

Supporting Information

Ligand-based Reactivity of a Platinum Bisdithiolene: Double Diene Addition Yields New C₂-Chiral Chelate Ligand

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Experimental Section

General. Samples were prepared in an inert (nitrogen) atmosphere using standard glovebox (MBraun Unilab) and Schlenk-type techniques. Reagents were purchased from Sigma-Aldrich if not specified otherwise. Solvents, including benzene-d₆ (C₆D₆, from Cambridge Isotopes), were dried over sodium/benzophenone and vacuum-transferred prior to use. Re-sealable NMR tubes equipped with a Teflon valve were used to keep NMR samples air-free. Pt[(S₂C₂(CF₃)₂)₂] (1) was prepared using the three-step procedure reported in the literature¹, starting from commercially available (Strem) Pt(PPh₃)₄ and 1,2-bis(trifluoromethyl)dithietene, S₂C₂(CF₃)₂. The latter compound was prepared according to Krespan's² procedure and freshly distilled before use. ¹H NMR spectra were collected on a Bruker Avance III 400 MHz instrument. NMR experiments were performed as described in the main text of the manuscript. Elemental analysis was performed at ANALEST, University of Toronto. Mass spectrometry (ESI) was performed at Advanced Instrumentation for Molecular Structure (AIMS), Toronto, ON, Canada, using an AB/Sciex QStar mass spectrometer.

Compound 3. 90.6 mg of Pt(tfd)₂ (0.139 mmol) were added to a 50 ml round bottom flask and dissolved in 12.5 ml of benzene. To the flask 4.5 equivalents of 1,2-dimethyl-1,3-butadiene (0.626 mmol, 70.8 μL) were added. The solution turned orange upon briefly swirling the mixture. The round bottom flask was connected to a vacuum adapter, sealed under N₂, and allowed to heat at 50°C in an oil bath for 20 hours. The solution appeared a pale yellow after heating. The solvent was removed and the yellow powder was allowed to dry under vacuum for about 1 hour. 99.8 mg of **3** · C₆H₆ (0.112 mmol) were collected (yield = 81 %). Identity and purity of the product were confirmed by ¹H- and ¹⁹F-NMR spectroscopy. NMR data are described in the main text of the manuscript. Results of the crystal structure determination of **3** (experimental details included) are available in CIF format at <http://pubs.acs.org>. Compound **3** co-crystallizes with one equivalent of C₆H₆, which is directly observed in the X-ray structure determination. Partial loss of benzene occurs upon storage. See Figure S1 for a thermal ellipsoid drawing that includes the benzene solvate. Anal. Calc. for C₂₀H₂₀F₁₂Pt₁S₄ · ²/₃ C₆H₆: C: 33.37 %, H: 2.80 %; Found: C: 33.30 %, H: 2.71%. High-resolution MS (ESI) for **3**-H⁺ (C₂₀H₂₁F₁₂Pt₁S₄⁺) matches prediction (Figure S2).

¹ Davison, A.; Edelstein, N.; Holm, R. H.; Maki, A. H. *Inorg. Chem.* **1964**, 3, 814.

² Krespan, C. G. *J. Am. Chem. Soc.* **1961**, 83, 3434

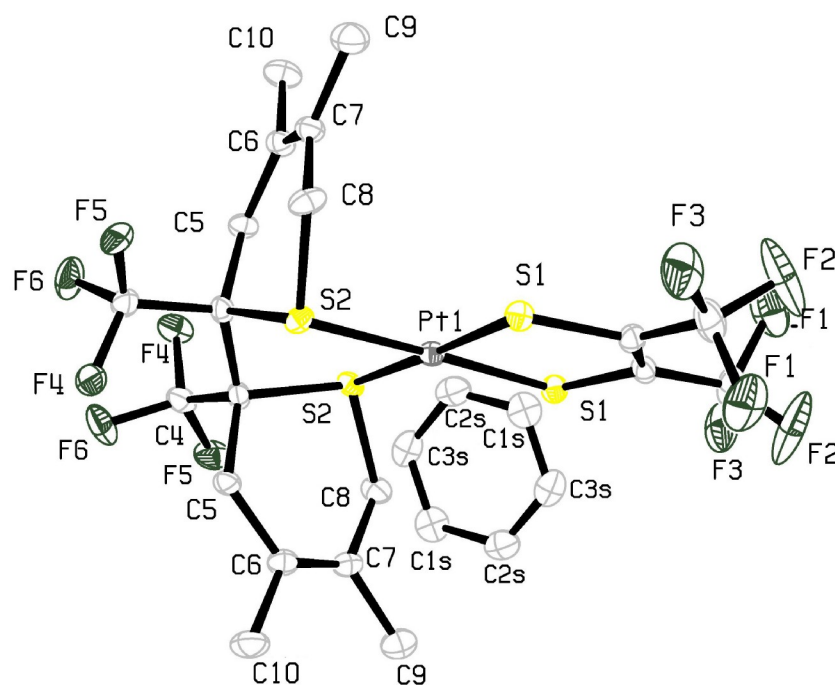


Figure S1. Molecular structure of **3**, showing the benzene solvate molecule as well

