Supporting Information

Molecular Architecture via Coordination: Self-Assembly of Pseudo Hexagonal Macrocycles

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General Comments. The ^{1}H NMR spectra were recorded at 300 MHz, and chemical shifts are reported relative to internal TMS δ 0.0 ppm or to the signal of a residual protonated solvent: $CDCl_3$ δ 7.27, d_6-acetone δ 2.05 or CD_2Cl_2 δ 5.32 ppm. The $^{13}C\{^{1}H\}$ NMR spectra were recorded at 75 MHz, and chemical shifts are reported relative to $CDCl_3$ δ 77.2, d_6-acetone δ 29.9 ppm or CD_2Cl_2 δ 54.0 ppm. The $^{31}P\{^{1}H\}$ NMR spectra were recorded at 121 MHz, and chemical shifts are reported relative to external 85% aqueous H_3PO_4 δ 0.0 ppm. The signals in the ^{1}H NMR due to water are omitted. Elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA. Melting points were obtained with a Mel-Temp capillary melting point apparatus and were not corrected. Electrospray mass spectra were obtained with a Micromass Quatro II with ionization performed under electrospray conditions (flow rate: 7.7 μL/min, capillary voltage: 3.0 kV, cone: 57 V, Extractor: 16 V). About 15 individual scans were averaged for the mass spectrum. The calibration of the mass range 500-4000 amu was done with a 1:1 mixture of an isopropanol:water solution of NaI (2μg/μL) and CsI (0.01μg/μL). Samples were prepared as 0.02 mmol/L solutions in a 1:1 acetone:methylene chloride solution just prior to the analysis.

Materials. Commercial reagents, trimethylsilylacetylene, 1,3,5-tribromobenzene, and 2,6-dibromopyridine were ACS reagent grade or higher and were used without further purification. Methylene chloride was purified according to literature procedure[1] and distilled over CaH_2. Diethyl ether was purified according to literature procedure[1] and distilled over Na/benzophenone. Deuterated solvents used for spectroscopic measurements were spectrophotometric grade. 4,4'-Diiodobenzophenone and di(4-pyridyl)ketone[2] (**7**), bis(triethylphosphine)platinum(II) diiodide[3], and tetrakis(triethylphoshine)platinum(0)[4] were prepared according to literature methods.

4,4'-Bis(*trans*-Pt(PEt_3)$_2$I)benzophenone (1). A 3-neck 25 mL round bottom flask was charged with 4,4'-diiodobenzophenone (47.3 mg, 0.11 mmol) and $Pt(PEt_3)_4$ (160.1 mg, 0.24 mmol) and dissolved in toluene (10 mL). The reaction mixture was allowed to stir at 60ºC overnight. The volume of the reaction mixture was reduced to 3ml and 10 ml of hexanes were added. The white precipitate was washed several times (3 x 15 mL) with hexanes and dried under vacuum to affording a white microcrystalline solid (72.7 mg, 51%): mp 240ºC (dec.); IR (neat) 2963 (Ar), 1638 (CO), 1573, 1452 (Ar ring stretch), 1034 (In-plane C-H bend), 763 (Out-of-plane C-H bend) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.49 (d, 4H, $^3J_{H\text{-}H}$=8.1 Hz, Pt-H$_o$), 7.42 (d, 4H, $^3J_{H\text{-}H}$=8.3 Hz, Pt-H$_m$), 1.86-1.74 (m, 24H, PCH_2), 1.06 (t, 36H, $^3J_{H\text{-}H}$=8.0 Hz, $^3J_{P\text{-}H}$=31.7 Hz, $PCH_2\mathit{CH_3}$); ^{13}C {^{1}H} NMR ($CDCl_3$) δ 197.7 (s, CO), 154.6 (s, $J_{Pt\text{-}C}$=945 Hz, Pt-C$_{ipso}$), 136.7 (s, $^3J_{Pt\text{-}C}$=38 Hz, Pt-C$_m$), 132.4 (s, Pt-C$_p$), 129.4 (s, $^2J_{Pt\text{-}C}$=77 Hz, Pt-C$_o$), 15.5 (t, $J_{P\text{-}C}$=34 Hz, PCH_2), 8.1 (s, PCH_2 $\mathit{CH_3}$); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 11.5 (s, $J_{P\text{-}Pt}$ =2691 Hz); FAB LRMS, *m/z* 1297 ([M+H]$^+$).

