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# Unexpected, Photochemically Induced Activation of the Tetrabutylammonium Cation by Hexachloroplatinate(IV)

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### **Supplementary Information**

#### Experimental

#### **Electron Paramagnetic Resonance Spectroscopy**

EPR spectroscopy was performed using a JEOL JES-RE1X-ESR spectrometer equipped with a 100 W Mercury lamps without a filter ( $\lambda > 250$  nm). A sample of a solution of the analyte was loaded into a flat, quartz cell. A background spectrum was recorded at room temperature followed by the spectrum of sample at 120 K. The spectra were processed using SpecView software.

#### **Mass Spectrometry**

Liquid injection field desorption/ionisation mass spectrometry (LIFDI-MS) analysis was carried out using a Bruker Daltronics microTOF-Agilent series 1200LC spectrometer.

#### Preparation of Tetrabutylammonium Hexachloroplatinate(IV)

In a round-bottom flask, potassium hexachloroplatinate (1.15 g; 2.37 mmol) was stirred with acetone (15 cm<sup>3</sup>). While stirring, tetrabutylammonium chloride (1.31 g; 4.73 mmol) was added into the flask. The mixture was stirred overnight to afford an orange solution and a colourless precipitate. The solution was filtered *in vacuo* to remove the precipitate and then the solvent was removed resulting in an orange precipitate. The solid was allowed to dry *in vacuo* in for two of hours to give a crystalline orange solid. Yield: 97% (2.04 g; 2.28 mmol). Anal. calc. for C<sub>32</sub>H<sub>72</sub>N<sub>2</sub>Cl<sub>6</sub>Pt: Calc.: C = 43.1, H = 8.1, N = 3.1%. Found: C = 43.1, H = 8.1, N = 3.0%. <sup>1</sup>H NMR,  $\delta_{H}$  (400 MHz, d<sub>6</sub>-acetone): 0.98 (24 H, t, -CH<sub>3</sub>), 1.45 (16 H, m, -CH<sub>2</sub>-), 1.80 (16 H, m, -CH<sub>2</sub>-), 3.46 (16 H, m, -NCH<sub>2</sub>-). <sup>195</sup>Pt NMR,  $\delta_{Pt}$  (107.5 MHz, d<sub>6</sub>-acetone, 298 K): 377.

#### Reaction of tetrabutylammonium hexachloroplatinate(IV) in dry acetone

Tetrabutylammonium hexachloroplatinate(IV) (202.9 mg; 0.2273 mmol) in dry acetone (40 cm<sup>3</sup>) was heated under reflux under an atmosphere of nitrogen and ambient light for 48 h. The mixture was concentrated using a rotary evaporator to afford a brown paste which was dissolved in a small amount of acetone and crystallised by addition of diethyl ether to give a pale-yellow precipitate and a supernatant. The precipitate was isolated by decanting of the solution, and it was then dried in air to afford (NBu<sub>4</sub>)<sub>2</sub>[ $\eta^2$ -Cl<sub>3</sub>Pt(C<sub>4</sub>H<sub>6</sub>)- $\eta^2$ -PtCl<sub>3</sub>], as a yellow, crystalline solid. The precipitation was then repeated a few times to obtain greater yields. Yield: 88.21 mg, 0.077 mmol, 68%. Anal. calc. for C<sub>36</sub>H<sub>78</sub>N<sub>2</sub>Cl<sub>6</sub>Pt<sub>2</sub>: Calc.: C = 37.9, H = 6.9, N = 2.5%. The CHN analysis was conducted for compounds randomly taken from three batches of precipitation. Found: 1: C = 37.5, H = 6.8, N = 2.3%. 2: C = 38.2, H = 6.9, N = 2.4%. 3: C = 38.0, H = 6.5, N = 2.2%.  $\delta_{\rm H}$  (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 295 K): *anti-trans*-butadiene-conformer: 5.56 (2H, m, H<sub>X</sub>, H<sub>X'</sub>), 4.80 (2H, dd, <sup>3</sup>J<sub>HH</sub> = 12.8 Hz, <sup>2</sup>J<sub>HH</sub> = 1.2 Hz, <sup>2</sup>J<sub>PtH</sub> = 60 Hz, H<sub>A</sub>, H<sub>A'</sub>), 4.44 (2H, dd, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, <sup>2</sup>J<sub>HH</sub> = 1.2 Hz, <sup>2</sup>J<sub>PtH</sub> = 60 Hz, H<sub>A</sub>, H<sub>A'</sub>), 4.44 (2H, m, H<sub>X</sub>, H<sub>X</sub>), 4.32 (2H, d, <sup>3</sup>J<sub>HH</sub> = 13.2 Hz, H<sub>A</sub>, H<sub>A'</sub>), 4.12 (2H, d, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, H<sub>M</sub>, H<sub>M'</sub>), *anti-cis*-butadiene-conformer:

conformer: 6.33 (2H, d of t,  ${}^{3}J_{HH} = 17.2 \text{ Hz}$ ,  ${}^{3}J_{HH} = 10.4$ ,  ${}^{3}J_{HH} = 10.4\text{Hz}$ ,  $H_{X}$ ,  $H_{X'}$ ), 5.80 (2H, d,  ${}^{3}J_{HH} = 17.2 \text{ Hz}$ ,  $H_{A}$ ,  $H_{A'}$ ), 5.52 (2H, d,  ${}^{3}J_{HH} = 10.4 \text{ Hz}$ ,  $H_{M}$ ,  $H_{M'}$ ).  ${}^{195}$ Pt NMR,  $\delta_{Pt}$  (107.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 295 K): -2521 (*anti-trans*-butadiene-conformer), -2591 (*syn-trans*-butadiene-conformer).



