

A Biomimetic Phenol Substituent Effect on the Reaction of a Dimethylplatinum(II) Complex with Oxygen: Proton Coupled Electron Transfer and Multiple Proton Relay

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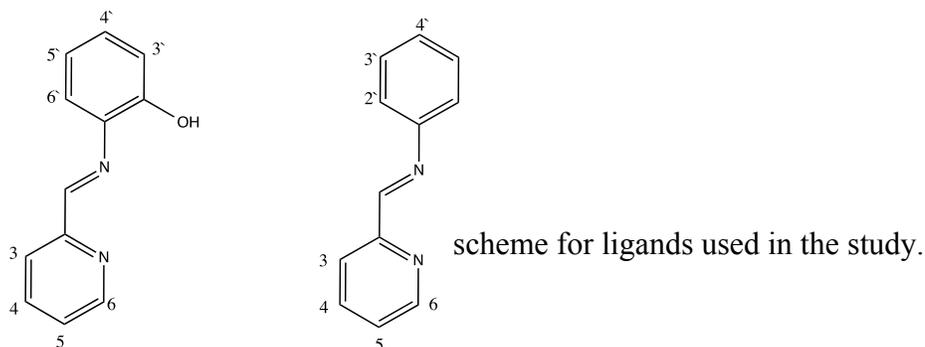
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Experimental :

General Procedures

NMR spectra were recorded using a Varian INOVA 600 MHz spectrometer. NMR labeling is shown in Chart 1. Assignments were confirmed by recording COSY spectra. Mass spectrometric analysis was carried out using an electrospray PE-Sciex mass spectrometer (ESI-MS) coupled with a TOF detector. The platinum complex, $[\text{Pt}_2\text{Me}_4(\mu\text{-SMe}_2)_2]$ was prepared according to the literature. ■

Chart 1. NMR labeling



2-(Pyridin-2-ylmethyleneimino)phenol

To a solution of 2-aminophenol (1.0 g, 9.174 mmol) in dry dichloromethane (50 mL) was added 2-pyridine carboxaldehyde (0.98 g, 9.174 mmol). The reaction mixture was heated under reflux for 24 h. then the solvent

¹ G.S. Hill, M.J. Irwin, C.J. Levy, L.M. Rendina and R.J. Puddephatt, *Inorg. Synth.*, 1998, **32**, 149.

was evaporated under reduced pressure. Pentane (50 mL) was added to the residue, and the mixture was sonicated for 5 min., then filtered to remove insoluble material. The filtrate solution was evaporated under reduced pressure to give the product. Yield: 1.68 g, 91 %. NMR (600 MHz, CDCl₃): δ (¹H) = 8.83 (s, 1H, CH=N), 8.71 (d, 1H, $J_{\text{HH}} = 7$ Hz, H⁶), 8.19 (d, 1H, $J_{\text{HH}} = 8$ Hz, H³), 7.81 (t, 1H, $J_{\text{HH}} = 8$ Hz, H⁴), 7.38 (m, 3H, H⁵, H^{3'} and OH), 7.23 (t, 1H, $J_{\text{HH}} = 8$ Hz, H⁴), 7.05 (d, 1H, $J_{\text{HH}} = 8$ Hz, H⁶), 6.94 (t, 1H, $J_{\text{HH}} = 8$ Hz, H⁵). HRMS (ESI): calc for C₁₂H₁₀N₂O [M]⁺ 198.0793; found 198.0797

Pyridin-2-ylmethyleneiminobenzene

To a solution of 2-pyridinecarboxaldehyde (0.98 g, 9.174 mmol) in toluene (50 mL) was added aniline (0.85 g, 9.174 mmol) and the reaction was heated under Dean-Stark reflux for 24h. The solvent was evaporated under reduced pressure to afford the product as a yellow oil. NMR (600 MHz, CDCl₃): δ (¹H) = 8.72 (d, 1H, $J = 8$ Hz, H⁶), 8.61 (s, 1H, CH=N), 8.22 (d, 1H, $J_{\text{HH}} = 8$ Hz, H³), 7.81 (t, 1H, $J_{\text{HH}} = 8$ Hz, H⁴), 7.40 (m, 2H, H^{3'}), 7.36 (t, 1H, $J_{\text{HH}} = 8$ Hz, H⁵), 7.28 (m, 3H, H^{2',4'})