4,4'-Bis(*trans*-Pt(PEt_3)$_2$(OTf))benzophenone (2). A 3-neck flask was charged with 4,4'-bis(*trans*-Pt(PEt_3)$_2$I)benzophenone (101 mg, 0.084 mmol) under nitrogen and dissolved in 13 mL CH_2Cl_2. The reaction was then cooled to 0ºC with an ice bath and AgOTf (47.5 mg, 0.185 mmol) was added. The reaction was allowed to stir for 3h and the AgI precipitate was filtered off. The solvent volume was reduced to 4 ml and the product precipitated with 15 ml of hexanes. The compound was isolated as a white powder in 82% yield. (92.4 mg): mp 184-186ºC (dec.); IR (thin film) 2970 (Ar C-H), 2877 (Aliphatic C-H), 1638 (CO), 1576, 1457 (Ar ring stretch), 1291, 1233 (OTf), 1031 (In-plane C-H bend), 761 (Out-of-plane C-H bend) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.45 (d, 4H, J_{H-H}=8.6 Hz, Pt-H_o), 7.31 (d, 4H, J_{H-H}=8.3 Hz, Pt-H_m), 1.71-1.61 (m, 24H, P-CH_2), 1.18-1.08 (m, 36H, P-CH_2CH_3); ^{13}C {^1H} NMR (CD_2Cl_2) δ 196.7 (s, CO), 136.4 (s, Pt-C_m), 133.8 (t, J_{P-C}=10 Hz, Pt-C_{ipso}), 133.2 (s, Pt-C_p), 129.6 (s, Pt-C_o), 120.1 (q, J_{C-F}=321 Hz, OTf), 14.2 (t, J_{P-C}=16 Hz, PCH_2), 8.0 (s, PCH_2 CH_3); ^{31}P{^1H} NMR (CD_2Cl_2) δ 21.9 (s, J_{P-Pt} =2798 Hz); ^{19}F {^1H} NMR (CD_2Cl_2) δ -76; FAB LRMS, *m/z* 1341 ($[M+H]^+$).

3,5-Bis[*trans*-Pt(PEt_3)$_2$I(ethynyl)]bromobenzene (3). To a 100 ml round-bottom Schlenk flask were added trans-diiodobis(triethylphosphine)platinum(II) (2.060 g, 3.01 mmol) and 3,5-bis(ethynyl)bromobenzene (153 mg, 0.75 mmol). Then, 30 ml of toluene and 20 ml of dry diethylamine were added under nitrogen. The solution was stirred for 10 min at room temperature, and 20 mg (0.11 mmol) of cuprous iodide was added in one portion. After 3 h at room temperature, a small amount of diethylammonium started to precipitate out of solution. The solvents were then removed in vacuo, and the remaining yellow residue was separated by column chromatography on silica gel. The first fraction containing excess trans-diiodobis(triethylphosphine)platinum(II) was recovered almost quantitatively by elution with