The four possible conformers of **1**: left-to-right: *anti,trans; syn,trans; anti,cis* and *syn,cis*. Note that the *syn,cis* conformer is not observed (sterically too crowded) and that there is relatively little of the *anti,cis*, which is why it is not readily observed by <sup>195</sup>PT NMR spectroscopy.

#### Photoreaction of Tetrabutylammonium Hexachloroplatinate(IV)

Tetrabutylammonium hexachloroplatinate(IV) (10.18 mg, 0.01140 mmol) in dry acetone (2.0 cm<sup>3</sup>) was irradiated with UV light with  $\lambda$  > 305 nm for 18 h; a parallel reaction in three Young's NMR tubes was carried out. The mixture was concentrated *in vacuo* to give a yellowish paste which was solidified by addition of diethyl ether to give a pale-yellow precipitate. The precipitate was isolated by decanting and dried in air to afford (NBu<sub>4</sub>)<sub>2</sub>[ $\eta$ <sup>2</sup>-Cl<sub>3</sub>Pt(C<sub>4</sub>H<sub>6</sub>)- $\eta$ <sup>2</sup>-PtCl<sub>3</sub>], I, as a yellow, crystalline solid. Yield: 4.52 mg, 0.004 mmol, 69%.  $\delta$ <sub>H</sub> (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 295 K): *anti-trans*-butadiene-conformer: 5.56 (2H, m, H<sub>X</sub>, H<sub>X'</sub>), 4.80 (2H, dd, <sup>3</sup>J<sub>HH</sub> = 12.8 Hz, <sup>2</sup>J<sub>HH</sub> = 1.2 Hz, <sup>2</sup>J<sub>PtH</sub> = 60 Hz, H<sub>A</sub>, H<sub>A'</sub>), 4.44 (2H, dd, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, <sup>2</sup>J<sub>PtH</sub> = 1.2 Hz, <sup>2</sup>J<sub>PtH</sub> = 60 Hz, H<sub>A</sub>, H<sub>A'</sub>), 4.44 (2H, dd, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, <sup>2</sup>J<sub>HH</sub> = 1.2 Hz, <sup>2</sup>J<sub>PtH</sub> = 60 Hz, H<sub>A</sub>, H<sub>A'</sub>), 4.44 (2H, dd, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, <sup>2</sup>J<sub>HH</sub> = 13.2 Hz, H<sub>A</sub>, H<sub>A'</sub>), 4.12 (2H, d, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, H<sub>M</sub>, H<sub>M'</sub>), *anti-cis*-butadiene-conformer: 6.33 (2H, d of t, <sup>3</sup>J<sub>HH</sub> = 17.2 Hz, <sup>3</sup>J<sub>HH</sub> = 10.4, <sup>3</sup>J<sub>HH</sub> = 10.4Hz, H<sub>X</sub>, H<sub>X'</sub>), 5.80 (2H, d, <sup>3</sup>J<sub>HH</sub> = 17.2 Hz, H<sub>A</sub>, H<sub>A'</sub>), 5.52 (2H, d, <sup>3</sup>J<sub>HH</sub> = 10.4 Hz, H<sub>M</sub>, H<sub>M'</sub>). <sup>195</sup>Pt NMR,  $\delta$ <sub>Pt</sub> (107.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 295 K): - 2521 (*anti-trans*-butadiene-conformer), - 2591 (*syn-trans*-butadiene-conformer).



Figure S1: The <sup>1</sup>H NMR spectrum (500 MHz) of **1** recorded in  $CD_2Cl_2$  at 295 K.



#### Figure S2: The <sup>1</sup>H NMR spectrum (500 MHz) of 1 recorded in in d<sub>6</sub>-acetone at 298 K

#### Single crystal X-ray diffraction

CCDC Deposition No.	1860540
Empirical formula	$C_{36}H_{78}CI_6N_2Pt_2$
Formula weight	1141.88
Temperature/K	109.9(4)
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /n
a/Å	13.1677(5)
b/Å	12.8495(6)
<i>c</i> /Å	13.3831(7)
α/°	90
β/°	98.427(4)
γ/°	90
Volume/Å <sup>3</sup>	2239.95(18)
Z	2
$ ho_{ m calc}$ /g cm <sup>-3</sup>	1.693
µ/mm⁻¹	6.622
F(000)	1132.0
Crystal size/mm <sup>3</sup>	0.1848 × 0.1316 × 0.0612
Radiation	ΜοΚα (λ = 0.71073)
2 $\theta$ range for data collection/°	6.918 to 59.992
Index ranges	-17 ≤ <i>h</i> ≤ 18, -18 ≤ <i>k</i> ≤ 11, -18 ≤ <i>l</i> ≤ 18
Reflections collected	11858
Independent reflections	6514 [ <i>R</i> <sub>int</sub> = 0.0382, <i>R</i> <sub>sigma</sub> = 0.0619]
Data/restraints/parameters	6514/0/221
Goodness-of-fit on $F^2$	1.068
Final R indexes [/>=2 $\sigma$ (I)]	$R_1 = 0.0360, wR_2 = 0.0719$
Final R indexes [all data]	$R_1 = 0.0481$ , w $R_2 = 0.0791$
Largest diff. peak/hole / e Å <sup>-3</sup>	3.52/-2.86



Figure S3 Molecular structure of  ${\bf 1}$  using thermal ellipsoid representation.