[PtMe₂(κ^2 -*N,N*-2-C₅H₄NCH=N-2-C₆H₄OH)], **1a**

To a stirred solution of 2-C₅H₄NCH=N-2-C₆H₄OH (1.00 mmol) in diethylether (10 mL) was added [Pt₂Me₄(μ -SMe₂)₂] (0.288 g, 0.50 mmol). The colour changed rapidly from colourless to red with precipitation of a red solid. The reaction mixture was stirred at room temperature for 6 h, then the product by filtration, washed with ether (3 × 2 mL) and pentane (3 × 2 mL), and dried under high vacuum. Yield: 0.33 g, 78 %. NMR (600 MHz, CDCl₃): δ (¹H) = 9.70 (s, 1H, ³ $J_{\text{PtH}} = 32$ Hz, -CH=N), 9.27 (d, 1H, $J_{\text{HH}} = 6$ Hz, ³ $J_{\text{PtH}} = 25$ Hz, H⁶), 8.39 (t, 1H, $J_{\text{HH}} = 8$ Hz, H⁴), 8.22 (d, 1H, $J_{\text{HH}} = 8$ Hz, H³), 7.92 (dd, 1H, $J_{\text{HH}} = 6$ Hz, 8 Hz, H⁵), 7.22 (t, 2H, $J_{\text{HH}} = 9$ Hz, H^{4',5'}), 7.01 (d, 2H, $J_{\text{HH}} = 9$ Hz, H^{3',6'}), 1.21 (s, 3H, ³ $J_{\text{PtH}} = 87$ Hz, PtMe), 0.82 (s, 3H, ³ $J_{\text{PtH}} = 89$ Hz, PtMe). HRMS (ESI): Calc for **1a**: C₁₄H₁₆N₂OPt, 423.0910; found, 423.1036.

[PtMe₂(κ^2 -*N,N*-2-C₅H₄NCH=NPh)], **1b**

This was prepared similarly, but using the ligand 2-C₅H₄NCH=NPh. Yield: 0.35 g, 86%. NMR (600 MHz, CDCl₃): δ (¹H) = 9.30 (d, 1H, $J_{\text{HH}} = 6$ Hz, ³ $J_{\text{PtH}} = 17$ Hz, H⁶), 9.27 (s, 1H, ³ $J_{\text{PtH}} = 30$ Hz, -CH=N), 8.11 (t, 1H, $J_{\text{HH}} = 6$ Hz, PyH⁴), 7.79 (d, 1H, $J_{\text{HH}} = 8$ Hz, PyH³), 7.67 (t, 1H, $J_{\text{HH}} = 6$ Hz, PyH⁵), 7.44 (t, 2H, $J_{\text{HH}} = 8$ Hz, H^{3'}), 7.34 (t, 1H, $J_{\text{HH}} = 8$ Hz, H⁴), 7.27 (d, 2H, $J_{\text{HH}} = 8$ Hz, H^{2'}), 1.39 (s, 3H, ³ $J_{\text{PtH}} = 88$ Hz, PtMe), 1.00 (s, 3H, ³ $J_{\text{PtH}} = 88$ Hz, PtMe). HRMS (ESI): Calc for **1b**: C₁₄H₁₆N₂Pt 407.0961; found 407.0495.

[Pt(OH)Me₂(κ³-N,N,O-2-C₅H₄NCH(CHCMeO)N-2-C₆H₄OH)], **2**

Complex **1a** (0.05 mmole) was dissolved in acetone (10 mL) and the reaction mixture was stirred in air for 24 h. The solvent was evaporated under reduced pressure, to give the product which was dried under vacuum. ¹H NMR (600 MHz, CD₂Cl₂): δ(¹H) = 8.61 (d, 1H, *J*_{HH} = 6 Hz, ³*J*_{PtH} = 28 Hz, H⁶), 7.94 (t, 1H, *J*_{HH} = 7 Hz, H⁴), 7.51 (d, 1H, *J*_{HH} = 7 Hz, H³), 7.42 (m, 2H, H^{4,5}), 7.15 (m, 1H, H⁵), 6.85 (m, 2H, H^{3,6}), 4.77(d, 1H, *J*_{HH} = 9 Hz, -CH-N), 4.17(d, 1H, *J*_{HH} = 9 Hz, -CH-CMe), 2.11(s, 3H, Me) 1.60 (s, 3H, ³*J*_{PtH} = 72 Hz, Pt-Me), 1.32 (s, 3H, ³*J*_{PtH} = 72 Hz, Pt-Me).

