Template-controlled synthesis of a planar [16]ane-P$_2$C$_2^{NHC}$ 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($\text{PMe}_3)_4]$Cl$_2$,$^1$ [Pt($\text{PMe}_2\text{Ph})_4]$($\text{PF}_6$)$_2$,$^2$ [Pt($\text{PMe}_2\text{Ph})_4]$($\text{PF}_6$)$_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 6(Cl)$_2$−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$_2$O (20 mL) was added. This mixture was cooled to −20 °C for 24 h after which the complexes 6(Cl)$_2$−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(PMe₃)₄]Cl₂ 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%). ¹H (400 MHz, CD₃OD): δ = 4.86 (s br, 4H, NH), 3.72 (s, 8H, CH₂), 1.58 (t, ²J_P,H = 4.1 Hz, Pt satellites ³J_P,H = 31.6 Hz, PMe₃); ¹³C{¹H} (100 MHz, CD₃OD): δ = 191.8 (t, ²J_P,C = 10.6 Hz, NCN), 45.4 (s, Pt satellites ³J_P,C = 36.8 Hz, CH₂), 14.1 (t, ¹J_P,C = 20.0 Hz, PMe₃); ³¹P{¹H} (162 MHz, CD₃OD): δ = –19.7 (s, Pt satellites ¹J_P,P = 2262 Hz, PMe₃); MS (ESI): m/z (%) 486 (24, [6a–H]+), 243 (100, [6a]⁺²).  

6b(PF₆)₂: Synthesized from 1.24 g (1.19 mmol, 1.0 eq) of [Pt(PMe₂Ph)₄](PF₆)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%). ¹H (400 MHz, DMSO-d₆): δ = 8.56 (s br, 4H, Ph), 7.55–7.47 (m, 6H, Ph), 3.38 (s br, 4H, NH), 3.20 (s, 8H, CH₂), 1.91–1.75 (m, 12H, PMe₂); ¹³C{¹H} (100 MHz, DMSO-d₆): 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 = 5.3 Hz, PPh), 43.6 (s, CH₂), 12.2 (t, ¹J_P,C = 19.6 Hz, PMe₂); ³¹P{¹H} (162 MHz, DMSO-d₆): δ = –10.0 (s, Pt satellites ¹J_P,P = 2311 Hz, PMe₂Ph), –144.2 (sept, PF₆); MS (ESI): m/z (%) 756 (13, [6b+PF₆]+), 610 (5, [6b–H]+), 305 (100, [6b]⁺²).  

6c(PF₆)₂: Synthesized from 400 mg (0.31 mmol, 1.0 eq) of [Pt(PMePh₂)₄](PF₆)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%). ¹H (400 MHz, DMSO-d₆): δ = 8.54 (s br, 4H, Ph), 7.57–7.46 (m, 16H, Ph), 3.37 (s br, 4H, NH), 2.69 (s, 8H, CH₂), 2.42–2.25 (m, 6H, PMe); ¹³C{¹H} (100 MHz, DMSO-d₆): δ = 189.2 (t, ²J_P,C = 10.3 Hz, NCN), 132.2 (t, ²J_P,C = 6.2 Hz, PPh₂), 131.4 (m, PPh₂), 130.9 (PPh₂), 128.4 (t, ²J_P,C = 5.3 Hz, PPh₂), 43.3 (s, Pt satellites ³J_P,C = 32.2 Hz, CH₂), 11.1 (t, ¹J_P,C = 19.2 Hz, PMe); ³¹P{¹H} (162 MHz, DMSO-d₆): δ = –0.07 (s, Pt satellites ¹J_P,P = 2510 Hz, PMePh₂), –144.2 (sept, PF₆); MS (ESI): m/z (%) 880 (7, [6c+PF₆]+), 734 (3, [6c–H]+), 367 (100, [6c]⁺²).  

1(PF₆)₂: A solution of 100 mg (0.11 mmol, 1.0 eq) of 6b(PF₆)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(PF₆)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(PF₆)₂ can also be obtained from 6c(PF₆)₂ under similar conditions at a reaction temperature of 70 °C, but the lower boiling point of PMe₂Ph makes the isolation of 1(PF₆)₂ starting from 6b(PF₆)₂ easier. Yield: 95 mg (0.99 mmol, 90%) starting from 6c(PF₆)₂. 

\[ ^1H \quad (400 \text{ MHz, DMSO-}d_6): \delta = 7.97−7.52 (m, 10H, Ph), 4.02−3.81 (m, 4H, NCH₂CH₂P), 3.97−3.62 (m, 8H, NCH₂CH₂P), 3.75−3.55 (m, 4H, NCH₂CH₂P), 3.21−2.97 (m, 4H, NCH₂CH₂P); \]

\[ ^{13}C\quad ^1H \quad (100 \text{ MHz, DMSO-}d_6): \delta = 180.2 \text{ (t, } ^2J_{P,C} = 9.4 \text{ Hz, NCN), 132.9, 132.1, 129.7, 129.4 \text{ (PPh), 51.0 \text{ (s, Pt satellites } ^3J_{P,C} = 27.9 \text{ Hz, NCH₂CH₂P), 46.2 \text{ (s, Pt satellites } ^3J_{P,C} = 54.9 \text{ Hz, NCH₂CH₂P), 22.2 \text{ (m, NCH₂CH₂P); } ^{31}P\quad ^1H \quad (162 \text{ MHz, DMSO-}d_6): \delta = 4.3 \text{ (s, Pt satellites } ^1J_{P,P} = 2272 \text{ Hz, PPh), −144.2 \text{ (sept, PF₆); MS (ESI): } m/z \% 660 (23, [1+H]^+), 329 (100, [1−H]^2+).} \]