hexanes/benzene 3:1. The second fraction with benzene as eluent gave the product **2** as slightly yellow crystals after recrystallization from dichloromethane. Yield: 712 mg (72%); mp 287-290 (dec); ^{1}H NMR (CD_2Cl_2) δ 7.21 (d, 2H, $^4J_{H\text{-}H}$=1.78 Hz, Br-H$_o$), 7.10 (t, 1H, $^4J_{H\text{-}H}$=1.78 Hz, Br-H$_p$), 2.21 (m, 24H, PCH_2), 1.18 (pq, 36H, PCH_2CH_3); ^{13}C NMR (CD_2Cl_2) δ 132.0 (s, Br-C$_{ipso}$), 130.7 (s, Br-C$_o$), 130.6 (s, Br-C$_p$), 122.0 (s, Br-C$_m$), 99.1 (s, PtC*C*), 93.0 (m, Pt*C*), 17.1 (pq, PCH_2), 8.6 (pt, PCH_2CH_3); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 11.6 (s, $J_{P\text{-}Pt}$ =2310 Hz); Anal. Calcd for $C_{34}H_{63}BrI_2P_4Pt_2$: C, 30.95; H, 4.81. Found: C, 31.58; H, 4.85.

2,6-Bis[*trans*-Pt(PEt$_3$)$_2$I(ethynyl)]pyridine (4). To a 100 ml round-bottom Schlenk flask were added trans-diiodobis(triethylphosphine)platinum(II) (1.820 g, 2.66 mmol) and 2,6-bis(ethynyl)pyridine (82 mg, 0.65 mmol). The compounds were dissolved in 30 ml of toluene and 20 ml of dry diethylamine under nitrogen. The solution was stirred for 10 min at room temperature, and 18 mg (0.10 mmol) of cuprous iodide was added in one portion. After 4 h at room temperature, the solvents were removed in vacuum, and the remaining yellow residue was separated by column chromatography on silica gel. The first fraction containing excess trans-diiodobis(triethylphosphine)platinum(II) was recovered almost quantitatively by elution with hexanes/benzene 3:1. The second fraction with benzene as eluent gave the product **3** as yellow crystals after recrystallization from dichloromethane. Yield: 516 mg (64%); mp 254-260 (dec); ^{1}H NMR ($CDCl_3$) δ 7.32 (t, 1H, $^3J_{H\text{-}H}$=9.0 Hz, H_), 6.96 (d, 2H, $^3J_{H\text{-}H}$=9.0 Hz, H_), 2.42 (m, 24H, PCH_2), 1.13 (pq, 36H, PCH_2CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 147.0 (s, C_), 135.0 (s, C_), 122.7 (s, C_), 101.5 (s, PtC*C*), 91.1 (s, Pt*C*), 16.6 (pq, PCH_2), 8.3 (pt, PCH_2CH_3); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 12.2 (s, $J_{P\text{-}Pt}$ =2312 Hz); Anal. Calcd for $C_{33}H_{63}I_2NP_4Pt_2$: C, 31.92; H, 5.11; N, 1.13. Found: C, 31.92; H, 5.06; N, 1.22.

3,5-Bis[*trans*-Pt(PEt_3)$_2$(OTf)(ethynyl)]bromobenzene (5). A 50 ml round bottom Schlenk flask was charged with 186 mg (0.146 mmol) of **2** and 15 ml of dichloromethane. To the solution, 83 mg (0.322 mmol) of AgOTf were added at once, resulting in a yellowish precipitate of AgI. After 2h at room temperature the suspension was filtered through a glass fiber filter and the volume of the solution reduced to 5 ml. Subsequent addition of diethylether resulted in the precipitation of the bistriflate salt **4** as a slightly yellow crystalline powder. Yield 189 mg (95%); mp 245-254ºC (dec.); ^{1}H NMR (CD_2Cl_2) δ 7.20 (d, 2H, $^4J_{H\text{-}H}$=1.78 Hz, Br-H$_o$), 7.10 (t, 1H, $^4J_{H\text{-}H}$=1.78 Hz, Br-H$_p$), 2.02 (m, 24H, PCH_2), 1.16 (pq, 36H, PCH_2CH_3); ^{13}C NMR (CD_2Cl_2) δ 131.2 (s, Br-C$_{ipso}$), 130.8 (s, Br-C$_o$), 129.2 (s, Br-C$_p$), 122.2 (s, Br-C$_m$), 97.1 (s, PtC*C*), 89.0 (m, Pt*C*), 15.4 (pq, PCH_2), 8.7 (pt, PCH_2CH_3); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 25.2 (s, $J_{P\text{-}Pt}$ =2310 Hz); Anal. Calcd for $C_{36}H_{63}BrO_6F_6S_2P_4Pt_2$: C, 31.70; H, 4.66; S, 4.70. Found: C, 31.78; H, 4.69; S, 4.57.

