Supporting Information

for

Tetrametallic Rectangular Box Complexes Assembled from Heteroligated Macrocycles

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Experimental Section

General Procedures. All reactions were performed under a nitrogen atmosphere in reagent grade solvents, using standard Schlenk or dry-box techniques.[1] All other solvents were purified by published methods.[2] Chemicals were purchased from Aldrich Chemical Co., unless otherwise mentioned or prepared by literature methods as referenced below. ^{1}H, ^{13}C, and ^{31}P{^{1}H} NMR spectra were recorded on a Varian Mercury 300 MHz spectrometer using deuterated solvents and H_3PO_4 as internal and external references, respectively. Electrospray mass spectra (ES MS) were recorded on a Micromas Quatro II triple quadrapole mass spectrometer. Electron ionization mass spectra (EIMS) were recorded on a Fisions VG 70-250 SE mass spectrometer. Elemental analyses were obtained from Quantitative Technologies Inc. of Whitehouse, NJ. Crystallographic material can be found on the WWW.

4a. To a stirred solution of complex **3**[3] $\cdot$ $[BF_4]_2$ (12.6 mg, 8.51 μmol) in CH_2Cl_2 (1 mL), a solution of 1,4-dicyanobenzene (1.1 mg, 8.58 μmol) in CH_2Cl_2 (1 mL) was added via syringe and the reaction stirred for 10 min. Pentane was then added to precipitate out the product. Filtering through a fritted funnel to remove solvent and subsequent drying *in vacuo* resulted in pure product **4a**. Yield 13.0 mg, 95%. ^{31}P{^{1}H} NMR: (CD_2Cl_2) δ 67.3 (dd, $J_{P\text{-}P} = 41$ Hz, $J_{Rh\text{-}P} = 166$ Hz) and δ 26.7 (dd, $J_{P\text{-}P} = 42$ Hz, $J_{Rh\text{-}P} = 164$ Hz). ^{1}H NMR: (CD_2Cl_2) δ 8.27-6.71 (m, aromatic), 5.08 (m), 4.87 (m), 2.93 (m), 2.70 (m), 2.30 (m), 1.11 (m). Due to the labile nature of the Rh-N bond, ESI mass spectra of complex **4a**, showed complex **3** which presumably forms owing to the harsh ionization conditions within the mass spectrometer. Diffraction quality crystals were grown from a concentrated solution of **4a** in dichloromethane and layered with pentane. Elemental analysis for $C_{152}H_{136}P_8S_4O_4N_4Rh_4B_4F_{16} \cdot 2CH_2Cl_2$ calcd: 54.60% C, 4.17% H. Found: 54.58% C, 4.098% H.

4b. To a stirred solution of complex **3** $\cdot$ $[BF_4]_2$ (10.5 mg, 7.09 μmol) in CH_2Cl_2 (1 mL), a solution of 4,4'-dicyanobiphenyl (1.45 mg, 7.10 μmol) in CH_2Cl_2 (1 mL) was added via syringe and the reaction stirred for 10 min. Pentane was then added to precipitate out the product. Filtering through a fritted funnel to remove solvent and subsequent drying *in vacuo* resulted in pure product **4b**. Yield 11.2 mg, 94%. ^{31}P{^{1}H} NMR: (CD_2Cl_2) δ 69.3 (dd, $J_{P\text{-}P} = 42$ Hz, $J_{Rh\text{-}P} = 169$ Hz) and δ 32.2 (dd, $J_{P\text{-}P} = 41$ Hz, $J_{Rh\text{-}}$

$_{\mathrm{P}}$ = 164 Hz). ^{1}H NMR: (CD_2Cl_2) δ 8.17-6.76 (m, aromatic), 5.47 (m), 4.60 (m), 2.97 (m), 2.83 (m), 2.42 (m), 1.37 (m). Due to the labile nature of the Rh-N bond, ESI mass spectra of complex **4b**, showed complex **3** which presumably forms owing to the harsh ionization conditions within the mass spectrometer. Elemental analysis for $C_{164}H_{144}P_8S_4O_4N_4Rh_4B_4F_{16} \cdot 1CH_2Cl_2$ calcd: 57.36% C, 4.26% H. Found: 57.53% C, 4.25% H.