Reaction of **1a** with acetone-*d*₆.

A solution of complex **1a** (0.025 mmole) in acetone-*d*₆ (1 mL) was added to an NMR tube in air and NMR spectra were recorded at regular intervals for 24 h. as complex **2-d**₆ was formed. ¹H NMR (600 MHz, acetone-*d*₆): δ(¹H) = 8.68 (d, 1H, *J*_{HH} = 6 Hz, ³*J*_{PtH} = 30 Hz, H⁶), 8.07 (t, 1H, *J*_{HH} = 8 Hz, H⁴), 7.36 (d, 1H, *J*_{HH} = 8 Hz, H³), 7.59 (dd, 1H, *J*_{HH} = 6 Hz, 8 Hz, H⁵), 7.48 (d, 1H, *J*_{HH} = 7 Hz, H³), 6.89 (t, 1H, *J*_{HH} = 7 Hz, H⁵), 6.72 (m, 2H, H^{4,6}), 4.79 (s, 1H, -CH-N), 1.58 (s, 3H, ³*J*_{PtH} = 72 Hz, Pt-Me), 1.13 (s, 3H, ³*J*_{PtH} = 72 Hz, Pt-Me).

A similar reaction was carried out using an atmosphere of pure O₂ in place of air to determine the dependence of rate on oxygen concentration. In a similar experiment with complex **1b**, no reaction was observed.

Structure determination¹

Data Collection and Processing. The sample was mounted on a Mitegen polyimide micromount with a small amount of Paratone N oil. All X-ray measurements were made on a Bruker Kappa Axis Apex2 diffractometer at a temperature of 110 K. The unit cell dimensions were determined from a symmetry constrained fit of 9857 reflections with 5.04° < 2θ < 66.44°. The data collection strategy was a number of ω and φ scans which collected data up to 78.936° (2θ). The frame integration was performed using SAINT. The resulting raw data was scaled and absorption corrected using a multi-scan averaging of symmetry equivalent data using SADABS. It was apparent that the sample crystal was twinned. However, a reasonable model for the twinning could not be found. Both non-merohedral twinning and twinning by pseudomerohedry were considered. The twinning was neglected in all subsequent steps of the analysis.

Structure Solution and Refinement. The structure was solved by using a dual space methodology using the SHELXT program. All non-hydrogen atoms were obtained from the initial solution. The hydrogen atoms were introduced at idealized positions and were allowed to ride on the parent atom. The hydrogen atoms of the water

of solvation(atom O1W) were disordered by imposition of crystallographic symmetry. This led to the hydroxy hydrogens on atoms O1B and O3B also being disordered. The structural model was fit to the data using full matrix least-squares based on F^2 . The calculated structure factors included corrections for anomalous dispersion from the usual tabulation. The structure was refined using the SHELXL-2014 program from the SHELX suite of crystallographic software.

1. Bruker-AXS, SAINT version 2013.8, **2013**, Bruker-AXS, Madison, WI 53711, USA; Bruker-AXS, SADABS version 2012.1, **2012**, Bruker-AXS, Madison, WI 53711, USA; Sheldrick, G. M., *Acta Cryst.* **2015**, *A71*, 3-8; Sheldrick, G. M., *Acta Cryst.* **2008**, *A64*, 112-122.

DFT Calculations

DFT calculations were carried out by using the Amsterdam Density Functional program based on the BLYP functional, with double-zeta basis set and first-order scalar relativistic corrections.¹ The calculations are for the gas phase, neutral molecules in the singlet state. Energy minima were confirmed by vibrational analysis. Transition states were not determined.

