

## Facile self-assembly of the first diphosphametacyclophane

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### Supplementary Information

#### Experimental Details

##### General

Standard Schlenk and vacuum line techniques were applied throughout, operating under an inert Ar atmosphere; all materials were stored and manipulated in a dry-nitrogen filled MBraun glovebox. Solvents were distilled under dinitrogen from appropriate drying agents and stored over either molecular sievers (THF) or potassium mirrors (non-halogenated). MeP(SiMe<sub>3</sub>)<sub>2</sub> was prepared from HP(SiMe<sub>3</sub>)<sub>2</sub><sup>S1</sup> and MeI. Isophthaloyl chloride was obtained from Sigma, recrystallised from toluene and stored under an inert atmosphere. NMR spectra were recorded on a Varian VNMRS 400 spectrometer operating at: <sup>1</sup>H 399.5 MHz, <sup>13</sup>C 100.46 MHz, <sup>31</sup>P 161.71 MHz, <sup>195</sup>Pt 85.53 MHz, referenced to external Me<sub>4</sub>Si, H<sub>3</sub>PO<sub>4</sub> and KPtCl<sub>6</sub> as appropriate. Carbon-13 spectra were assigned with recourse to 2D (HSQC, HMBC) techniques. Infrared spectra were recorded on a Perkin-Elmer Spectrum one FT-IR spectrometer. Mass spectrometric data were recorded by Dr A.-A. Sada of the departmental service, microanalyses were performed by Mr S. Boyer of the London Metropolitan University Elemental Analysis Service.

##### Synthesis and Characterisation

Compound **1** *m*-{-C(O)-C<sub>6</sub>H<sub>4</sub>(C(O)PMe)}<sub>2</sub>

A diethyl ether solution of isophthaloyl chloride (0.46 g, 2.27 mmol) was added, slowly, to a pre-cooled (-78 °C) ethereal solution of MeP(SiMe<sub>3</sub>)<sub>2</sub> (0.66 g, 2.27 mmol). During addition the solution assumes a yellow colouration, concomitant with deposition of a yellow precipitate. After stirring at -78 °C for 30 mins the mixture was allowed to attain ambient temperature and stirred for a further 12 h, whereupon the precipitate was collected by filtration, washed with diethyl ether dried *in vacuo*. Yield 320 mg, 79 %. <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>, 30°C, 399.5 MHz): δ<sub>H</sub> 1.58 (d, 6H, <sup>2</sup>J<sub>HP</sub> = 3.1 Hz) 6.45 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 1.75 Hz), 7.17 (d, 4H, <sup>3</sup>J<sub>HH</sub> = 1.67 Hz), 9.28 (br., 2H). <sup>31</sup>P{<sup>1</sup>H}-NMR (C<sub>6</sub>D<sub>6</sub>, 30°C, 161.73 MHz): δ<sub>P</sub> 32.7 (s). <sup>13</sup>C{<sup>1</sup>H}-NMR (C<sub>6</sub>D<sub>6</sub>, 30°C, 150.81 MHz): δ<sub>C</sub> 1.7 (d, <sup>1</sup>J<sub>CP</sub> 4.5 Hz, Me), 130.3 (*J*<sub>CP</sub> = 1.6 Hz, C<sup>m</sup>), 130.6 (dd, *J*<sub>CP</sub> ~ 2 Hz, C<sup>o,p</sup>), 134.0 (t, <sup>3</sup>J<sub>CP</sub> = 13.9 Hz, C<sup>o</sup>), 137.6 (d, *J*<sub>CP</sub> = 37.9 Hz, C<sup>i</sup>), 205.9 (d, *J*<sub>CP</sub> = 46.0 Hz, C=O). IR (ν<sub>C=O</sub>) 1654 (s, B<sub>1</sub> asymm.) 1637 (s, B<sub>2</sub> asymm.). EI-MS *m/z* 356 ([M]<sup>+</sup>). Anal. Found: C, 60.59 %; H, 3.82 %. Calcd for C<sub>18</sub>H<sub>14</sub>O<sub>4</sub>P<sub>2</sub>: C, 60.67 %; H, 3.93 %.

Compound **2** *trans*-PtCl<sub>2</sub>(**1**)<sub>2</sub>

(a) A solution of **1** (60 mg, 1.68 x 10<sup>-4</sup> mol) in THF was added to a pre-cooled (-78 °C) solution of PtCl<sub>2</sub>(NCPH)<sub>2</sub> (79 mg, 1.68 x 10<sup>-4</sup> mol) in THF and stirred for 30 mins, before being allowed to warm to ambient temperature. Stirring was continued for a further 12 h. then the volatiles removed under reduced pressure to afford crude **2**, in admixture with unreacted PtCl<sub>2</sub>(NCPH)<sub>2</sub>.

(b) A solution of **1** (60 mg, 1.68 x 10<sup>-4</sup> mol) in THF was added to a pre-cooled (-78 °C) solution of PtCl<sub>2</sub>(NCPH)<sub>2</sub> (79 mg, 1.68 x 10<sup>-4</sup> mol) in THF and stirred for 30 mins, before being allowed to warm to ambient temperature. Stirring was continued for a further 12 h. then the volatiles removed under reduced pressure to afford crude **2**, as a yellow solid, which was dried *in vacuo*. Recrystallisation from concentrated

