Electronic Supplementary Material (ESI) for Dalton Transactions

Metallo-macrocycles with labile coordination sites through self assembly: binuclear phenyl bridged bisbipyridine manganese complexes

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Supporting information

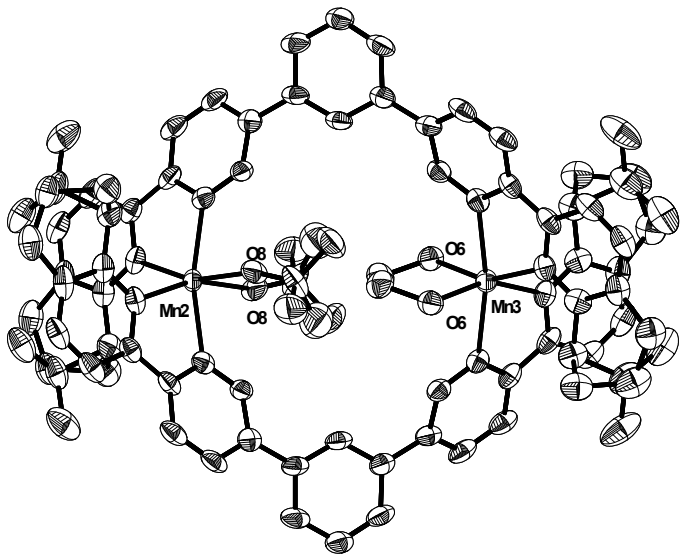

Figure 1S The ORTEP plots of cation of *P*-**2** showing partial atom labeling. The thermal ellipsoids are drawn at the 30% probability level.

Experimental Section

Procedure for synthesis of achiral bromo-bipyridine. *n*-Butyllithium (1.6 M in hexane, 3.9 ml) was added to a solution of 2-bromo-pyridine (5.5 mmol, 0.9 g) in dried THF at −78 ^{o}C under nitrogen. The solution was stirred at −50 ^{o}C for 1 h, and then cooled back to −78 ^{o}C. The orange solution was transferred to a solution of $ZnCl_2$ (6.1 mmol, 1.0 g) in dried THF (15 ml). The reaction temperature was raised to room temperature after stirring of the solution at −78 ^{o}C for 1 h. The purple color solution was transferred to a solution of 2,5-dibromo-pyridine (8.5 mmol, 2.0 g), $Pd(PPh_3)_4$ (0.2 mmol, 0.3 g) in dried THF (29 ml). The mixture was stirred overnight. The reaction was quenched by saturated sodium bicarbonate solution. The mixture was extracted by CH_2Cl_2 and dried with $MgSO_4$ and filtered. The solvent was removed under reduced pressure and the yellow residue was purified by column chromatograph with light petroleum ether and ethyl acetate (10:1, R_f = 0.3). The achiral bromo-bipyridine was isolated as white solid. Yield: 0.7 g (50%), ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.61 (s, 1H), 8.55 (d, 1H, J = 4.5 Hz), 8.24 (d, 1H, J = 8.1 Hz), 8.19 (d, 1H, J = 8.4), 7.82 (d, 1H, J = 8.4 Hz), 7.71 (t, 1H, J = 7.5 Hz), 7.22 (t, 1H, J = 5.1 Hz). ESI-MS m/z: 236 (M^+ + 1).

Procedure for synthesis of chiral bromo-bipyridine. 3-Bromo-(6-pyridinioacetyl) pyridine iodide (10 mmol, 4.1 g), α,β-unsaturated ketone (13 mmol, 2.1 g) and ammonium acetate (13 g) was dissolved in glacial acetic acid (13 ml). The mixture was stirred and heated at 100 ^{o}C for 8 h. The reaction was quenched by NaOH. The mixture was extracted with diethyl ether (3 × 150 ml) and dried with $MgSO_4$ and filtered. The solvent was removed under reduced pressure and the brown residue obtained was purified by column chromatography with light petroleum ether and ethyl acetate (20:1, R_f = 0.3). Yield: 3.0 g (90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.69 (s, 1H), 8.28 (d, 1H, J = 8.1 Hz), 8.12 (d, 1H, J = 8.1 Hz), 7.90 (d, 1H, J = 8.4 Hz), 7.54 (d, 1H, J = 6.9 Hz), 3.10 (t, 1H, J = 5.4 Hz), 2.99 (d, 2H, J = 2.4 Hz), 2.75 (m, 1H),2.36 (m, 1H), 1.45 (s, 1H), 1.33 (d, 1H, J = 9.6 Hz), 0.70 (s, 1H). ESI-MS m/z: 329 (M^+ + 1).

General procedure for synthesis of **L1** and **L2**. Degassed MeOH (2 ml) and H_2O (2 ml) was added to a solution of bromo-bipyridine (1.2 mmol), $Pd(PPh_3)_4$ (0.05 g, 3 mol%), 1,3-phenyldiboronic acid (0.09 g, 0.6 mmol), sodium carbonate (0.25 g, 2.3 mmol) in degassed toluene (5 ml). The mixture was heated at 95 ^{o}C for overnight. The reaction was cooled to room temperature. Ammonia solution in saturated Na_2CO_3 solution was added and the solution was stirred for 5 min. The mixture was extracted with

dichloromethane (three times by 50 ml) and dried under vacuum. White precipitate was isolated by filtration after addition of methanol (100 ml).