4c. To a stirred solution of complex **3** $\cdot$ $[BF_4]_2$ (9.20 mg, 6.21 μmol) in CH_2Cl_2 (1 mL), a solution of zinc salen pyridyl terminated bridging ligand **5**^{4} (4.06 mg, 6.21 μmol) in CH_2Cl_2 (1 mL) was added via syringe and the reaction stirred for 10 min. Pentane was then added to precipitate out the product. Filtering through a fritted funnel to remove solvent and subsequent drying *in vacuo* resulted in pure product **4c**. Yield 12.2 mg, 92%. $^{31}P\{^1H\}$ NMR: (CD_2Cl_2) δ 70.7 (dd, $J_{\mathrm{P-P}}$ = 42 Hz, $J_{\mathrm{Rh-P}}$ = 156 Hz) and δ 37.9 (dd, $J_{\mathrm{P-P}}$ = 42 Hz, $J_{\mathrm{Rh-P}}$ = 175 Hz). ^{1}H NMR: (CD_2Cl_2) δ 8.19-6.42 (m, aromatic), 5.80 (m), 4.60 (m), 3.19 (m), 2.90 (m), 2.42 (m), 1.56 (s), 1.49 (s), 1.32 (s). ESI MS for $[C_{212}H_{216}S_4O_8P_8N_8Rh_4]^{4+}$ calcd (M - 2 Zn + 2H): 948.8. Found: 948.6. Elemental analysis for $C_{212}H_{216}N_8O_8P_8S_4Rh_4Zn_2B_4F_{16} \cdot 1CH_2Cl_2$ calcd: 59.63 % C, 5.12 % H. Found: 59.47% C, 5.10% H.

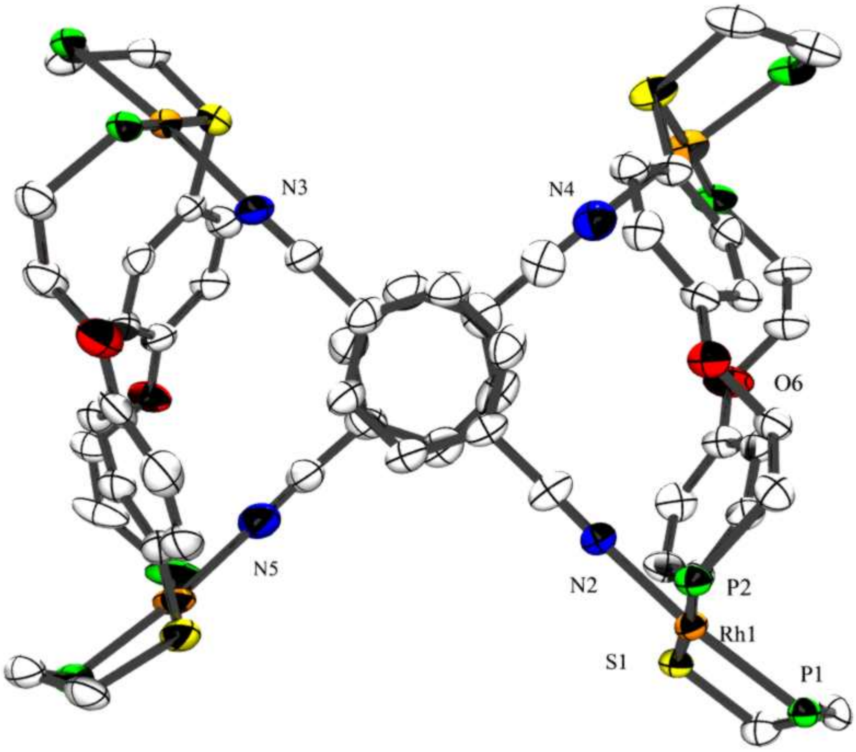

Figure S1. ORTEP diagram side view of **4a** depicting the torsion angle about each bridging ligand. Hydrogen atoms, solvent molecules, counter ions, and phenyl rings appended to each P atom have been omitted for clarity. Labeling and coloring scheme is as follows: Rh (orange); P (green); O (red); S (yellow); N (blue).[5]

References:

(1) Errington, R. J. *Advanced Practical Inorganic and Metalorganic Chemistry*; Chapman & Hall: New York, 1997.
(2) Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*; Butterworth-Heinemann: Oxford, 1996.
(3) Brown, A. M.; Ovchinnikov, M. V.; Stern, C. L.; Mirkin, C. A.; *J. Am. Chem. Soc.* **2004**, *126*, 14316-14317.
(4) Sun, S. S.; Stern, C. L.; Nguyen, S. B. T.; Hupp, J. T.; *J. Am. Chem. Soc.* **2004**, *126*, 6314-6326.
(5) Sheldrick, G.M. (1998), SADABS (2.01), Bruker/Siemens Area Detector Absorption Correction Program, Bruker AXS, Madison, Wisconsin, USA.