1. (a) G. Te Velde, F.M. Bickelhaupt, E.J. Baerends, S. van Gisbergen, C.F. Guerra, J.G. Snijders and T. Ziegler, *J. Comput. Chem.*, 2001, **22**, 931. (b) A. Becke, *Phys. Rev. A* 1988, **38**, 3098.

¹H NMR Spectroscopic Data

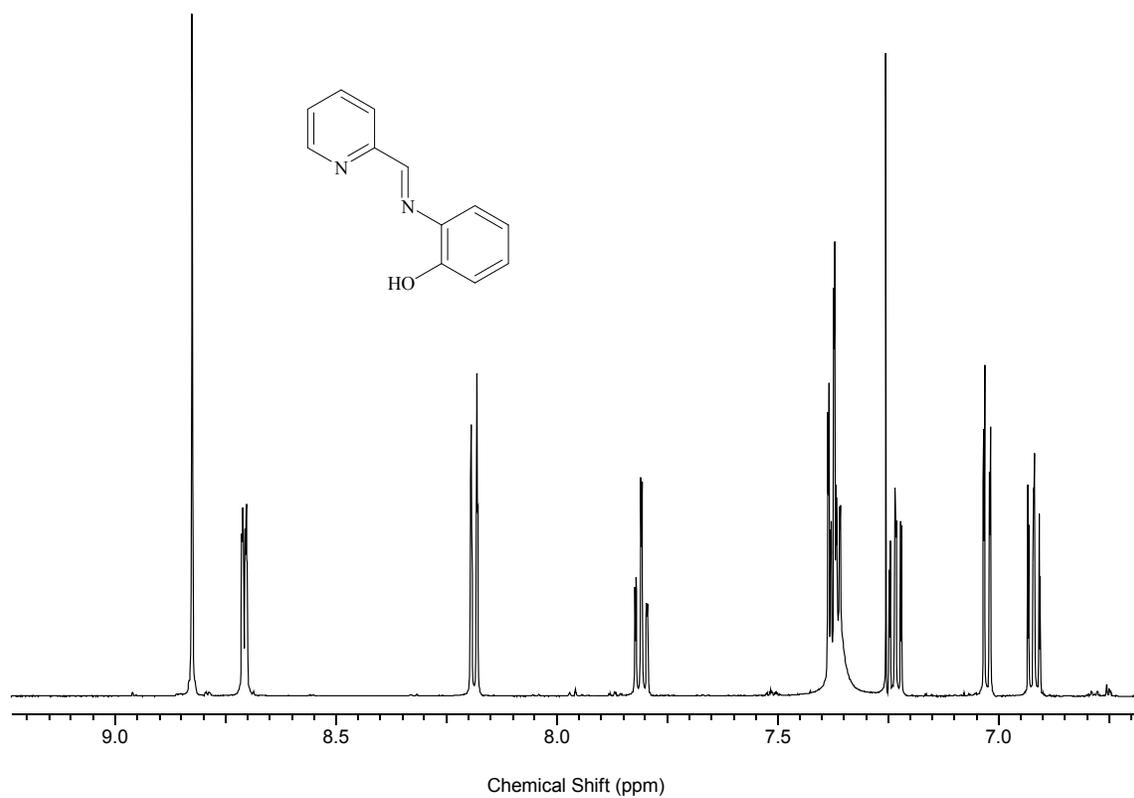


Figure 1S: ¹H NMR spectrum (600 MHz-chloroform-*d*) of 2-(Pyridine-2-ylmethyleneamino)-phenol ligand.

