Supplementary Material (ESI) for Chemical Communications

Supporting Information

Half-rotation in a [2]catenane via interconvertible Pd(II) coordination modes

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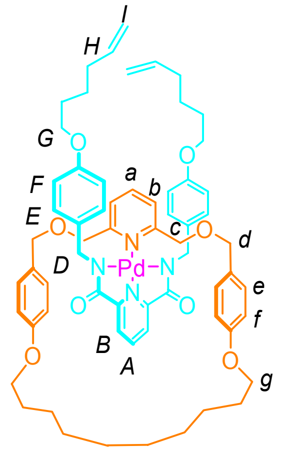
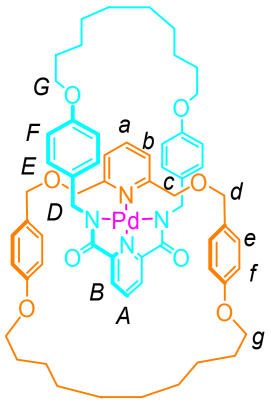
Unless stated otherwise, all reagents and anhydrous solvents were purchased from Aldrich Chemicals and used without further purification. All ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV 400 instrument, at a constant temperature of 25 °C. Chemical shifts are reported in parts per million from low to high field and referenced to TMS. Coupling constants (*J*) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: m = multiplet, br = broad, d = doublet, q = quadruplet, t = triplet, s = singlet. All melting points were determined using Sanyo Gallenkamp apparatus and are reported uncorrected. Compounds S**1**,[1] Pd**1**,[2] **1**H_2[2] and **2**[2] were prepared using literature procedures and showed identical spectroscopic characteristics to those described therein.



S1Pd**2**

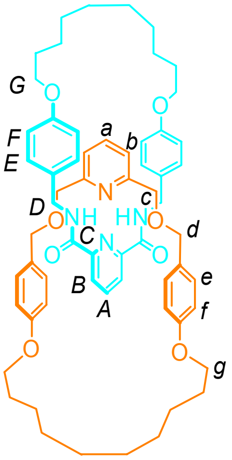
A solution of **2** (0.279 g, 5.70 x10^{-1} mmol) and **S1**Pd(CH_3CN) (0.392 g, 5.70 x10^{-1} mmol) in anhydrous dichloromethane (25 mL) was stirred for 1 h at room temperature. The resulting crude residue was purified by column chromatography (95:5 CH_2Cl_2:EtOAc) to yield **S1**Pd**2** as a yellow solid (0.478 g, yield = 74%). m.p. 58-60 °C; ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ = 1.19-1.48 (m, 12H, *alkyl*-H), 1.50-1.82 (m, 12H, *alkyl*-H), 2.13 (m, 4H, *alkyl*-H), 3.55 (s, 4H, H$_{D}$), 3.80-3.91 (m, 8H, H$_{G}$ +H$_{g}$), 4.18 (b, 4H, H$_{c}$), 4.39 (s, 4H, H$_{d}$), 5.00 (m, 4H, H$_{I}$), 5.86 (m, 2H, H$_{H}$), 6.21 (br, 4H, H$_{E}$), 6.41 (d, 8H, J = 8.0 Hz, H$_{F}$), 6.52 (d, 4H, J = 8.3 Hz, H$_{f}$), 7.07 (d, 4H, J = 8.3 Hz, H$_{e}$), 7.25 (d, 2H, J = 7.8 Hz, H$_{b}$), 7.71-7.78 (m, 3H, H$_{B+a}$), 8.11 (t, 1H, J = 7.8 Hz, H_{A}). ^{13}C NMR (100 MHz, CD_2Cl_2, 298 K): δ = 25.7, 26.0, 28.9, 29.0, 29.1, 29.9, 33.8, 48.5, 67.6, 68.1, 70.4, 73.1, 114.2, 114.4, 114.8, 123.5, 124.3, 128.6, 131.4, 133.6, 139.1, 139.3, 140.4, 153.0, 157.9, 158.2, 159.3, 159.8, 170.8; LRFAB-MS (3-NOBA matrix): m/z = 1135 $[M+1]^+$; HRFAB-MS (3-NOBA matrix): m/z = 1135.47843 (calcd. for $C_{64}H_{77}N_4O_8Pd$, 1135.47734).



