# Structure and Protonation of the Bis-Ethylene Adduct $[Pt(\mu-PBu_2^t)(\eta^2-CH_2=CH_2)]_2$ . Pt–H–P Agostic Interaction and Proton Scrambling.

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## **Supporting Information**

#### **Experimental section**

 $[Pt(\mu-PBu_2^t)(CO)]_2$  was prepared treating  $Pt_2(\mu-PBu_2^t)_2(CO)(PBu_2^tH)^1$  with CO (80 atm, room temperature).<sup>2</sup> NMR spectra were acquired using a Varian Gemini 200 BB spectrometer (200 MHz for <sup>1</sup>H) at room temperature (about 293 K) on CD<sub>2</sub>Cl<sub>2</sub> solutions. <sup>#</sup> is used to label <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P peaks with <sup>195</sup>Pt satellites.

## Synthesis of $[Pt(\mu-PBu_2^t)(\eta^2-CH_2CH_2)]_2$ , (4).

An orange solution of  $[Pt(\mu-PBu_2^t)(CO)]_2$  (100 mg, 0.136 mmol) in toluene (5 ml) was saturated with ethylene (60 atm) and stirred for 4 hours at room temperature. The resulting yellow solution was evaporated and the yellow residue identified as  $[Pt(\mu-PBu_2^t)(\eta^2-CH_2CH_2)]_2$  (92 mg; 92% yield). Elemental analysis calcd (%) for C<sub>20</sub>H<sub>44</sub>P<sub>2</sub>Pt<sub>2</sub>: C 32.6; H 6.02; found: C 32.4; H 6.35. <sup>1</sup>H NMR:  $\delta = 1.23$  (vt, <sup>3</sup>J<sub>HP</sub> + <sup>5</sup>J<sub>HP</sub> = 7 Hz, 36 H, CH<sub>3</sub>), 2.57<sup>#</sup> (s, <sup>2</sup>J<sub>HPt</sub> = 65 Hz, 8 H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR:  $\delta = 26.7^{#}$  (t, <sup>2</sup>J<sub>CP</sub> = 6 Hz, <sup>1</sup>J<sub>CPt</sub> = 197 Hz, <sup>1</sup>J<sub>CH</sub> = 159 Hz, CH<sub>2</sub>), 32.2 (m, <sup>1</sup>J<sub>CH</sub> = 127 Hz, CH<sub>3</sub>), 40.1<sup>#</sup> (m, <sup>2</sup>J<sub>CPt</sub> = 38 Hz, PC). <sup>31</sup>P NMR:  $\delta = 292.7^{#}$  ppm (s, <sup>1</sup>J<sub>PPt</sub> = 2280 Hz). <sup>195</sup>Pt NMR:  $\delta = -5925$ ppm (t; <sup>1</sup>J<sub>PPt</sub> = 2280 Hz).

### Synthesis of $[Pt_2(\mu - PBu_2^t)(\mu - PBu_2^t)(\eta^2 - CH_2CH_2)_2](CF_3SO_3), (5).$

Triflic acid (17  $\mu$ L; d = 1.69 g/ml; 0.19 mmol) was added to a CH<sub>2</sub>Cl<sub>2</sub> solution (3 mL) of Pt<sub>2</sub>( $\mu$ -PBu<sup>t</sup><sub>2</sub>)<sub>2</sub>( $\eta$ <sup>2</sup>-CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub> (140 mg, 0.19 mmol). The solution was concentrated and added with Et<sub>2</sub>O (1 mL), yielding a yellow precipitate, which was filtered off, dried in vacuo and identified as [Pt<sub>2</sub>( $\mu$ -

