Supporting Information

belonging to

[2]Rotaxanes with Palladium(II)-NHC stoppers

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Experimental procedures, spectroscopic data, and crystallographic analyses

General Considerations. Unless otherwise noted all operations were performed without taking precautions to exclude air or moisture, and all solvents and chemicals were used as received without any further treatment. Dimer **1**,[S1] Compound **A**[S2] and **B**[S3] were prepared according to a literature procedure. ^{1}H, and ^{13}C NMR spectra were recorded on a Bruker ACF 300 or AMX 500 spectrometer and the chemical shifts (*δ*) were internally referenced to the residual protio-solvent signals relative to tetramethylsilane. Mass spectra were measured using a Finnigan MAT LCQ (ESI) spectrometer. Elemental analyses were performed on a Perkin-Elmer PE 2400 elemental analyzer at the Department of Chemistry, National University of Singapore.

[2]rotaxane (2). HBF_4 (26 μL, 0.2 mmol) was added in one portion to a solution of spacer **A** (13 mg, 0.1 mmol) in CH_3CN (4 mL), and the resulting mixture was stirred overnight. DB24C8 (224 mg, 0.5 mmol) was added to give a clear solution, which was stirred for a further 24 h. Complex **1** (94 mg, 0.1 mmol) was then added to the reaction mixture and stirred at 60°C for 24 h. After cooling, all volatiles were removed in vacuo.

The crude product was washed with toluene (5 × 20 mL) and CH_2Cl_2 (3 × 20 mL). The residue was dried in vacuo and crystallized from a mixed CH_3CN/toluene solution to yield the pure product as yellow crystals (10 mg, 0.005 mmol, 5%). ^{1}H NMR (300 MHz, CD_3CN): δ 9.08–7.14 (m, 16 H, Ar-H), 6.89 (s, 8 H, Ar-H_{DB24C8}), 4.41–3.03 (m, 12 H, $CH_2 + NH_2$), 6.27 (m, ^3J(H,H) = 6.6 Hz, 2 H, NC*H*(CH_3)$_2$), 6.13 (m, ^3J(H,H) = 7.2 Hz, 2 H, NC*H*(CH_3)$_2$), 4.08 (m, 8 H, OC*H*$_2$CH$_2$), 3.81 (m, 8 H, OCH$_2$C*H*$_2$), 3.71 (s, 8 H , OC*H*$_2$CH$_2$O), 1.74 (d, ^3J(H,H) = 7.2 Hz, 12 H, CH_3), 1.69 (d, ^3J(H,H) = 6.6 Hz, 12 H, CH_3). Anal. Calc for $C_{64}H_{89}B_2Br_4F_8N_8O_8Pd_2$: C, 42.62; H, 4.92; N, 6.21. Found: C, 42.58; H, 5.01; N, 5.98. MS (ESI): *m/z* = 631 [M – ($PdBr_2L$) – DB24C8 – Br – 2H]$^+$.

Tetranuclear complex (3). Spacer **A** (13 mg, 0.054 mmol) was added to a suspension of complex **1** (101 mg, 0.11 mmol) in CH_2Cl_2 (4 mL) to give a clear yellow solution, which was stirred at ambient temperature overnight. The solvent was removed in vacuo and the crude product was washed with excess CH_3CN (4 × 10 mL) and filtered. The residue was dried under vacuum to give a yellow powder (55 mg, 0.026 mmol, 48%). ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ 9.28 (d, ^3J(H,H) = 7.0 Hz, 4 H, 2,6-py-H), 7.89 (d, ^3J(H,H) = 7.0 Hz, 4 H, 3,5-py-H), 7.62 (dd, 4 H, Ar-H), 7.55 (dd, 4 H, Ar-H), 7.25 (dd, 4 H, Ar-H), 7.20 (dd, 4 H, Ar-H), 6.34 (m, ^3J(H,H) = 7.0 Hz, 4 H, C*H*(CH_3)$_2$), 4.80 (m, 2 H, N-H), 4.44 (ps t, 2 H, C*H*H), 4.27 (ps d, 2 H, CH*H*), 3.91 (ps dd, 2 H, C*H*H), 3.58 (ps t, 2 H, CH*H*), 1.79 (ps m, 24 H, CH_3), 1.69 (d, ^3J(H,H) = 7.0 Hz, 12 H, CH_3), 1.66 (d, ^3J(H,H) = 7.0 Hz, 12 H, CH_3). $^{13}C\{^1H\}$ NMR (125.76 MHz, CD_2Cl_2, 298 K): 160.4 (NCN), 159.9 (NCN), 152.9, 147.9, 133.8, 133.5, 126.6, 122.7, 122.6, 113.0, 112.9 (s, Ar-C), 54.9 (*C*H(CH_3)$_2$), 54.8 (*C*H(CH_3)$_2$), 52.5 (NH*C*H$_2$), 41.4 (CH$_2$*C*H$_2$NH), 20.7