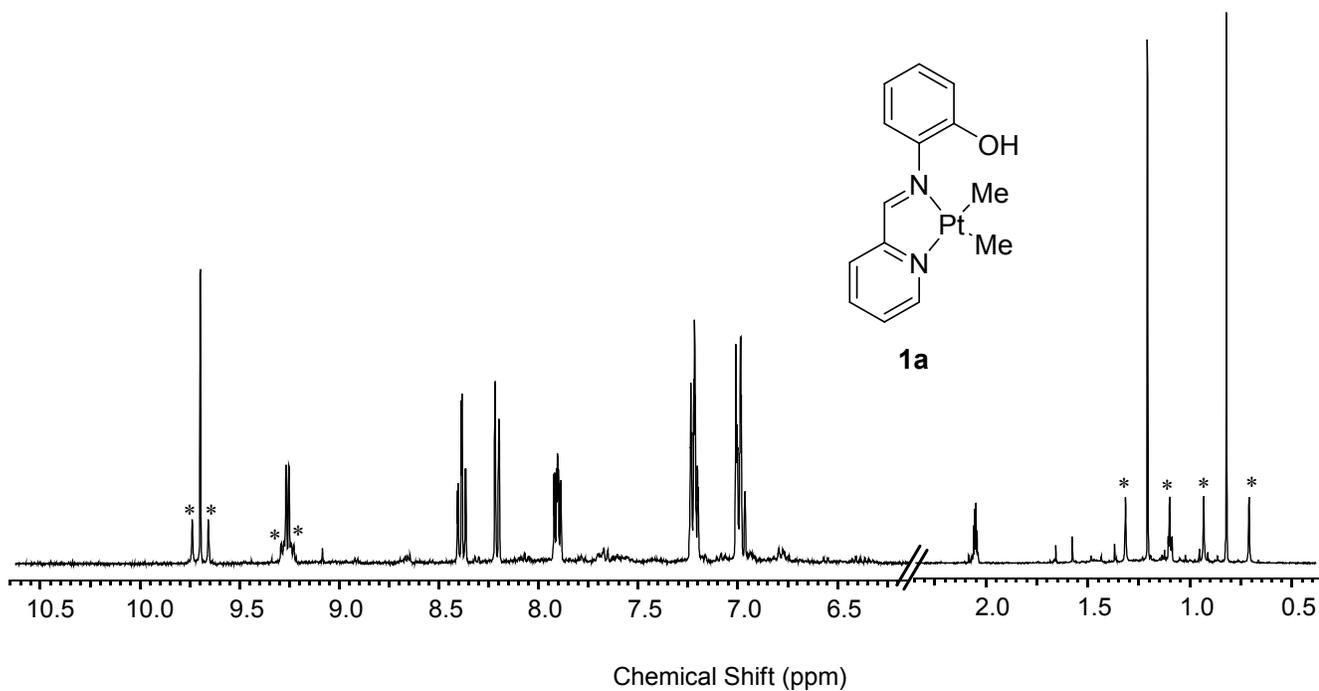


Figure 2S: ^1H NMR spectrum (600 MHz- acetone- d_6) complex **1a**. ^{195}Pt satellite spectra of the are indicated by asterisks.

