Supplementary Material (ESI) for Chemical Communications

Synthesis of a [2]rotaxane through first- and second-sphere coordination

Barry A. Blight, James A. Wisner* and Michael C. Jennings

Supplemental Information:

All reactions were performed in dry solvents, and under an inert $N_{2(g)}$ atmosphere. All organic reagents were purchased from Aldrich Chemical Company, while palladium(II)dichloride was purchased from Pressure Chemical Company and all used without further purification. 1D-NMR spectral analyses were performed on a Varian Mercury 400MHz instrument in chloroform-*d* as the solvent. High resolution mass determinations were performed on a Finnigan MAT 8200 instrument using EI-ionization, and cold-spray ionization (CSI-MS) mass determinations with samples dissolved in a dichloromethane/acetone matrix, were performed with Micromass LCT instrumentation with carrier gases cooled to 200 K. Single crystal X-ray diffraction information can be found in the reference section and the .cif file for **3** is available on the Cambridge Crystallographic Database #CCDC-611645

Experimental Procedures and Characterization Data:

4-(3,5-di-*t-butyl*-benzyloxy)pyridine (2):

4-Hydroxypyridine(1.68g, 17.7mmol) was dissolved with heat in dry *N,N*-dimethylformamide (30ml) and the solution was cooled to 0°C. Sodium hydride (55% oil dispersion, 0.85g 17.7 mmol) was added to the reaction mixture in small portions over a 20 minute period. At 0°C, 3,5-di-*t*-butylbenzylbromide (5.00g, 17.7mmol)[A. Gourdon, *Eur. J. Org. Chem.* 1998, **12**, 2797], also dissolved in DMF (30ml), was added dropwise over 30 minutes. The reaction was stirred at 0°C for 1 hour, and warmed to room temperature overnight. The solvent was removed under reduced pressure, and the residue dissolved in dichloromethane (150ml), extracted with H_2O (3X100ml), dried with $MgSO_4$, and filtered. Solvent was removed under reduced pressure, and the residue purified by flash column chromatography (eluant 20:1 DCM/EtOAc) to yield the desired product. (2.36g, 8.0 mmol, 45%)

^{1}H NMR ($CDCl_3$, 400MHz) δ 8.46 (d, J = 5.7 Hz, 2H), 7.44 (s, 1H), 7.26 (s, 2H), 6.92 (d, J = 5.7 Hz, 2H), 5.07 (s, 2H), 1.34 (s, 18H). ^{13}C NMR ($CDCl_3$, 400MHz) δ 151.3, 151.0, 134.5, 122.6,

122.2, 110.5, 109.7, 70.6, 34.9, 31.4. M.P. 107-109 °C. LRMS M^+ *m/z*: 297.2, HRMS M^+ *m/z* calc: 297.2086 found: 297.2090.

***trans*-Bis-(3,5-di-*t-butyl*-4-benzyloxypyridine) palladium(II)dichloride (4)**:

trans-Bis-benzonitrilepalladium(II)dichloride (12mg, 0.033mmol) [see ref. **5**] was dissolved in dry acetonitrile (3ml) and a solution of 4-(3,5-di-*t-butyl*-benzyloxy)pyridine (20mg, 0.067mmol) in acetonitrile (1ml) was added dropwise to the reaction mixture and stirred at room temperature for 1 hour. The precipitate was collected by vacuum filtration to afford the desired metal complex (24mg, 0.031mmol, 93% yield).

^{1}H NMR ($CDCl_3$, 400MHz) δ 8.59 (d, *J* = 7.0 Hz, 4H), 7.45 (s, 2H), 7.22 (s, 4H), 6.90 (d, *J* = 7.0 Hz, 4H), 5.07 (s, 4H), 1.33 (s, 36H). ^{13}C NMR ($CDCl_3$, 400MHz) δ 166.4, 153.9, 151.5, 133.4, 123.1, 111.7, 71.7, 34.9, 31.4. CSI-MS $[M+Na]^+$ *m/z* = 794.4

[2]Rotaxane (3):

Tetralactam macrocyle (50.0mg, 0.049mmol) [see ref **4**] and *trans*-bis-benzonitrilepalladium(II)dichloride (9.4mg, 0.024mmol) [see ref. **5**] were dissolved in choroform (8ml) and allowed to stir at room temperature for 10 minutes. 4-(3,5-Di-*t-butyl*-benzyloxy)pyridine (20mg, 0.067mmol) was then dissolved separately in $CHCl_3$ (2ml), added dropwise to the reaction solution over 10 minutes and the reaction stirred for a further 4 hours at room temperature. The solvent was removed at reduced pressure, the residue dissolved in a minimum amount of hot $CHCl_3$ (2-3ml), and placed in the freezer overnight to selectively precipitate free macrocycle. The mixture was vacuum-filtered, and the filtrate rinsed with cold $CHCl_3$. The mother liquor was concentrated under reduced pressure to approximately 1mL and added slowly to stirring hexane (35ml), precipitating pure [2]rotaxane (37.9mg, 0.021mmol, 89%).

^{1}H NMR ($CDCl_3$, 400MHz) δ 8.23 (s, 4H), 8.159 (s, 4H), 7.95 (s, 2H), 7.45 (s, 2H), 7.20 (s, 4H), 7.16 (s, 8H), 6.90 (d, *J* = 6.8 Hz, 4H), 6.55 (d, *J* = 6.8 Hz, 4H), 5.11 (s, 4H), 2.46, (b, 8H), 2.05 (s, 12H), 1.70 (b, 8H), 1.56 (b, 4H), 1.37 (s, 18H), 1.30 (s, 36H). ^{13}C NMR ($CDCl_3$, 400MHz) δ 166.5, 165.8, 165.8, 153.7, 152.2, 152.2, 135.3, 134.6, 133.3, 131.8 (2C), 129.2, 124.0 (2C), 121.9, 112.4, 72.1, 45.1, 35.5, 35.2, 35.0, 31.6, 31.5, 26.6, 23.1, 19.3. CSI-MS $[M+2H]^{2+}$ *m/z* = 895.5 (Note no singly charged rotaxane species were observed in the mass spectrum despite several variations in the conditions employed.)