(CH_3), 20.6 (CH_3). 20.5 (CH_3). Anal. Calc for $C_{66}H_{90}Br_8N_{12}Pd_4$: C, 37.46; H, 4.29; N, 7.94. Found: C, 37.39; H, 4.30; N, 7.83. MS (ESI): *m/z* = 1178 $[M - 2(PdBr_2L) + H]^+$.

[2]rotaxane (4). Spacer **B** (60 mg, 0.12 mmol) and DB24C8 (104 mg, 0.23 mmol) were dissolved in CH_3CN (10 mL). The reaction mixture was left to stir at ambient temperature for 2 hours. Complex **1** (109 mg, 0.12 mmol) was then added and the reaction mixture stirred at ambient temperature for 24 h. After filtration over celite and slow evaporation of the filtrate, the product was obtained as yellow crystals (155 mg, 0.082 mmol, 70%). ^{1}H NMR (500 MHz, d$_6$-DMSO): δ 9.25 (d, ^3J(H,H) = 4.4 Hz, 4 H, 2,6-Py-H), 9.19 (d, 4 H, 3,5-Py-H), 8.75 (d, 4 H, 3,5-Py-H), 8.20 (d, 4 H, 3,5-Py-H), 7.90 (dd, 4 H, Ar-H), 7.33 (dd, 4 H, Ar-H), 6.94 (m, 4 H, Ar-H_{DB24C8}), 6.87 (m, 4 H, Ar-H_{DB24C8}), 6.22 (m, 4 H, $C\mathit{H}(CH_3)_2$), 5.29 (s, 4 H, NCH_2), 4.06 (m, 8 H, Ar-$OC\mathit{H}_2CH_2$), 3.76 (m, 8 H, Ar-$OCH_2C\mathit{H}_2$), 3.66 (s, 8 H, OCH_2CH_2O), 1.73 (d, 24H, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, d$_6$-DMSO): 158.7 (NCN), 153.3, 148.5, 146.1, 146.0, 132.5, 126.1, 123.3, 122.8, 121.1, 114.1, 112.9 (Ar-C, one aromatic resonance absent due to accidental overlap), 70.3, 69.1, 68.7 ($O\mathit{C}H_2$), 59.4 (NCH_2), 54.0 ($\mathit{C}H(CH_3)_2$), 19.9 (CH_3). Anal. Calcd for $C_{72}H_{88}B_2Br_4F_8N_8O_8Pd_2$: C, 45.48; H, 4.77; N, 5.89. Found: C, 45.45, H, 4.59; N, 5.91. MS (ESI): *m/z* = 1364 $[M - DB24C8 - BF_4]^+$; 638 $[M - DB24C8 - 2BF_4]^{2+}$.

Dinuclear complex (5). Spacer **B** (60 mg, 0.12 mmol) and Complex **1** (109 mg, 0.12 mmol) were dissolved in DMF (6 mL) and stirred at ambient temperature overnight. The reaction mixture was filtered over Celite and the crude product was precipitated by mixing the filtrate with diethyl ether (150 mL). The crude product was washed with diethyl ether (2 × 10 mL) and water (2 × 10 mL). The residue was dried in vacuo to yield the product as a yellow powder (140 mg, 0.096 mmol, 80%) Yellow crystals suitable for X-ray diffraction studies were obtained from concentrated acetonitrile/toluene solution of **5**. ^{1}H NMR (500 MHz, d$_6$-DMSO): δ 9.25 (d, 4 H, 2,6-Py-H), 9.19 (d, 4 H, 2,6-Py-H), 8.75 (d, 4 H, 3,5-Py-H), 8.21 (d, 4 H, 3,5-Py-H), 7.90 (dd, 4 H, Ar-H), 7.33 (dd, 4 H, Ar-H),), 6.22 (m, 4 H, C*H*(CH$_3$)$_2$), 5.31 (s, 4 H, NCH$_2$), 1.73 (d, 24 H, CH$_3$). ^{13}C{^{1}H} NMR (126 MHz, d$_6$-DMSO): 158.8 (NCN), 153.3, 151.8, 146.1, 142.9, 132.5, 126.1, 123.3, 122.8, 112.9 (Ar-C), 59.4 (NCH$_2$), 54.0 (*C*H(CH$_3$)$_2$), 19.9 (CH$_3$). Anal. Calcd for $C_{48}H_{56}B_2Br_4F_8N_8Pd_2$: C, 39.73; H, 3.89; N, 7.72. Found: C, 39.97; H, 4.26; N, 7.42. MS (ESI): *m/z* = 1364 $[M – BF_4]^+$; 638 $[M – 2BF_4]^{2+}$.