Pd**1**

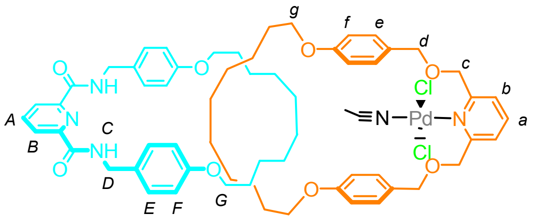
(i) A solution of **S1**Pd**2** (0.352 g, 3.10x10^{-1} mmol) in anhydrous dichloromethane (150 mL) was added via a double ended needle to a solution of first generation Grubbs catalyst (0.030 g, 3.6x10^{-2} mmol) in anhydrous dichloromethane (500 mL) under an atmosphere of nitrogen. The solution was stirred at room temperature for 18 h, concentrated *in vacuo* and the crude residue purified by column chromatography (96:4 CH_2Cl_2:EtOAc) to yield a yellow solid (0.34 g).

(ii) The yellow solid obtained from part (i) (0.34 g) was treated with 10% w/w Pd-C (0.050 g) over H_2 in THF (20 mL) to yield Pd**1** (0.268 g, 78% over 2 steps). m.p. 134-135 °C; ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ = 1.04-1.50 (m, 24H, *alkyl*-H), 1.60 (m, 4H, *alkyl*-H), 1.70 (m, 4H,*alkyl*-H), 3.60 (s, 4H, H_D), 3.81 (t, 4H, J = 6.3 Hz, H_G), 3.89 (t, 4H, J = 6.3 Hz, H_g), 4.36-4.42 (m, 8H, H_d+ H_c), 5.94 (d, 4H, J = 8.6 Hz, H_F), 6.10 (d, 4H, J = 8.6 Hz, H_E), 6.63 (d, 4H, J = 8.6 Hz, H_f), 7.05 (d, 2H, J = 7.8 Hz, H_b), 7.15 (d, 2H, J = 8.6 Hz, H_e), 7.60 (t, 1H, J = 7.8 Hz, H_a), 7.76 (d, 2H, J = 7.6 Hz, H_B), 8.13 (t, 1H, J = 7.6 Hz, H_A); ^{13}C NMR (100 MHz, CD_2Cl_2, 298 K): δ = 25.8, 26.0, 28.5, 28.7, 28.9, 29.2, 30.0, 30.1, 49.4, 67.1, 67.7, 69.6, 72.9, 114.5, 114.8, 121.2, 124.5, 128.2, 128.6, 131.7, 132.9, 138.8, 140.6, 153.1, 157.4, 159.5, 160.0, 171.1. LRFAB-MS (3-NOBA matrix): m/z = 1109 $[M+1]^+$; HRFAB-MS (3-NOBA matrix): m/z = 1109.46152 (calcd. for $C_{62}H_{75}N_4O_8$ Pd, 1109.46169).



1H_2

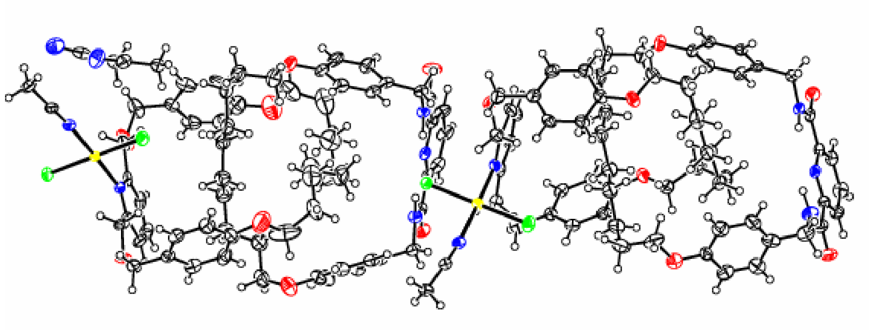
To a solution of Pd**1** (0.210 g, 1.90x10^{-1} mmol) in dichloromethane (10 mL) and methanol (10 mL) was added potassium cyanide (0.190 g, 2.92 mmol). in methanol (2 mL). The solution was stirred at room temperature for 1 h, until it was colorless, and then heated gently to reduce the overall volume to less than 5 mL. The resultant mixture was dispersed in water (25 mL) and washed with dichloromethane (3 x 25 mL). The combined organic extracts were washed with further water (25 mL) and dried over anhydrous magnesium sulfate. After filtration, the solution was concentrated *in vacuo* and the crude residue recrystallised from acetonitrile to give the title compound as a colorless solid (0.185 g, yield = 97%). m.p.125-126 °C; ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ = 1.22-1.55 (m, 24H, *alkyl*-H), 1.63-1.76 (m, 8H, *alkyl*-H), 3.75-2.89 (m, 12H, H_g + H_c + H_G), 4.02 (d, 2H, J = 6.3, H_D), 4.16 (s, 4H, H_d), 6.32-6.42 (m, 8H, H_f+ H_F), 6.48 (d, 4H, J = 8.6 Hz, H_E), 6.74 (d, 4H, J = 8.6 Hz, H_e), 6.85 (d, 2H, J = 7.8 Hz, H_b), 7.40 (t, 1H, J = 7.8 Hz, H_a), 7.91 (t, 1H, J = 7.8 Hz, H_A), 8.15 (d, 2H, J = 7.8 Hz, H_B), 9.01 (t, 2H, J = 6.3 Hz, H_C); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 25.6, 25.8, 28.3, 28.5, 28.6, 28.7, 29.2, 29.4, 42.2, 67.0, 67.1, 70.0, 72.6, 113.6, 114.1, 118.9, 124.1, 128.3, 128.8, 129.8, 130.4, 136.5, 137.3, 148.6, 157.3, 157.5, 158.4, 163.2; LRFAB-MS (3-NOBA matrix): m/z = 1006 $[M+1]^+$; HRFAB-MS (3-NOBA matrix): m/z = 1005.57494 (calcd. for $C_{62}H_{77}N_4O_8$, 1005.57414).