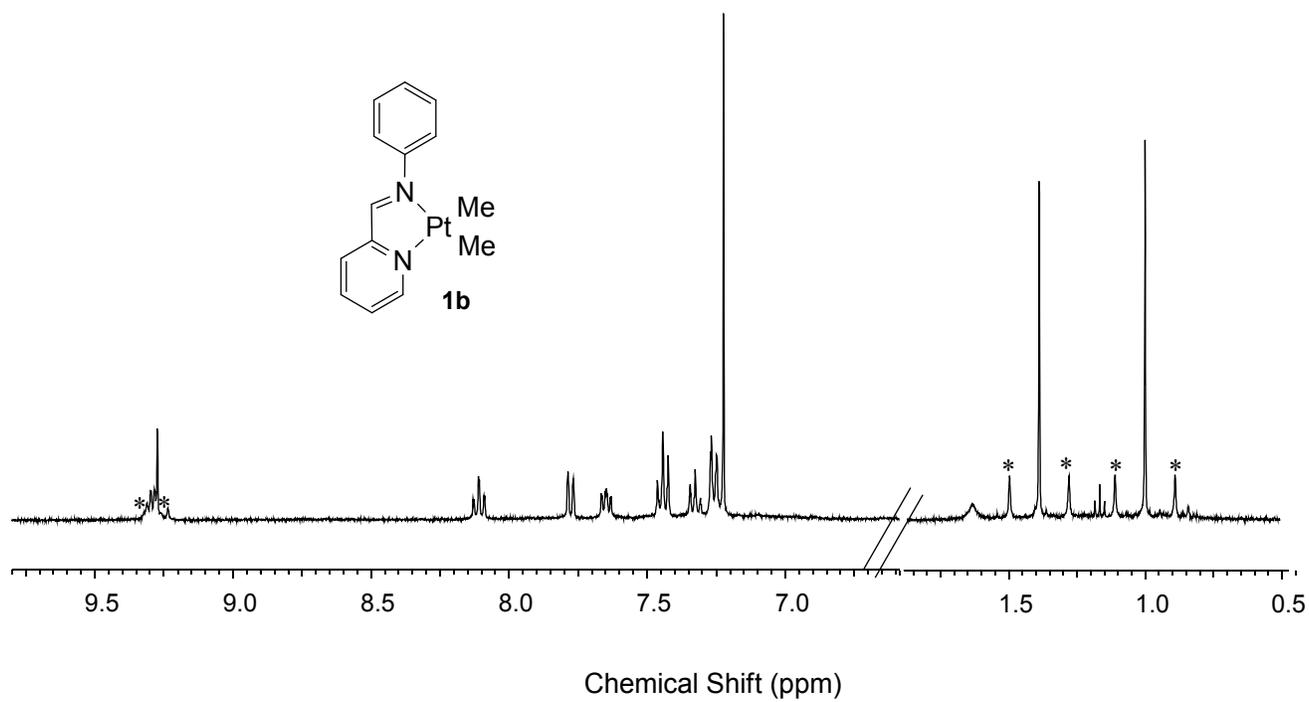


Figure 3S: ^1H NMR spectrum (600 MHz- chloroform-*d*) complex **1b**. ^{195}Pt satellite spectra of the are indicated by asterisks.

