Supplementary Material (ESI) for Chemical Communications

Template-controlled synthesis of a planar [16]ane-$P_2C^{NHC}_2$ macrocycle

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Supplementary Information

General: All preparations were carried out under an argon atmosphere using conventional Schlenk techniques. Methanol was dried over CaH_2 under argon and was freshly distilled prior to use. Dry DMF and phenyldivinylphosphine (PVP) were purchased from Aldrich. Complexes $[Pt(PMe_3)_4]Cl_2$,[1] $[Pt(PMe_2Ph)_4](PF_6)_2$,[2] $[Pt(PMe_2Ph)_4](PF_6)_2$[2] and 2-azidoethyl isocyanide[3] were prepared following published procedures. NMR spectra were recorded with a Bruker Avance I 400 NMR spectrometer. IR spectra were measured with a Bruker Vector 22 spectrometer. Electrospray mass spectra were obtained with a Bruker Daltonics Micro Tof (ESI-MS) spectrometer.

General procedure for the preparation of compounds $\mathbf{6}(Cl)_2$–$\mathbf{6}(PF_6)_2$: A sample of a platinum tetraphosphine complex $[Pt(PR_3)_4]X_2$ was dissolved in methanol. The appropriate amount of 2-azidoethyl isocyanide in methanol was slowly added via a dropping funnel over the period of 6 h. After complete addition the solution was stirred at ambient temperature for 4 h. The volume of the solution was reduced to about 7 mL and Et_2O (20 mL) was added. This mixture was cooled to –20 °C for 24 h after which the complexes $\mathbf{6}(Cl)_2$–$\mathbf{6}(PF_6)_2$ crystallized and were collected by filtration. The platinum dicarbene complexes are white solids which are stable in air.

6a$(Cl)_2$: Synthesized from 258 mg (0.45 mmol, 1.0 eq) of $[Pt(PMe_3)_4]Cl_2$ dissolved in 20 mL of methanol and 96 mg (0.99 mmol, 2.2 eq) of **3** dissolved in 40 mL of methanol. Yield: 164 mg (0.29 mmol, 65%). ^{1}H (400 MHz, CD_3OD): δ = 4.86 (s br, 4H, NH), 3.72 (s, 8H, CH_2), 1.58 (t, $^2J_{P,H}$ = 4.1 Hz, Pt satellites $^3J_{Pt,H}$ = 31.6 Hz, PMe_3); $^{13}C\{^1H\}$ (100 MHz, CD_3OD): δ = 191.8 (t, $^2J_{P,C}$ = 10.6 Hz, NCN), 45.4 (s, Pt satellites $^3J_{Pt,C}$ = 36.8 Hz, CH_2), 14.1 (t, $^1J_{P,C}$ = 20.0 Hz, PMe_3); $^{31}P\{^1H\}$ (162 MHz, CD_3OD): δ = –19.7 (s, Pt satellites $^1J_{Pt,P}$ = 2262 Hz, PMe_3); MS (ESI): *m/z* (%) 486 (24, [**6a**–H]$^+$), 243 (100, [**6a**]$^{2+}$).

6b$(PF_6)_2$: Synthesized from 1.24 g (1.19 mmol, 1.0 eq) of $[Pt(PMe_2Ph)_4](PF_6)_2$ dissolved in 70 mL of methanol and 0.24 g (2.50 mmol, 2.1 eq) of **3** dissolved in 50 mL of methanol. Yield: 752 mg (0.83 mmol, 70%). ^{1}H (400 MHz, DMSO-d_6): δ = 8.56 (s br, 4H, Ph), 7.55–7.47 (m, 6H, Ph), 3.38 (s br, 4H, NH), 3.20 (s, 8H, CH_2), 1.91–1.75 (m, 12H, PMe_2); $^{13}C\{^1H\}$ (100 MHz, DMSO-d_6): δ = 188.8 (t, $^2J_{P,C}$ = 10.6 Hz, NCN), 131.5 (t, $^1J_{P,C}$ = 29.4 Hz, PPh), 130.7, 130.5 (t, $^2J_{P,C}$ = 5.8 Hz, PPh), 128.5 (t, $^3J_{P,C}$ = 5.3 Hz, PPh), 43.6 (s, CH_2), 12.2 (t, $^1J_{P,C}$ = 19.6 Hz, PMe_2); $^{31}P\{^1H\}$ (162 MHz, DMSO-d_6): δ = –10.0 (s, Pt satellites $^1J_{Pt,P}$ = 2311 Hz, PMe_2Ph), –144.2 (sept, PF_6); MS (ESI): *m/z* (%) 756 (13, [**6b**+PF_6]$^+$), 610 (5, [**6b**–H]$^+$), 305 (100, [**6b**]$^{2+}$).

