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$^3$). 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$_{32}$H$_{72}$N$_2$Cl$_6$Pt: Calc.: C = 43.1, H = 8.1, N = 3.1%. Found: C = 43.1, H = 8.1, N = 3.0%. $^1$H NMR, $\delta$ (400 MHz, d$_6$-acetone): 0.98 (24 H, t, -CH$_3$), 1.45 (16 H, m, -CH$_2$-), 1.80 (16 H, m, -CH$_2$-), 3.46 (16 H, m, -NCH$_2$-). $^{195}$Pt NMR, $\delta$ (107.5 MHz, d$_6$-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$^3$) 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$_4$)$_2$[$\eta^2$-Cl$_2$Pt(C$_4$H$_5$)-$\eta^2$-PtCl$_3$], as a yellow, crystalline solid. The precipitation was then repeated a few times to obtain greater yields. Yield: 88.21 mg, 0.0777 mmol, 68%. Anal. calc. for C$_{36}$H$_{78}$N$_2$Cl$_6$Pt$_2$: 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%. $\delta$ (500 MHz, CD$_2$Cl$_2$, 295 K): anti-trans-butadiene-conformer: 5.56 (2H, m, H$_x$, H$_x'$), 4.80 (2H, dd, $^3$J$_{HH}$ = 12.8 Hz, $^2$J$_{HH}$ = 1.2 Hz, $^2$J$_{HH}$ = 60 Hz, H$_A$, H$_A'$), 4.44 (2H, dd, $^3$J$_{HH}$ = 7.1 Hz, $^2$J$_{HH}$ = 1.2 Hz, $^2$J$_{HH}$ = 60 Hz, H$_M$, H$_M'$), syn-trans-butadiene-conformer: 5.80 (2H, m, H$_x$, H$_x'$), 4.32 (2H, d, $^3$J$_{HH}$ = 13.2 Hz, H$_A$, H$_A'$), 4.12 (2H, d, $^3$J$_{HH}$ = 7.6 Hz, H$_M$, H$_M'$), anti-cis-butadiene-
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 $^{195}$Pt NMR spectroscopy.

**Photoreaction of Tetrabutylammonium Hexachloroplatinate(IV)**

Tetrabutylammonium hexachloroplatinate(IV) (10.18 mg, 0.01140 mmol) in dry acetone (2.0 cm$^3$) 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$_4$)$_2$[η$^2$-Cl$_3$Pt(C$_4$H$_6$)-η$^2$-PtCl$_3$], I, as a yellow, crystalline solid. Yield: 4.52 mg, 0.004 mmol, 69%. $\delta_1$ (500 MHz, CD$_2$Cl$_2$, 295 K): anti-trans-butadiene-conformer: 5.56 (2H, m, H$_X$, H$_X'$), 4.80 (2H, dd, $^3$J$_{HH}$ = 12.8 Hz, $^2$J$_{HH}$ = 1.2 Hz, $^2$J$_{PtH} = 60$ Hz, H$_A$, H$_A'$), 4.44 (2H, dd, $^3$J$_{HH}$ = 7.1 Hz, $^2$J$_{HH}$ = 1.2 Hz, $^2$J$_{PtH} = 60$ Hz, H$_M$, H$_M'$), syn-trans-butadiene-conformer: 5.80 (2H, m, H$_X$, H$_X'$), 4.32 (2H, d, $^3$J$_{HH}$ = 13.2 Hz, H$_A$, H$_A'$), 4.12 (2H, d, $^3$J$_{HH}$ = 7.6 Hz, H$_M$, H$_M'$), anti-cis-butadiene-conformer: 6.33 (2H, d of t, $^3$J$_{HH}$ = 17.2 Hz, $^3$J$_{HH}$ = 10.4 Hz, H$_A$, H$_A'$), 5.80 (2H, d, $^3$J$_{HH}$ = 17.2 Hz, H$_A$, H$_A'$), 5.52 (2H, d, $^3$J$_{HH}$ = 10.4 Hz, H$_M$, H$_M'$). $^{195}$Pt NMR, $\delta_{Pt}$ (107.5 MHz, CD$_2$Cl$_2$, 295 K): -2521 (anti-trans-butadiene-conformer), -2591 (syn-trans-butadiene-conformer).
Figure S1: The $^1$H NMR spectrum (500 MHz) of 1 recorded in CD$_2$Cl$_2$ at 295 K.
Figure S2: The $^1$H NMR spectrum (500 MHz) of 1 recorded in d$_6$-acetone at 298 K
Single crystal X-ray diffraction

CCDC Deposition No. 1860540

Empirical formula C_{36}H_{78}Cl_{6}N_{2}Pt_{2}

Formula weight 1141.88

Temperature/K 109.9(4)

Crystal system monoclinic

Space group P2_{1}/n

a/Å 13.1677(5)
b/Å 12.8495(6)
c/Å 13.3831(7)
α/° 90
β/° 98.427(4)
γ/° 90

Volume/Å³ 2239.95(18)

Z 2

ρ_{calc} /g cm⁻³ 1.693

μ/mm⁻¹ 6.622

F(000) 1132.0

Crystal size/mm³ 0.1848 × 0.1316 × 0.0612

Radiation MoKα (λ = 0.71073)

2θ range for data collection/° 6.918 to 59.992

Index ranges -17 ≤ h ≤ 18, -18 ≤ k ≤ 11, -18 ≤ l ≤ 18

Reflections collected 11858

Independent reflections 6514 [R_{int} = 0.0382, R_{sigma} = 0.0619]

Data/restraints/parameters 6514/0/221

Goodness-of-fit on F² 1.068

Final R indexes [I>2σ(I)] R₁ = 0.0360, wR₂ = 0.0719

Final R indexes [all data] R₁ = 0.0481, wR₂ = 0.0791

Largest diff. peak/hole / e Å⁻³ 3.52/-2.86
Figure S3 Molecular structure of 1 using thermal ellipsoid representation.