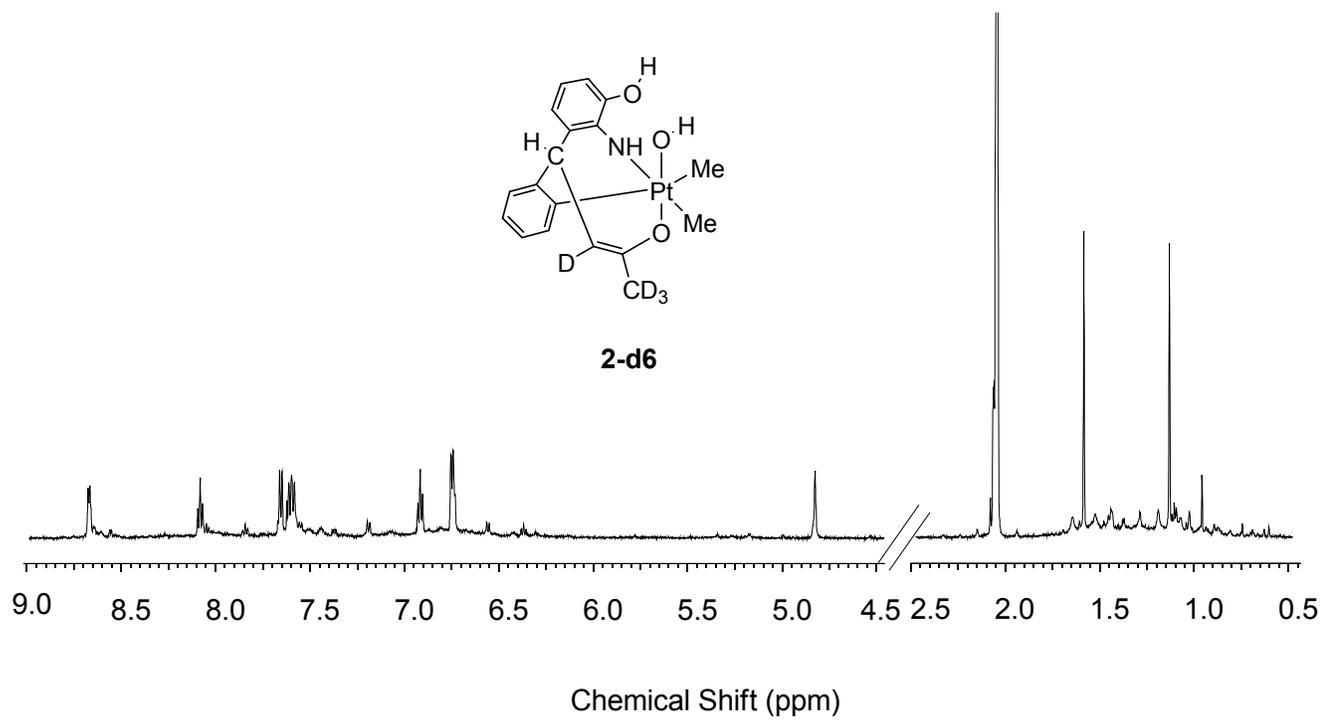


Figure 4S: ^1H NMR spectrum (600 MHz- acetone- d_6) complex **2-d6**.

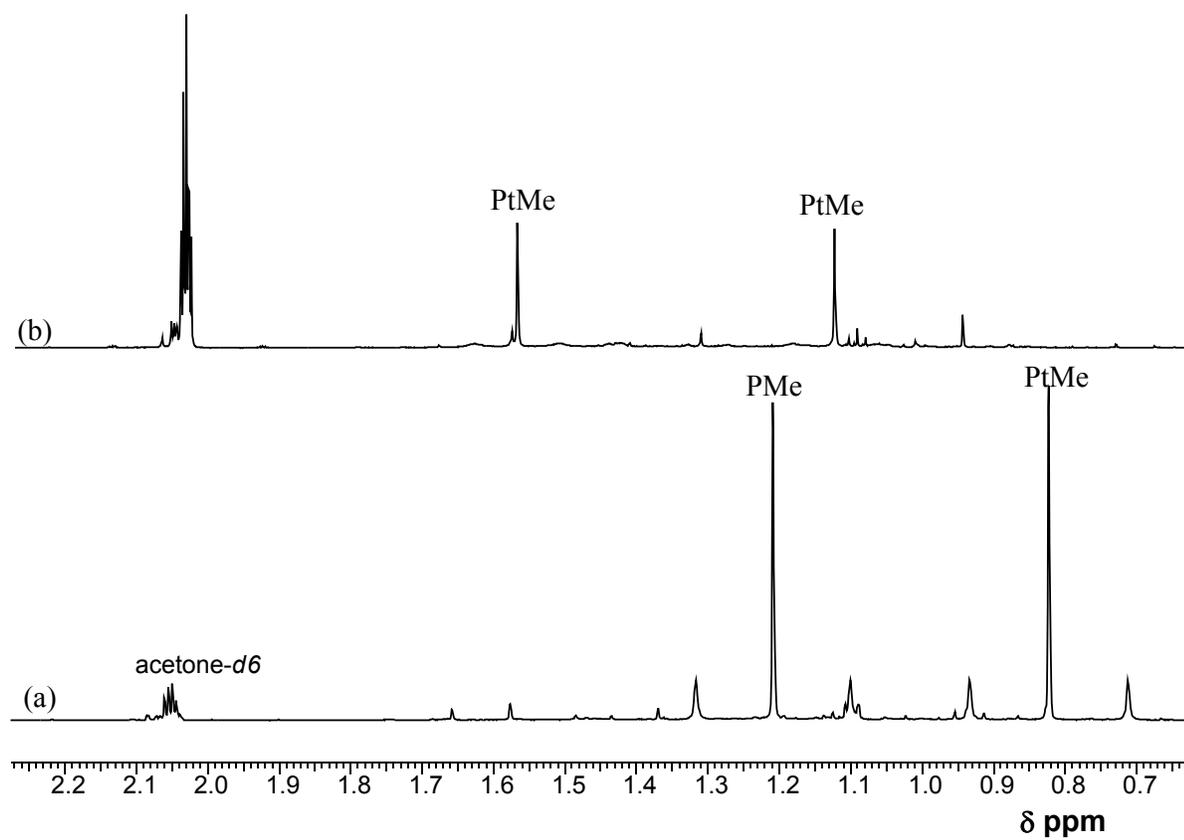


Figure 5S: Changes in the ¹H NMR spectrum in the methylplatinum region of complex **1a**

during reaction with acetone-*d*₆ (a) before O₂ gas addition (b) after 25 min of O₂ gas addition (mostly complex **2-d6**).