Procedure for synthesis of **L1**. The above procedure was followed by using achiral bipyridine (0.28 g, 1.2 mmol). Yield: 0.13 g (54%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.01 (s, 2H), 8.73 (d, 2H, J = 4.0 Hz), 8.54 (d, 2H, J = 8.4 Hz), 8.48 (d, 2H, J = 8.0 Hz), 8.12 (d, 2H, J = 8.4 Hz), 7.92 (s, 1H), 7.87 (t, 2H, J = 6.0 Hz), 7.73 (d, 2H, J = 7.2 Hz), 7.66 (t, 1H, J = 6.8 Hz), 7.36 (t, 2H, J = 6.7). ^{13}C NMR (300 MHz, $CDCl_3$): δ 155.78, 155.31, 149.28, 147.71, 138.65, 137.01, 136.11, 135.39, 129.95, 126.93, 125.87, 123.82, 121.13, 121.08. ESI-MS m/z: 387 (M^+ + 1).

Procedure for synthesis of **L2**. The above procedure was followed by using chiral bipyridine (0.39 g, 1.2 mmol). Yield: 0.07 g (43%). ^{1}H NMR (300MHz, $CDCl_3$): δ 8.98 (d, 2H, J = 2.32 Hz), 8.48 (d, 2H, J = 8.3 Hz), 8.21 (d, 2H, J = 7.8 Hz), 8.07 (d, 2H, J = 8.3 Hz), 7.89 (t, 1H, J = 1.6 Hz), 7.71–7.57 (m, 3H), 3.13 (t, 2H, J = 5.6 Hz), 3.02 (d, 4H, J = 2.72 Hz), 2.79 (m, 2H), 2.37 (m, 2H), 1.46 (s, 6H), 1.37 (d, 2H, J = 9.72 Hz), 0.73 (s, 6H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 166.04, 155.94, 151.66, 147.65, 138.82, 136.01, 135.49, 135.22, 130.77, 139.85, 126.74, 125.77, 120.93, 118.83, 50.57, 40.18, 39.23, 31.33, 30.90, 26.07, 21.33. ESI-MS m/z: 575 (M^+ + 1).

Procedure for the synthesis of $[Mn_2(\mathbf{L1})_2(H_2O)_4](ClO_4)_4$. **L1** (0.10 mmol, 0.039 g) and $Mn(ClO_4)_2{\cdot}6H_2O$ (0.10 mmol, 0.036 g) was stirred in MeCN for 2 h. The crude product was isolated as a pale yellow solid by filtration after precipitation by addition of diethyl ether. The compound was crystallised by diffusion of diisopropyl ether into an acetonitrile solution. Yellow crystalline product was isolated by filtration. Yield: 0.031 g (44%). ESI-MS: m/z 986 $[Mn(C_{26}H_{18}N_4)_2](ClO_4)^+$, 1181, $[Mn_2(C_{26}H_{18}N_4)_2](ClO_4)_3^+$; CHN elemental analysis: calc. for $Mn_2(C_{26}H_{18}N_4)_2(H_2O)_4(ClO_4)_4{\cdot}3H_2O$: C, 43.84; H, 3.72; N, 7.86; Found: C, 43.89, H, 3.63, N, 7.88%.

Procedure for the synthesis of $[Mn_2(\mathbf{L2})_2](H_2O)(MeOH)(ClO_4)_4$. **L2** (0.10 mmol, 0.057 g) and $Mn(ClO_4)_2{\cdot}6H_2O$ (0.10 mmol, 0.036 g) was stirred in MeCN for 2 h. The crude product was isolated as pale yellow solid by filtration after precipitation by addition of diethyl ether. The compound was crystallised by ether diffusion into a mixture of MeOH and CH_2Cl_2 solution. Yellow crystalline product was isolated by filtration. Yield: 0.032 g (38%). ESI-MS: 1558.4 $[Mn_2(C_{40}H_{38}N_4)_2](ClO_4)_3^+$; CHN elemental analysis: calc. for $Mn_2(C_{46}H_{42}N_4)_2(H_2O)(MeOH)(ClO_4)_4{\cdot}2H_2O{\cdot}0.5CH_2Cl_2$: C, 54.82; H, 4.91; N, 6.27. Found: C, 54.77, H, 4.91, N, 6.35%.

Procedure for the epoxidation. Alkene (0.05 mmol) was added to a pear-shape flask containing a MeCN (0.1 ml) solution of **1** or **2** (5×10^{-4} mmol), and Na_2HPO_4 (0.15 g, 0.84 mmol). Four equivalent of peracetic acid (2 M, 0.2 mmol) was added, and then the mixture was stirred at room temperature. Solution drawn from the reaction mixture was diluted with diethyl ether and filtered through a basic alumina plug. The conversion and product yield was based on GC analysis. The product of the reaction was identified by comparison to the GC retention time and mass spectrum of standard.