6c$(PF_6)_2$: Synthesized from 400 mg (0.31 mmol, 1.0 eq) of $[Pt(PMePh_2)_4](PF_6)_2$ dissolved in 60 mL of methanol and 63 mg (0.65 mmol, 2.1 eq) of **3** dissolved in 60 mL of methanol. Yield: 236 mg (0.23 mmol, 74%). ^{1}H (400 MHz, DMSO-d_6): δ = 8.54 (s br, 4H, Ph), 7.57–7.46 (m, 16H, Ph), 3.37 (s br, 4H, NH), 2.69 (s, 8H, CH_2), 2.42–2.25 (m, 6H, PMe); $^{13}C\{^1H\}$ (100 MHz, DMSO-d_6): δ = 189.2 (t, $^2J_{P,C}$ = 10.3 Hz, NCN), 132.2 (t, $^2J_{P,C}$ = 6.2 Hz, PPh_2), 131.4 (m, PPh_2), 130.9 (PPh_2), 128.4 (t, $^2J_{P,C}$ = 5.3 Hz, PPh_2), 43.3 (s, Pt satellites $^3J_{Pt,C}$ = 32.2 Hz, CH_2), 11.1 (t, $^1J_{P,C}$ = 19.2 Hz, PMe); $^{31}P\{^1H\}$ (162 MHz, DMSO-d_6): δ = –0.07 (s, Pt satellites $^1J_{Pt,P}$ = 2510 Hz, $PMePh_2$), –144.2 (sept, PF_6); MS (ESI): *m/z* (%) 880 (7, [**6c**+PF_6]$^+$), 734 (3, [**6c**–H]$^+$), 367 (100, [**6c**]$^{2+}$).

1$(PF_6)_2$: A solution of 100 mg (0.11 mmol, 1.0 eq) of **6b**$(PF_6)_2$ and 72 mg (0.44 mmol, 4

eq) of phenyldivinylphosphine in 5 mL of DMF were heated to 85 °C for 2 d in a Schlenck tube fitted with a bubbler. Subsequently, the DMF was removed at 40 °C under reduced pressure and the resulting solid was suspended in 5 mL of MeOH (sonic bath). Compound **1**$(PF_6)_2$ was isolated by filtration and dried under reduced pressure. The solid obtained was washed one more time with MeOH and again dried under reduced pressure. Compound **1**$(PF_6)_2$ can also be obtained from **6c**$(PF_6)_2$ under similar conditions at a reaction temperature of 70 °C, but the lower boiling point of PMe_2Ph makes the isolation of **1**$(PF_6)_2$ starting from **6b**$(PF_6)_2$ easier. Yield: 95 mg (0.99 mmol, 90%) starting from **6c**$(PF_6)_2$. ^{1}H (400 MHz, DMSO-d_6): δ = 7.97–7.52 (m, 10H, Ph), 4.02–3.81 (m, 4H, NC*H*HC*H*HN), 3.97–3.62 (m, 8H, NCH_2CH_2P), 3.75–3.55 (m, 4H, NCH*H*CH*H*N), 3.21–2.97 (m, 4H, NCH$_2$C*H*HP), 2.67–2.45 (m, 4H, NCH$_2$CH*H*P); ^{13}C{^{1}H} (100 MHz, DMSO-d_6): δ= 180.2 (t, $^2J_{P,C}$ = 9.4 Hz, NCN), 132.9, 132.1, 129.7, 129.4 (PPh), 51.0 (s, Pt satellites $^3J_{Pt,C}$ = 27.9 Hz, N*C*H$_2$CH$_2$P), 46.2 (s, Pt satellites $^3J_{Pt,C}$ = 54.9 Hz, NCH$_2$CH$_2$N), 22.2 (m, NCH$_2$*C*H$_2$P); ^{31}P{^{1}H} (162 MHz, DMSO-d_6): δ = 4.3 (s, Pt satellites $^1J_{Pt,P}$ = 2272 Hz, PPh), –144.2 (sept, PF_6); MS (ESI): *m/z* (%) 660 (23, [**1**+H]$^+$), 329 (100, [**1**–H]$^{2+}$).

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