2,6-Bis[*trans*-Pt(PEt_3)$_2$(OTf)(ethynyl)]pyridine (6). 125.6 mg (0.101 mmol) of **2** were dissolved in 15 ml of dichloromethane in a 50 ml round bottom Schlenk flask under nitrogen. Then, 65.1 mg (0.254 mmol) of AgOTf were added at once, resulting in a yellowish precipitate of AgI. After 1h at room temperature the suspension was filtered through a glass fiber filter and the volume of the solution reduced to 5 ml. Subsequent addition of diethylether resulted in the precipitation of the bistriflate salt **4** as a yellow crystalline powder. Yield 109 mg (84%); mp 210ºC (dec.); ^{1}H NMR (CD_2Cl_2) δ 7.41 (t, 1H, $^3J_{H\text{-}H}$=7.8 Hz, H_), 6.93 (d, 2H, $^3J_{H\text{-}H}$=7.8 Hz, H_), 2.09 (m, 24H, PCH_2), 1.24 (pq, 36H, PCH_2CH_3); ^{13}C NMR (CD_2Cl_2) δ 146.6 (s, C_), 135.7 (d, $^1J_{C\text{-}H}$=30.4 Hz, C_), 123.9 (d, $^1J_{C\text{-}H}$=33.7 Hz, C_), 119.5 (q, $^1J_{C\text{-}F}$=349.3 Hz, CF_3), 103.9 (s,

PtC*C*), 64.7 (m, Pt*C*), 15.8 (m, PCH_2), 8.7 (m, PCH_2CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 25.3 (s, $J_{P\text{-}Pt}$ =2366 Hz);

Cyclotris[[di(4-pyridyl)ketone][4,4'-bis(trans-Pt(PEt_3)$_2$(OTf))benzophenone]] (8). To a solution of corner unit **2** (3.3 mg, 0.018 mmol) in 0.6 ml of CD_2Cl_2, di(4-pyridyl)ketone (**7**) (24.1 mg, 0.018 mmol) was added at 25ºC and agitated for 15 min. The solvent was removed *in vacuo* leaving an off-white, transparent, solid film (26.1 mg, 95%): mp 260ºC - 300ºC (dec.).; IR (CD_2Cl_2, thin film) 3060 (Aromatic C-H stretch), 2963 (C-H stretch), 1686 (CO_{pyr}), 1645 (Pt-CO), 1577, 1456, 1416 (Aromatic ring stretch), 1275, 1155, 1030 (OTf), 857 (CH_2 rock), 640 (Out of plane aromatic ring bend) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 9.02 (d, 12H, $^3J_{H\text{-}H}$=5.9 Hz, $H_{\alpha pyr}$), 8.25 (d, 12H, $^3J_{H\text{-}H}$=6.1 Hz, $H_{\beta pyr}$), 7.58 (d, 12H, $^3J_{H\text{-}H}$=8.3 Hz, Pt-H_o), 7.52 (d, 12H, $^3J_{H\text{-}H}$=8.1 Hz, Pt-H_m), 1.38 (m, 72H, P-CH_2), 1.16 (m, 108H, P-CH_2CH_3); ^{13}C $\{^1H\}$ NMR (CD_2Cl_2) δ 196.7 (s, Pt-CO), 190.8 (s, CO_{pyr}), 153.9 (s, $C_{\alpha pyr}$), 143.6 (s, $C_{\gamma pyr}$), 141.7 (m, Pt-C_i), 136.4 (s, Pt-C_o), 134.0 (s, Pt-C_p), 130.0 (s, Pt-C_m), 128.0 (s, $C_{\beta pyr}$), 121.5 (q, $J_{C\text{-}F}$=322 Hz, C_{OTF}), 13.0 (t, $J_{C\text{-}P}$=17 Hz, P-CH_2), 8.0 (s, P-CH_2CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 15.3 (s, $J_{P\text{-}Pt}$ =2640 Hz); ^{19}F $\{^1H\}$ NMR (CD_2Cl_2) δ -77. Anal. Calcd for $C_{150}H_{228}F_{18}N_6O_{24}P_{12}Pt_6S_6$: C, 39.37; H, 5.02; N, 1.84; S, 4.20. Found: C, 38.91; H, 5.03; N, 1.78; S, 4.13; MS (ES) *m/z* 3086 [M-**2**-OTf]$^+$ calcd 3086, 2140 [M-2OTf]$^{2+}$ calcd. 2140, 1560 [M-2**2**-**7**-OTf]$^+$ calcd. 1559, 1376 [M-3OTf]$^{3+}$ calcd. 1376, 1191 [**2**-OTf]$^+$ calcd. 1191, 995 [M-4OTf]$^{4+}$ calcd. 994, 521 [**2**-2OTf]$^{2+}$ calcd. 521.