X-ray Diffraction Studies. X-ray data were collected with a Bruker AXS SMART APEX diffractometer with the SMART suite of Programs.[4] Data were processed and corrected for Lorentz and polarisation effects with SAINT,[5] and for absorption effect with SADABS.[6] Structural solution and refinement were carried out with the SHELXTL suite of programs.[7] The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. All hydrogen atoms were put at calculated positions. All non-hydrogen atoms were generally given anisotropic displacement parameters in the final model. A summary of the most important crystallographic data is given in the Table S1.

References

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S5 *SAINT*+ version 6.22a; Bruker AXS Inc.: Madison, WI, 2001.

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Table S1. Selected Crystallographic Data for **2**·2$C_6H_5CH_3$, **3**·5CH_3CN, **4**·2.5CH_3CN and **5**·4CH_3CN.

	2·2$C_6H_5CH_3$	**3**·5CH_3CN	**4**·2.5CH_3CN	**5**·4CH_3CN
formula	$C_{78}H_{104}B_2Br_4F_8N_8O_8Pd_2$	$C_{74}H_{102}Br_8N_{16}Pd_4$	$C_{82}H_{103}B_2Br_4F_8N_{13}O_8Pd_2$	$C_{64}H_{80}B_2Br_4F_8N_{16}Pd_2$
fw	1987.75	2280.60	2104.83	1779.50
color, habit	yellow, block	yellow, block	yellow, block	yellow, block
cryst size [mm]	0.36 x 0.20 x 0.10	0.60 x 0.40 x 0.16	0.22 x 0.14 x 0.08	0.40 x 0.36 x 0.04
temp [K]	223(2)	223(2)	100(2)	223(2)
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic
space group	*Pbca*	*P*2(1)/*n*	*P*2(1)/*n*	*P*2(1)/*c*
a[Å]	16.4824(10)	20.3588(6)	21.8574(15)	21.8931(16)
b [Å]	11.9020(7)	17.5310(5)	12.0368(9)	12.5992(10)
c [Å]	45.221(3)	26.8606(8)	17.6400(13)	14.5756(11)
α [deg]	90	90	90	90
β [deg]	90	107.9010(10)	94.218(2)	105.640(2)
γ [deg]	90	90	90	90
V[Å^3]	8871.2(9)	9122.7(5)	4628.4(6)	3871.6(5)
Z	4	4	2	2
D_c [g cm^{-3}]	1.488	1.660	1.510	1.526
radiation used	Mo Kα	Mo Kα	Mo Kα	Mo Kα
μ [mm^{-1}]	2.278	4.326	2.189	2.596
θ range [deg]	1.53–27.50	1.57–27.50	1.87–27.50	1.88–27.50
no. of unique data	10199	20954	32347	26567
max., min. transmn	0.8042, 0.4943	0.5444, 0.1811	0.8443, 0.6445	0.9033, 0.4233
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0545$, $wR_2 = 0.1389$	$R_1 = 0.0513$, $wR_2 = 0.1217$	$R_1 = 0.0421$, $wR_2 = 0.1021$	$R_1 = 0.0385$, $wR_2 = 0.0891$
R indices (all data)	$R_1 = 0.0938$, $wR_2 = 0.1561$	$R_1 = 0.0910$, $wR_2 = 0.1354$	$R_1 = 0.0628$, $wR_2 = 0.1102$	$R_1 = 0.0581$, $wR_2 = 0.0977$
goodness-of-fit on F^2	1.032	0.995	1.041	1.17
peak/hole [e Å^{-3}]	0.847/–0.634	1.187/–0.736	1.594/–0.460	0.935/–0.524