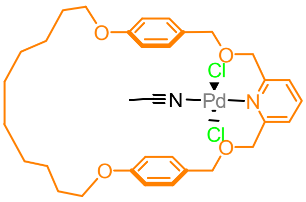
Pd(**1**H_2)Cl_2MeCN

To a solution of $PdCl_2.(CH_3CN)_2$ (0.015 g 0.057 mmol) in MeCN (5 mL) was added a solution of **1**H_2 (0.038 g, 0.038 mmol) dissolved in dichloromethane (5 mL) and the mixture stirred for 1 h. The crude residue was then concentrated *in vacuo* and recrystallized from acetonitrile to give the title product as orange plates (0.039 g, yield = 85%). m.p. 162-163 °C; ^{1}H NMR (400 MHz, 9:1 CD_2Cl_2:CD_3CN, 298 K): δ = 0.72-0.88 (m, 16H, alkyl-H), 1.01-1.24 (m, 12H, alkyl-H), 1.37-1.49 (m, 4H, alkyl-H), 1.94 (s, 3H, Pd-NCC$\underline{H}_3$), 3.15 (t, 4H, J = 6.8 Hz, H_g), 3.57 (t, 4H, J = 6.0 Hz, H_G), 4.08 (d, 4H, J = 6.3 Hz, H_D), 4.60 (s, 4H, H_d), 5.62 (s, 4H, H_c), 6.25 (d, 4H, J = 8.6 Hz, H_F), 6.41 (d, 4H, J = 8.6 Hz, H_E), 6.53 (d, 4H, J = 8.6 Hz, H_f), 7.13 (d, 4H, J = 8.6 Hz, H_e) 7.21 (d, 2H, J = 7.8 Hz, H_b), 7.48 (t, 1H, J = 7.8 Hz, H_a), 8.01 (t, 1H, J = 7.8 Hz, H_A), 8.25 (t, 2H, J = 6.3 Hz, H_C), 8.32 (d, 2H, J = Hz, 7.8 H_B); ^{13}C NMR (100 MHz, 9:1 CD_2Cl_2:CD_3CN, 298 K) δ = 0.5, 24.3, 24.5, 27.1, 27.2, 27.3, 27.5, 27.8, 28.2, 41.2, 65.7, 65.8, 70.3, 72.1, 113.3, 115.6, 120.6, 123.9, 128.2, 128.4, 128.7, 129.3 (x2), 137.7, 137.9, 148.2, 156.7, 157.3, 159.8, 162.0.

Ellipsoid plot of Pd(**1**H_2)Cl_2MeCN:



Single crystals of sufficient quality for X-Ray analysis were grown by slow cooling a saturated MeCN solution of Pd(**1**H_2)Cl_2MeCN. $C_{64}H_{79}Cl_2N_5O_8Pd.CH_3CN$, M = 1264.68, orange plate, crystal size 0.2×0.1×0.0.03 mm, triclinic, P-1, a = 9.8106(8), b = 25.305(2), c = 26.820(2) Å, α = 73.971(4), β = 82.771(6), γ = 88.050(6), V = 6348.3(9) $Å^3$, Z = 4, ρ_{calcd} = 1.323 Mg m^{-3}; $Mo_{K\alpha}$ radiation (confocal optic, λ = 0.71073 Å), μ = 0.435 mm^{-1}, T = 93(2) K. 40751 data (21993 unique, R_{int} =0.0258, 1.58<θ<25.35°), were collected on a Rigaku MM007/Mercury diffractometer and were corrected for absorption. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 values of all data (G. M. Sheldrick, SHELXTL, Bruker AXS Madison WI, USA, 2001, version 6.1) to give $wR = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ = 0.1351, conventional R = 0.0525 for F values of reflections with $F_o^2>2\sigma(F_o^2)$ [40751 observed reflections], S = 1.036 for 1516 parameters. Residual electron density extremes were 2.301 and -0.992 $eÅ^{-3}$.