Cyclotris[[di(4-pyridyl)ketone][3,5-bis[*trans*-Pt(PEt_3)$_2$(OTf)(ethynyl)]bromobenzene]] (9). To 81.9 mg (0.06 mmol) of **5** in 5 ml of methylene chloride was slowly added a solution of 11.1 mg (0.06 mmol) of di(pyridyl)ketone (**7**) in 4 ml of methylene chloride under nitrogen. The reaction mixture was stirred for 2h and the product precipitated with 5 ml of diethylether.

Isolation of the precipitate gave 90.2 mg (0.058 mmol) of **8** as a slightly yellow microcrystalline powder. Yield 97%; mp 272 - 296ºC (dec.).; IR (CD_2Cl_2, thin film) 3055 (Aromatic C-H stretch), 2975 (C-H stretch), 1679 (CO), 1577, 1466, 1421 (Aromatic ring stretch), 1277, 1161, 1030 (OTf); ^{1}H NMR (CD_2Cl_2) δ 8.91 (d, 12H, $^3J_{H\text{-}H}$=6.6 Hz, $H_{\alpha pyr}$), 8.20 (d, 12H, $^3J_{H\text{-}H}$=6.6 Hz, $H_{\beta pyr}$), 7.25 (d, 6H, $J_{H\text{-}H}$=1.2 Hz, Br-H_o), 7.07 (ps, 3H, Br-H_p), 1.82 (m, 72H, P-CH_2), 1.19 (pq, 108H, P-CH_2*CH_3*); ^{13}C {^{1}H} NMR (CD_2Cl_2) δ 190.4 (s, CO), 154.1 (s, $C_{\alpha pyr}$), 143.6 (s, $C_{\gamma pyr}$), 132.6 (s, Br-C), 132.1 (s, $C_{aromatic}$), 129.1 (s, $C_{aromatic}$), 128.3 (s, $C_{\beta pyr}$), 122.0 (s, $C_{aromatic}$), 121.4 (q, $J_{C\text{-}F}$=352.6 Hz, C_{OTF}), 105.5 (s, PtC*C*), 78.0 (s, Pt-C), 14.6 (pt, P-CH_2), 8.2 (s, P-CH_2*CH_3*); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 18.2 (s, $J_{P\text{-}Pt}$ =2291 Hz); ^{19}F {^{1}H} NMR (CD_2Cl_2) δ -79. Anal. Calcd for $C_{141}H_{213}Br_3F_{18}N_6O_{21}P_{12}Pt_6S_6$: C, 36.46; H, 4.62; N, 1.81; S, 4.14. Found: C, 36.47; H, 4.66; N, 2.24; S, 4.08; MS (ES) *m/z* 3131 [M-**5**-OTf]$^+$ calcd 3128, 2946 [M-**5**-**7**-OTf]$^+$ calcd. 2944, 2173 [M-2OTf]$^{2+}$ calcd. 2174, 1583 [M-2**5**-**7**-OTf]$^+$ calcd. 1581, 1400 [M-3OTf]$^{3+}$ calcd. 1399, 1215 [**5**-OTf]$^+$ calcd. 1215, 1012 [M-4OTf]$^{4+}$ calcd. 1013, 717 [M-2**5**-**7**-2OTf]$^{2+}$ calcd. 716.