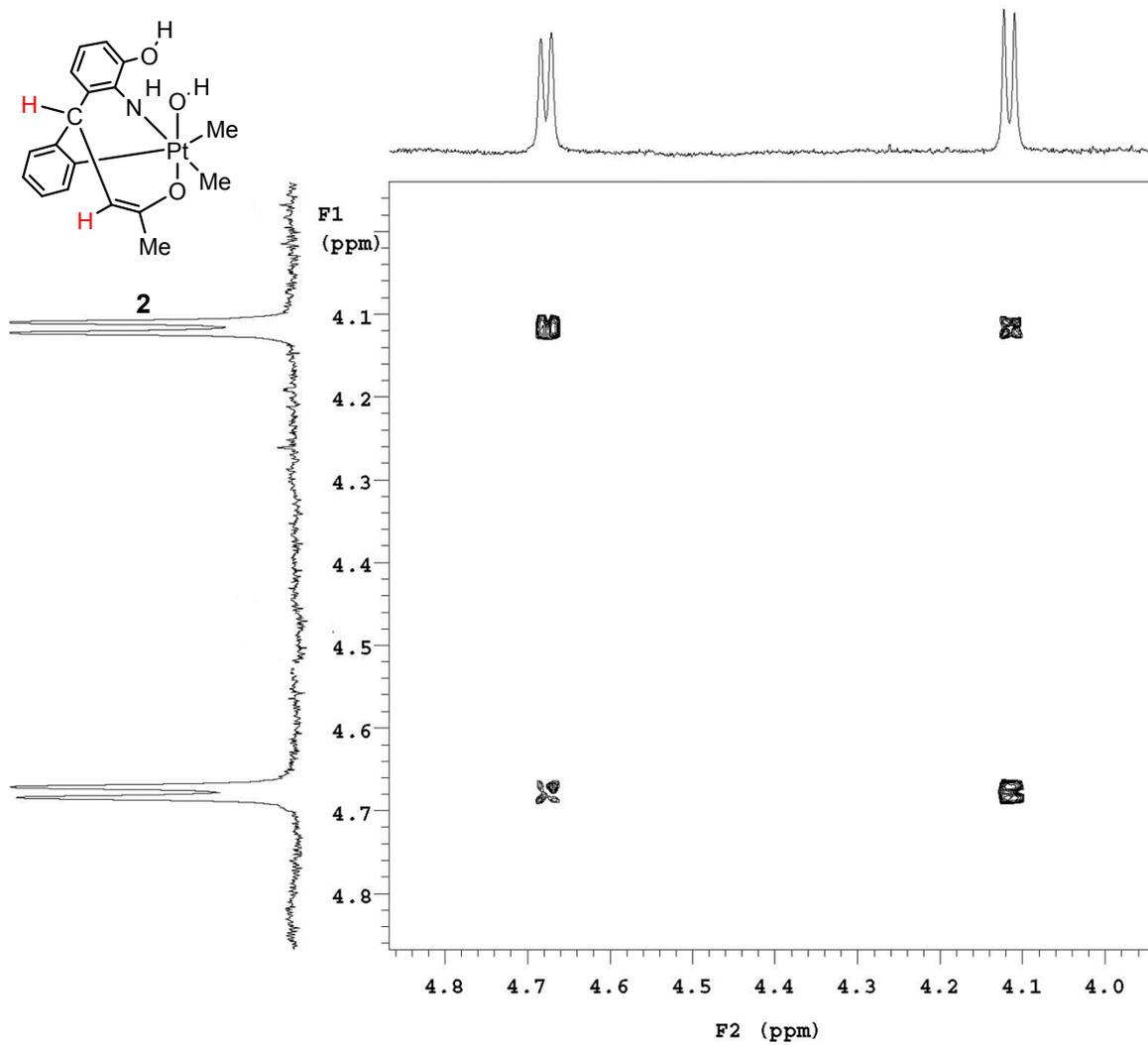


Figure 6S: COSY spectrum of complex **2** ((600 MHz- dichloromethane-*d*₂) in the region δ 3.9-4.9 ppm shows the coupling of CH-CH hydrogens (highlighted in red).