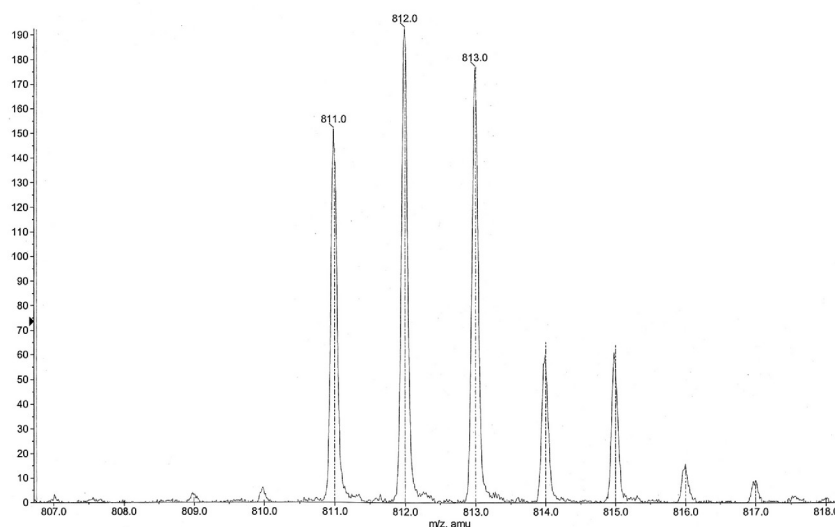


Figure S2. Experimental (spectrum) vs. calculated (dotted lines) mass spectrum (ESI) for **3-H⁺**

Equilibrium constant for 1 + 2,3-dimethyl-1,3-butadiene $\xrightleftharpoons{\text{R}}$ 2

Pt(tfd)₂ (compound **1**) (4.8 mg, 0.0074 mmol) was weighed into a weigh-boat and then transferred to a vial. To the vial was added C₆D₆ (5.0 mL). 3,5-Bis(trifluoromethyl)bromobenzene (BTBB) (Sigma Aldrich, 99 %) (4.0 µL, 6.8 mg, 0.023 mmol) was added to the mixture, followed by 2,3-dimethyl-1,3-butadiene (Alpha Aesar, 98%) (1.5 µL, 1.1 mg, 0.013 mmol). The mixture was shaken vigorously for ca. 2 min to ensure complete mixing, to give a solution having the initial concentrations [1]₀ = 1.5 mM, [diene]₀ = 2.6 mM, [BTBB] = 4.6 mM. Immediately upon addition of the diene, the color changed from purple to brown-yellow and the solution was homogenous by visual inspection. From this solution, 0.50 mL were taken and placed in a J. Young NMR tube, which was sealed under nitrogen. Within 20 min of adding the diene (sample kept at RT), ¹H and ¹⁹F NMR spectra were collected at 296(1) K to obtain equilibrium concentrations of diene (from ¹H NMR) and compounds **1** and **2** (from ¹⁹F NMR), using integration values relative to the internal standard, BTBB. The following concentrations were obtained from NMR integration and were used to calculate the equilibrium constant:

$$K_{\text{eq}} = [\mathbf{2}]_{\text{eq}} / \{[\mathbf{1}]_{\text{eq}}[\text{diene}]_{\text{eq}}\} = (0.0012 \text{ M}) / \{(9.5 \times 10^{-5} \text{ M})(0.0014 \text{ M})\} = 9.0 \times 10^3 \text{ M}^{-1}$$

As additional confirmation, another NMR sample was prepared by diluting 0.25 mL of the above stock solution with 0.25 mL of C₆D₆, in order to re-establish equilibrium in a more dilute solution. The equilibrium rapidly adjusted, and the new concentrations were again obtained via NMR integration to yield an identical (within 4 %) equilibrium constant:

$$K_{\text{eq}} = [\mathbf{2}]_{\text{eq}} / \{[\mathbf{1}]_{\text{eq}}[\text{diene}]_{\text{eq}}\} = (0.00058 \text{ M}) / \{(9.5 \times 10^{-5} \text{ M})(0.00070 \text{ M})\} = 8.7 \times 10^3 \text{ M}^{-1}$$

The largest source of error resides in the addition of the small amount of internal standard and the determination of the equilibrium concentration via NMR integration. From the magnitude of these errors, the overall error is estimated to be ca. 23 %, and we report the equilibrium constant as $9 (\pm 2) \times 10^3 \text{ M}^{-1}$.