Cyclotris[[di(4-pyridyl)ketone][2,6-bis[*trans*-Pt(PEt_3)$_2$(OTf)(ethynyl)]pyridine]] (10). To a solution of **6** (115.5 mg, 0.09 mmol) in 5 ml of methylene chloride was slowly added a solution of di(4-pyridyl)ketone (**7**) (16.5 mg, 0.09 mmol) in 3 ml of methylene chloride over a period of 10 min. After 10 min, the product was precipitated with diethylether and isolated as a yellow powder. Yield 129 mg (98%); mp 284ºC - 296ºC (decomposes).; IR (CD_2Cl_2, thin film) 3051 (Aromatic C-H stretch), 2988 (C-H stretch), 1676 (CO), 1586, 1474, (Aromatic ring stretch), 1277, 1155, 1032 (OTf); ^{1}H NMR (CD_2Cl_2) δ 8.93 (d, 12H, $^3J_{H\text{-}H}$=6.3 Hz, $H_{\alpha pyr}$), 8.22 (d, 12H, $^3J_{H\text{-}H}$=6.3 Hz, $H_{\beta pyr}$), 7.50 (t, 3H, $^3J_{H\text{-}H}$=7.8 Hz, Pt-$H_{\_pyr}$), 7.06 (d, 6H, $^3J_{H\text{-}H}$=7.8 Hz, Pt-$H_{\_pyr}$), 1.88 (m, 72H, P-CH_2), 1.21 (pq, 108H, P-CH_2*CH_3*); ^{13}C {^{1}H} NMR (CD_2Cl_2) δ 190.1 (s, CO),

153.1 (s, $C_{\alpha pyr}$), 147.1 (s, C_{ortho}), 143.9 (s, $C_{\gamma pyr}$), 134.4 (s, C_{para}), 129.1 (s, $C_{\beta pyr}$), 127.5 (s, C_{meta}), 121.2 (q, $J_{C\text{-}F}$=353.3 Hz, C_{OTF}), 104.1 (s, PtC*C*), 80.1 (s, Pt-C), 15.2 (pt, P-CH_2), 9.3 (s, P-CH_2*CH_3*); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 18.8 (s, $J_{P\text{-}Pt}$ =2284 Hz); ^{19}F $\{^1H\}$ NMR (CD_2Cl_2) δ -79. Anal. Calcd for $C_{138}H_{213}F_{18}N_9O_{21}P_{12}Pt_6S_6 \cdot 6H_2O$: C, 36.68; H, 5.01; N, 2.79; Found: C, 36.53; H, 4.91; N, 2.82; MS (ES) *m/z* 2976 [M-**6**-OTf]$^+$ calcd 2973, 2791 [M-**6**-**7**-OTf]$^+$ calcd. 2789, 2056 [M-2OTf]$^{2+}$ calcd. 2057, 1964 [M-**7**-2OTf]$^{2+}$ calcd. 1963, 1413 [M-**6**-2OTf]**2+** calcd. 1412, 1320 [M-3OTf]$^{3+}$ calcd. 1320, 1137 [**6**-OTf]$^+$ calcd. 1136, 678 [M-2**6**-**7**-2OTf]$^{2+}$ calcd. 678.

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