THF solution at  $-20^{\circ}\text{C}$  afforded analytically pure samples of **2** as X-ray quality crystals. Yield: 121 mg, 73.8 %.  $^1\text{H-NMR}$  ( $d_8$ -THF,  $30^{\circ}\text{C}$ , 399.5 MHz):  $\delta_{\text{H}}$  1.50 (d, 6H,  $^2J_{\text{HP}} = 3.2$  Hz, 2 x  $\text{PCH}_3$ ), 2.39 (t, 6H,  $J_{\text{PH}} = 3.1$  Hz, 2 x  $\text{Pt-PCH}_3$ ), 7.41 (d, 4H,  $J_{\text{HH}} = 7.5$  Hz), 7.67 (dm, 8H,  $J_{\text{HH}} = 7.5$  Hz), 10.64 (br., 4H).  $^{31}\text{P}\{^1\text{H}\}$ -NMR ( $d_8$ -THF,  $30^{\circ}\text{C}$ , 161.73 MHz):  $\delta_{\text{P}}$  28.4 (s), 33.2 (s,  $^1J_{\text{PtP}} = 2296$  Hz). IR ( $\nu_{\text{C=O}}$ ) 1661 (s) 1644 (s). Anal. Found: C, 44.28 %; H, 2.80 %. Calcd for  $\text{C}_{18}\text{H}_{14}\text{O}_4\text{P}_2$ : C, 44.17 %; H, 2.86 %.

### Compound **3** [ $\mu$ - $P,P'$ -(**1**){ $\text{PtCl}_2(\text{PEt}_3)_2$ }]

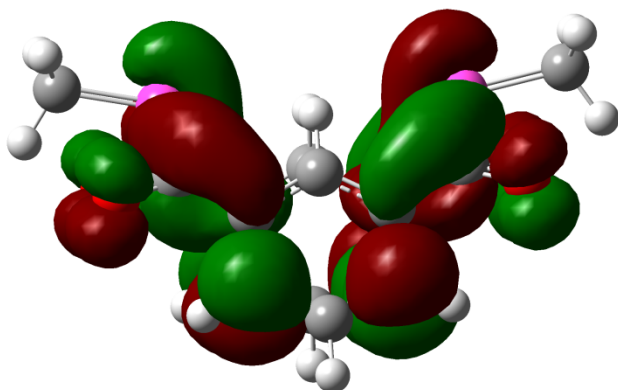
A THF solution of **1** (43 mg,  $1.23 \times 10^{-4}$  mol) was added to a pre-cooled ( $-78^{\circ}\text{C}$ ) solution of  $[\text{PtCl}_2(\text{PEt}_3)_2]_2$  (97 mg,  $1.23 \times 10^{-4}$  mol) in THF and the mixture then allowed to warm to ambient temperature slowly, while stirring over 12 h. The volatiles were removed under pressure afforded **3** as a yellow solid. Yield: 61 mg, 88.2 %.  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ,  $30^{\circ}\text{C}$ , 399.5 MHz):  $\delta_{\text{H}}$  0.99 (dt, 18H,  $^3J_{\text{HH}} = 9.0$  Hz,  $^2J_{\text{HP}} = 17.2$  Hz), 1.67 (m, 12 H), 2.02 (d,  $^2J_{\text{HP}} = 7.2$  Hz), 6.59 (t, 2H,  $J = 7.9$  Hz), 7.89 (d, 4H,  $J = 7.5$  Hz), 9.36 (s., 2H).  $^{31}\text{P}\{^1\text{H}\}$ -NMR ( $\text{C}_6\text{D}_6$ ,  $30^{\circ}\text{C}$ , 161.73 MHz):  $\delta_{\text{P}}$  15.9 (d,  $^2J_{\text{PP}} = 441$  Hz,  $^1J_{\text{PtP}} = 1936$  Hz, 2P), 51.3 (d,  $^2J_{\text{PP}} = 441$  Hz,  $^1J_{\text{PtP}} = 2810$  Hz, 2P).  $^{195}\text{Pt}\{^1\text{H}\}$ -NMR ( $\text{C}_6\text{D}_6$ ,  $30^{\circ}\text{C}$ , 85.53 MHz):  $\delta_{\text{Pt}}$   $\square$ 3933 (dd,  $^1J_{\text{PtP}} = 1936, 2810$  Hz). Anal. Found: C, 32.13 %; H, 3.82 %. Calcd for  $\text{C}_{18}\text{H}_{14}\text{O}_4\text{P}_2$ : C, 32.03 %; H, 3.91 %.

### Computational Details

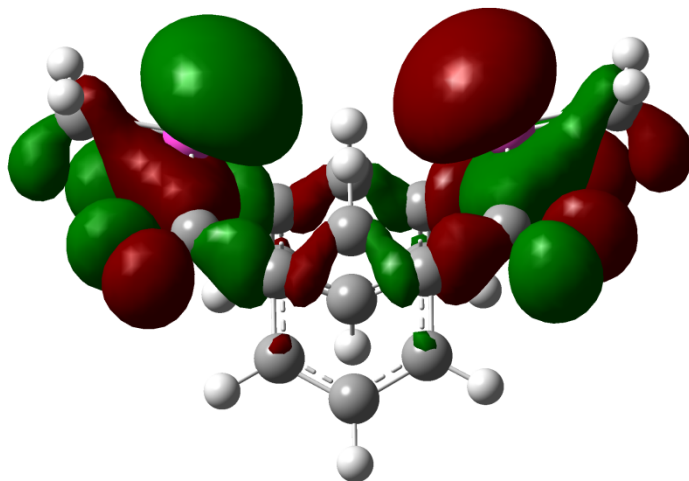
Calculations were performed using Gaussian 03W (multi-processor) running on an Intel Core i5 with 4 GB RAM. Outputs were visualised using Gaussview 4.1. Geometry optimization was performed using an unrestricted B3LYP functional with the 6-311G(3d,3p) basis set, augmented with diffuse functions on all atoms. Stationary points were characterised as minima by frequency calculation, and full NBO analysis was performed.

**Molecular orbitals:** Representative MO surfaces for LUMO, HOMO and HOMO-4

#### LUMO:



#### HOMO:



**HOMO-4:**