PBu<sup>1</sup><sub>2</sub>)(μ-PBu<sup>1</sup><sub>2</sub>H)(η<sup>2</sup>-CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>](CF<sub>3</sub>SO<sub>3</sub>) (143 mg, 85% yield). Elemental analysis calcd (%) for C<sub>21</sub>H<sub>45</sub>F<sub>3</sub>O<sub>3</sub>P<sub>2</sub>Pt<sub>2</sub>S: C 28.4; H 5.11; found: C 28.2; H 5.35. <sup>1</sup>H NMR (200 K):  $\delta = -2.06^{\#}$  (dd, <sup>1</sup>*J*<sub>HP</sub> = 86, <sup>2</sup>*J*<sub>HP</sub> = 29, <sup>1</sup>*J*<sub>HPt</sub> = 363, <sup>2</sup>*J*<sub>HPt</sub> = 29 Hz, P–H–Pt), 1.34 (d, <sup>3</sup>*J*<sub>HP</sub> = 16 Hz, CH<sub>3</sub>), 3.18<sup>#</sup> (s, <sup>2</sup>*J*<sub>HPt</sub> = 68 Hz, CH<sub>2</sub>), 4.02<sup>#</sup> ppm (s, <sup>2</sup>*J*<sub>HPt</sub> = 65 Hz, CH<sub>2</sub>). <sup>13</sup>C NMR (200 K):  $\delta = 30.8$  (d, <sup>2</sup>*J*<sub>CP</sub> = 5.5 Hz, CH<sub>3</sub>), 31.1 (d, <sup>2</sup>*J*<sub>CP</sub> = 5.5 Hz, CH<sub>3</sub>), 37.3<sup>#</sup> (m, <sup>1</sup>*J*<sub>CPt</sub> = 168 Hz, CH<sub>2</sub>), 38.2<sup>#</sup> (m, <sup>1</sup>*J*<sub>CPt</sub> = 175 Hz, CH<sub>2</sub>), 42.3<sup>#</sup> (m, PC), 45.0<sup>#</sup> (s, <sup>2</sup>*J*<sub>CPt</sub> = 17.4 Hz, PC), 119.9 ppm (q, <sup>1</sup>*J*<sub>CF</sub> = 319 Hz, CF<sub>3</sub>). <sup>31</sup>P NMR:  $\delta = 303.1$  (d, <sup>2</sup>*J*<sub>PP</sub> = 112 Hz, <sup>1</sup>*J*<sub>PPt</sub> = 2505, 345 Hz), 402.2 ppm (d, <sup>2</sup>*J*<sub>PP</sub> = 112 Hz, <sup>1</sup>*J*<sub>PPt</sub> = 2440, 2346 Hz). <sup>195</sup>Pt NMR:  $\delta = -5962$  (dd; <sup>1</sup>*J*<sub>PPt</sub> = 2346, 2505 Hz, <sup>1</sup>*J*<sub>PtPt</sub> = 750 Hz), -6495 ppm (dd; <sup>1</sup>*J*<sub>PPt</sub> = 345, 2440 Hz, <sup>1</sup>*J*<sub>PtPt</sub> = 750 Hz).

#### Crystal and Molecular Structure of complex 4.

X-ray measurements were carried out with a Bruker P4 diffractometer using the Mo- $K_{\alpha}$  graphitemonochromated radiation ( $\lambda = 0.71073$  Å), the sample being sealed in a glass capillary under dinitrogen atmosphere. The crystal used for the measurement was a rather large yellow prism  $0.50 \times$  $0.42 \times 0.10$  mm<sup>3</sup>. Cell parameters were calculated on the setting angles of 32 strong reflections with  $5.4 \,^{\circ} \leq \theta \leq 16.8^{\circ}$ . Crystal data: C<sub>20</sub>H<sub>44</sub>P<sub>2</sub>Pt<sub>2</sub>, M = 736.67, T = 293(2) K, space group  $P\overline{1}$  (No. 2), a =8.250(2), b = 8.406(1), c = 9.973(1) Å,  $\alpha = 95.41(2)$ ,  $\beta = 99.22(2)$ ,  $\gamma = 111.03(2)^{\circ}$ , V = 628.6(2) Å<sup>3</sup>, Z = 1,  $D_c = 1.946$  g· cm<sup>-3</sup>,  $\mu$ (Mo- $K_{\alpha}$ ) = 11.244 mm<sup>-3</sup>, F (000) = 350. The intensities of 2669 reflections with  $2.0^{\circ} \leq \theta \leq 25^{\circ}$  were collected. After merging the equivalent ones and after correction for Lorentz, polarisation, and absorption effects with an integration method base on the crystal shape,<sup>3</sup> an internal R value of 0.0340 was obtained.

The structure was solved by standard direct and Fourier methods and refined by full-matrix leastsquares procedures. The hydrogen atoms have been placed in calculated positions and were let to ride on the connected carbon atoms. In the final refinement cycle anisotropic thermal parameters were used for all heavy atoms, giving a conventional *R* factor ( $F_0$ ) of 0.0375, calculated for 110 parameters on the 1984 observed reflections  $[I > 2\sigma(I)]$ , and a value of 0.0427 for all 2168 data. The residual peaks in the final difference Fourier map range between 1.90 and  $-1.83 e \cdot \text{Å}^{-3}$ . The calculations were done by means of SHELX97<sup>4</sup> contained in the WINGX<sup>5</sup> suite.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-236901. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

### **References and Notes**

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5a NMR spectra (CD<sub>2</sub>Cl<sub>2</sub>, 213 K)



 $^{1}$ H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 233 – 283 K)





