl H^5), 7.05 (2 H, d, $J = 8.6$ Hz; phenyl H^5), 3.87 (6 H, s; Me).

H_2L^1 . This preparation is based on a published method.² Pyridinium chloride was prepared by heating a mixture of pyridine (16 cm^3) and concentrated HCl (17.6 cm^3) under a stream of N_2 at 195 °C for 2h. After this time, Me_2L^1 (0.10 g, 0.27 mmol) was added and the mixture was heated for a further 3h at 195 °C under N_2 . On cooling the mixture solidified; it was dissolved in water and neutralised with aqueous KOH, and then extracted with several portions of CH_2Cl_2 which were combined and dried over MgSO_4 . The resultant solid was purified by column chromatography [silica, $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (99:1)] to give pure H_2L^1 (0.060 g, 65%).

EIMS: m/z 340 (M^+). ^1H NMR (270 MHz, CDCl_3): δ 14.1 (2 H, br s; OH), 8.67 (2 H, d, $J = 5.4$ Hz; pyridyl H^6), 8.15 (2 H, s; pyridyl H^3), 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^5), 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 $\text{C}_{22}\text{H}_{16}\text{O}_2\text{N}_2$: C, 77.6; H, 4.7; N, 8.2%.

H_2L^2 was prepared from Me_2L^2 using pyridinium chloride, exactly as described above for conversion of Me_2L^1 to H_2L^1 , in 40% yield.

EIMS: ^1H NMR (270 MHz, CDCl_3): δ 14.4 (2 H, br s; OH), 8.54 (2 H, ddd, $J = 5.1, 1.9, 1.0$ Hz; pyridyl H^6), 8.02 (2 H, d, $J = 8.6$ Hz; pyridyl H^3), 7.97 (2 H, d, $J = 2.3$ Hz; phenyl H^2), 7.87 (2 H, td, $J = 7.9, 1.9$; pyridyl H^4), 7.53 (2 H, dd, $J = 8.6, 2.3$ Hz; phenyl H^6), 7.27 (2 H, ddd, $J = 7.3, 5.0, 1.0$ Hz; pyridyl H^5), 7.11 (2 H, dd, $J = 8.5$ Hz; phenyl H^5). Found: C, 77.3; H, 4.6; N, 7.8%. Required for $\text{C}_{22}\text{H}_{16}\text{O}_2\text{N}_2$: C, 77.6; H, 4.7; N, 8.2%.

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- (2) Dietrich-Buchecker, C.; Sauvage, J.-P. *Tetrahedron* **1990**, 46, 503.