Pd**2**Cl_2MeCN

To a solution of $PdCl_2.(CH_3CN)_2$ (0.039 g 0.15 mmol) in MeCN (5 mL) was added **2** (0.050 g, 0.10 mmol) in dichloromethane (5 mL) and the mixture stirred for 1 h. The crude residue was concentrated *in vacuo* and recrystallized from acetonitrile to give the title product as a pale orange solid (0.058 g, yield = 82%). m.p. 158 °C (decomp); ^{1}H NMR (400 MHz, 9:1 CD_2Cl_2:CD_3CN, 298 K): δ = 1.10-1.31 (m, 8H, alkyl-H), 1.55-1.67 (m, 8H, alkyl-H), 1.92 (s, 3H, Pd-NC$\underline{H_3}$), 3.83 (t, 4H, J = 6.6 Hz, H_g), , 4.68 (s, 4H, H_d), 5.62 (s, 4H, H_c) 6.69 (d, 4H, J = 8.6 Hz, H_f), 7.13 (d, 4H, J = 8.6 Hz, H_e) 7.21 (m, 6H, H_b + H_e), 7.46 (t, 1H, J = 7.8 Hz, H_a); ^{13}C NMR (100 MHz, 9:1 CD_2Cl_2:CD_3CN, 298 K) δ = 0.62, 24.5, 27.5 (x2), 28.1, 66.5, 70.5, 72.1, 113.5, 115.9, 120.8, 128.2, 129.4, 137.7, 157.9, 159.2.

Interconversion of catenane species:

1H_2→Pd**1**: To a stirred solution of **1**H_2 (0.050 g, 5.0x10^{-2} mmol) in anhydrous acetonitrile (10 mL) and dichloromethane (10 mL), palladium(II) acetate (0.011 g, 5.0x10^{-2} mmol) was added and the solution refluxed for 18 h under an atmosphere of nitrogen. The resulting precipitate was filtered, washed with acetonitrile (25 mL) and dried under suction to yield Pd**1** (0.044 g, 79%).

Pd**1**→Pd(**1**H_2)Cl_2MeCN: A solution of *ca.* 0.1 M HCl in $CDCl_3$ was added dropwise to a solution of Pd**1** (0.015 g, 1.4x10^{-2} mmol) in $CDCl_3$/CD_3CN until conversion to Pd(**1**H_2)Cl_2MeCN was complete as indicated by ^{1}H NMR spectroscopy. The resultant orange solution was filtered through a plug of $NaHCO_3$ and concentrated *in vacuo* to yield Pd(**1**H_2)Cl_2MeCN (0.012 g, 78%).

Pd(**1**H_2)Cl_2MeCN→Pd**1**: Sodium hydride (0.0018 g, 4.5x10^{-2} mmol) (60% dispersion in oil) was added to a solution of Pd(**1**H_2)Cl_2MeCN (0.018 g, 1.5 x10^{-2} mmol) in dry CH_3CN/CH_2Cl_2 (2 mL/1 mL) and the reaction mixture stirred for 20 minutes under an atmosphere of nitrogen. The crude solution was filtered, concentrated *in vacuo* and purified using column chromatography (99:1 CH_2Cl_2:MeOH) to yield Pd**1** (0.009 g, 54%).

Pd(**1**H_2)Cl_2MeCN→**1**H_2: To a solution of Pd(**1**H_2)Cl_2MeCN (0.015 g, $1.3x10^{-2}$ mmol) in dichloromethane (2 mL) and methanol (1 mL) was added potassium cyanide (0.01 g, $1.4x10^{-1}$ mmol) in methanol (0.5 mL). The solution was stirred at room temperature for 1 h, until it was colorless, and then heated gently to reduce the overall volume to less than 1 mL. The resultant mixture was dispersed in water (5 mL) and washed with dichloromethane (3 x 10 mL). The combined organic extracts were washed with further water (5 mL) and dried over anhydrous magnesium sulfate. After filtration, the solution was concentrated *in vacuo* and the crude residue recrystallised from acetonitrile to give **1**H_2 as a colorless solid (0.012 g, yield = 95%).

References

1 A.-M. Fuller, D. A. Leigh, P. J. Lusby, I. D. H. Oswald, S. Parsons and D. B. Walker, *Angew. Chem. Int. Ed*, 2004, **43**, 3914.

2 A.-M. L. Fuller, D. A. Leigh, P. J. Lusby, A. M. Z. Slawin, and D. B. Walker, submitted for publication.