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Supporting Information


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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 S1,\(^1\) Pd1,\(^2\) \(^1\)H\(^2\) and \(^2\) were prepared using literature procedures and showed identical spectroscopic characteristics to those described therein.

A solution of \(^2\) (0.279 g, 5.70 x10\(^{-1}\) mmol) and S1Pd(CH\(_3\)CN) (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\(_2\)Cl\(_2\):EtOAc) to yield S1Pd2
as a yellow solid (0.478 g, yield = 74%). m.p. 58-60 °C; $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 298 K):
$\delta$ = 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$_e$), 4.39 (s, 4H, H$_d$), 5.00 (m, 4H, H$_j$), 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$_j$), 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$_B$ + H$_a$), 8.11 (t, 1H, J = 7.8 Hz, H$_A$). $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$, 298 K): $\delta$ = 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$_6$H$_7$N$_7$O$_8$Pd, 1135.47734).

(i) A solution of S1Pd2 (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$_2$Cl$_2$: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 Pd1 (0.268 g, 78% over 2 steps). m.p. 134-135 °C; $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 298 K): $\delta$ = 1.04-1.50 (m, 24H, alkyl-H), 1.60 (m, 4H, alkyl-H), 1.70 (m,
To a solution of Pd1 (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; ¹H NMR (400 MHz, CD₂Cl₂, 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, H₉ + H₇ + H₈), 4.02 (d, 2H, J = 6.3, H₂), 4.16 (s, 4H, H₄), 4.36-4.42 (m, 8H, H₈ + H₆), 5.94 (d, 4H, J = 8.6 Hz, H₇), 6.10 (d, 4H, J = 8.6 Hz, H₈), 6.63 (d, 4H, J = 8.6 Hz, H₉), 7.05 (d, 2H, J = 7.8 Hz, H₆), 7.15 (d, 2H, J = 8.6 Hz, H₇), 7.60 (t, 1H, J = 7.8 Hz, H₃), 7.76 (d, 2H, J = 7.6 Hz, H₈), 8.13 (t, 1H, J = 7.6 Hz, H₄); ¹³C NMR (100 MHz, CD₂Cl₂, 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 (calcld. for C₆₂H₇₅N₄O₈ Pd, 1109.46169).
To a solution of PdCl$_2$(CH$_3$CN)$_2$ (0.015 g, 0.057 mmol) in MeCN (5 mL) was added a solution of 1H$_2$ (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$_2$Cl$_2$:CD$_3$CN, 298 K): $\delta$ = 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-NCCH$_3$), 3.15 (t, 4H, $J$ = 6.8 Hz, H$_g$), 3.57 (t, 4H, $J$ = 6.0 Hz, H$_c$), 4.08 (d, 4H, $J$ = 6.3 Hz, H$_d$), 4.60 (s, 4H, H$_d$), 5.62 (s, 4H, H$_b$), 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$_d$), 8.25 (t, 2H, $J$ = 6.3 Hz, H$_c$), 8.32 (d, 2H, $J$ = Hz, 7.8 Hz $H_b$); $^{13}$C NMR (100 MHz, 9:1 CD$_2$Cl$_2$:CD$_3$CN, 298 K) $\delta$ = 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(1H2)Cl2MeCN:

Single crystals of sufficient quality for X-Ray analysis were grown by slow cooling a saturated MeCN solution of Pd(1H2)Cl2MeCN. C64H79Cl2N5O8Pd.CH3CN, M = 1264.68, orange plate, crystal size 0.2×0.1×0.03 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) Å3, Z = 4, ρ calc = 1.323 Mg m-3; MoKα radiation (confocal optic, λ = 0.71073 Å), μ = 0.435 mm-1, T = 93(2) K. 40751 data (21993 unique, Rint =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 F2 values of all data (G. M. Sheldrick, SHELXTL, Bruker AXS Madison WI, USA, 2001, version 6.1) to give wR = {Σ[w(Fo2−Fc2)2]/Σ[w(Fo2)2]}1/2 = 0.1351, conventional R = 0.0525 for F values of reflections with Fo2>2σ(Fo2) [40751 observed reflections], S = 1.036 for 1516 parameters. Residual electron density extremes were 2.301 and -0.992 eÅ-3.

Pd2Cl2MeCN

To a solution of PdCl2(CH3CN)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); \textsuperscript{1}H NMR (400 MHz, 9:1 CD\textsubscript{2}Cl\textsubscript{2}:CD\textsubscript{3}CN, 298 K): \(\delta = 1.10-1.31\) (m, 8H, alkyl-H), 1.55-1.67 (m, 8H, alkyl-H), 1.92 (s, 3H, Pd-NCC\textsubscript{3}H\textsubscript{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, \(H_a\)); \textsuperscript{13}C NMR (100 MHz, 9:1 CD\textsubscript{2}Cl\textsubscript{2}:CD\textsubscript{3}CN, 298 K) \(\delta = 0.62, 24.5, 27.5\) (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:

\textbf{1H\textsubscript{2}}\textrightarrow PdI: To a stirred solution of \textbf{1H\textsubscript{2}} (0.050 g, 5.0x10\textsuperscript{-2} mmol) in anhydrous acetonitrile (10 mL) and dichloromethane (10 mL), palladium(II) acetate (0.011 g, 5.0x10\textsuperscript{-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 PdI (0.044 g, 79%).

PdI\textrightarrow Pd(1H\textsubscript{2})Cl\textsubscript{2}MeCN: A solution of \textit{ca.} 0.1 M HCl in CDCl\textsubscript{3} was added dropwise to a solution of PdI (0.015 g, 1.4x10\textsuperscript{-2} mmol) in CDCl\textsubscript{3}/CD\textsubscript{3}CN until conversion to Pd(1H\textsubscript{2})Cl\textsubscript{2}MeCN was complete as indicated by \textsuperscript{1}H NMR spectroscopy. The resultant orange solution was filtered through a plug of NaHCO\textsubscript{3} and concentrated \textit{in vacuo} to yield Pd(1H\textsubscript{2})Cl\textsubscript{2}MeCN (0.012 g, 78%).

Pd(1H\textsubscript{2})Cl\textsubscript{2}MeCN\textrightarrow PdI: Sodium hydride (0.0018 g, 4.5x10\textsuperscript{-2} mmol) (60% dispersion in oil) was added to a solution of Pd(1H\textsubscript{2})Cl\textsubscript{2}MeCN (0.018 g, 1.5 x10\textsuperscript{-2} mmol) in dry CH\textsubscript{3}CN/CH\textsubscript{2}Cl\textsubscript{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$_2$Cl$_2$:MeOH) to yield Pd$^1$ (0.009 g, 54%).

Pd(1H$_2$)Cl$_2$MeCN$\rightarrow$1H$_2$: To a solution of Pd(1H$_2$)Cl$_2$MeCN (0.015 g, 1.3x10$^{-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 1H$_2$ as a colorless solid (0.012 g, yield = 95%).

References
