

## Supporting information

### **Organometallics in Superacidic Media: Characterization of Remarkably Stable Platinum-Methyl Bonds in HF/SbF<sub>5</sub> Solution**

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***The following are some notes regarding the use of sapphire NMR tubes. Even though the burst rating of the tubes (4500 psi) is well above the pressures that most users will employ, there is always the possibility that rupture could occur at lower pressures, and the valve and/or its epoxy attachment to the sapphire tube body is a potential weak point. It is strongly recommended that these tube/valve assemblies be tested at pressures significantly higher than the desired operating pressure before each use.***

**Sample prep:** The NMR tube is filled with a solvent mixture and placed in a spinner (NOTE: Depending on the final dimensions of the valve and tube, a spinner might have to be machined to fit this tube). The NMR tube valve is attached to a gas cylinder (or vacuum line, if a condensable gas is used) with a 1/8" Swagelok fitting. We generally place the sapphire tube assembly in the hood behind a Plexiglas safety shield, flush out the line with the desired gas, then tighten the fitting. The valve is then opened (using a wrench: in our design the valve is slotted for a wrench; not much force is required: the wrench is just for leverage), and the tube is pressurized to the desired level. For additional safety, we typically over-pressurize if we are below 2000 psi as a safety check. If everything looks good, the valve is closed and the swagelok fitting is removed. Venting after the experiment is carried out in a hood.

For transportation, the tube is placed in a cylindrical Plexiglas (or Lexan) carrier. We just have one end that the spinner fits in with a set screw, and the other end swing away on a screw so the tube can be lowered into the probe.

We don't use any special shielding around the NMR probe. The tube/metal valve assembly is much heavier than a normal tube, so some care should be taken lowering it into the probe. We prefer to attach monofilament fishing line onto the 1/8" swagelok fitting and to lower the tube. If the tube is not spun, one can simply leave the string hanging out of the bore and use it to retrieve the tube after the experiment. Ejecting using pneumatic pressure may be okay (use the safety carrier both to lower the tube out of bottom of it and to catch the ejected tube), but for heavier tube/valve assemblies we don't recommend this.

As far as student training, Both the Roe article and the Horvath review should be read before using sapphire tubes. They should also get approval for their particular experiment: pressures of condensable gases at operating temperatures, in particular, should be carefully verified.

The following is a list of relevant literature on the subject of solution high-pressure NMR using sapphire tubes:

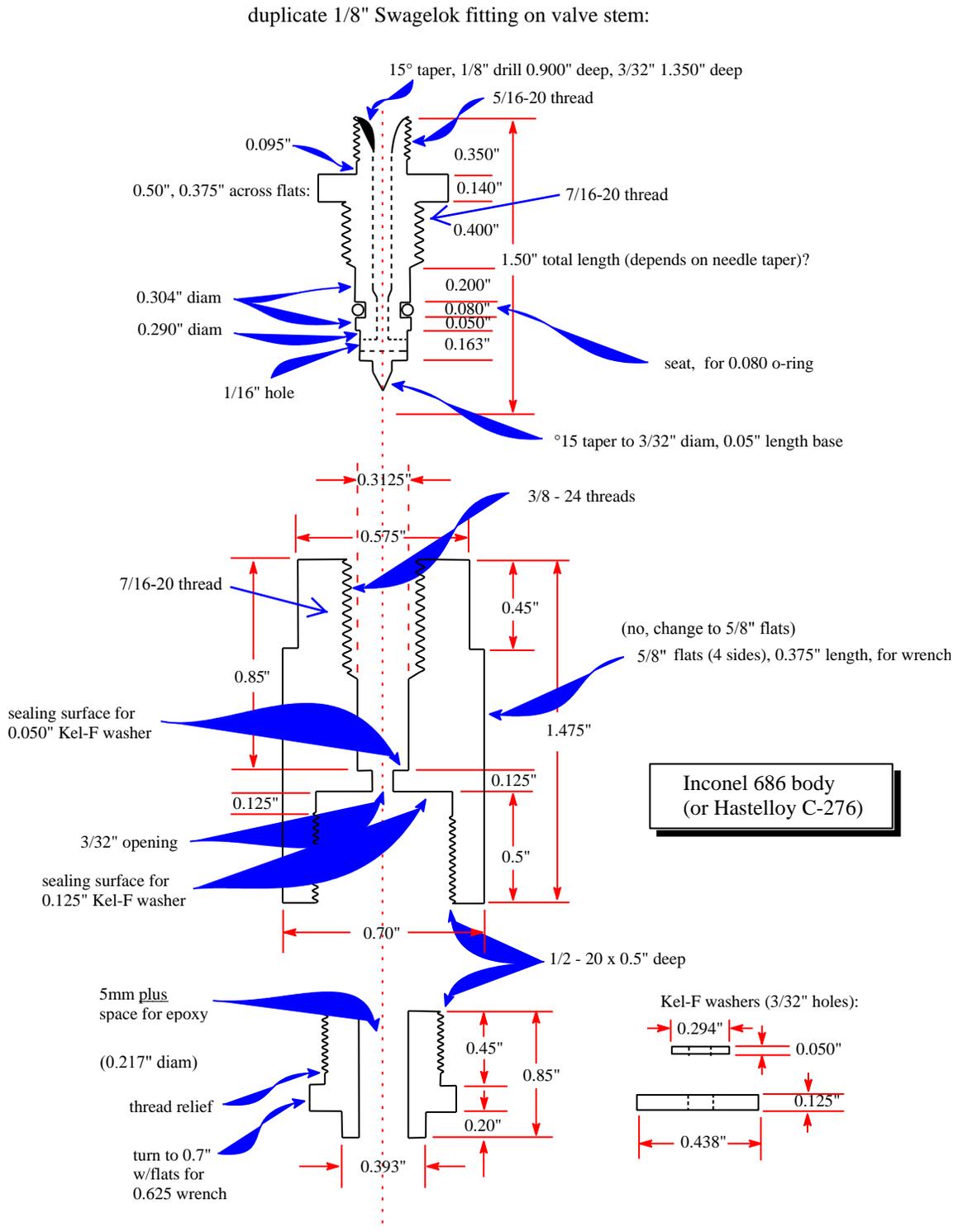
- 1) D. Christopher Roe, "Sapphire NMR Tube for High-Resolution Studies at Elevated Temperatures", *J. Mag. Res.* 63, 388-391 (1985)
- 2) I. T. Horvath and J. M. Millar, "NMR under High Gas Pressure", *Chem. Rev.* 91, 1339-1351 (1991)
- 3) I. T. Horvath and E. C. Ponce, "New Valve Design for High-Pressure Sapphire Tubes for NMR Measurements", *Rev. Sci. Instrum.* 62, 1104-1105 (1991)

- 4) Y. H. Lim, N. E. Nugara, and A. D. King, Jr., "NMR Chemical Shifts of Xenon-129 in Liquid Carbon Dioxide, Nitrous Oxide, Ethane, and Propane at 23 C", *J. Phys. Chem.*, 97, 8816-8819 (1993)
- 5) A. Cusanelli, U. Frey, D. T. Richens, A. E. Merbach, "The Slowest Water Exchange at a Homoleptic Mononuclear Metal Center: Variable-Temperature and Variable-Pressure  $^{17}\text{O}$  NMR Study on  $[\text{Ir}(\text{H}_2\text{O})_6]^{3+}$ ", *J. Am. Chem. Soc.* 118, 5265-5271 (1996)

Reference #4 describes the simplest valve design. We use the Aremko epoxy referenced in Horvath's article.

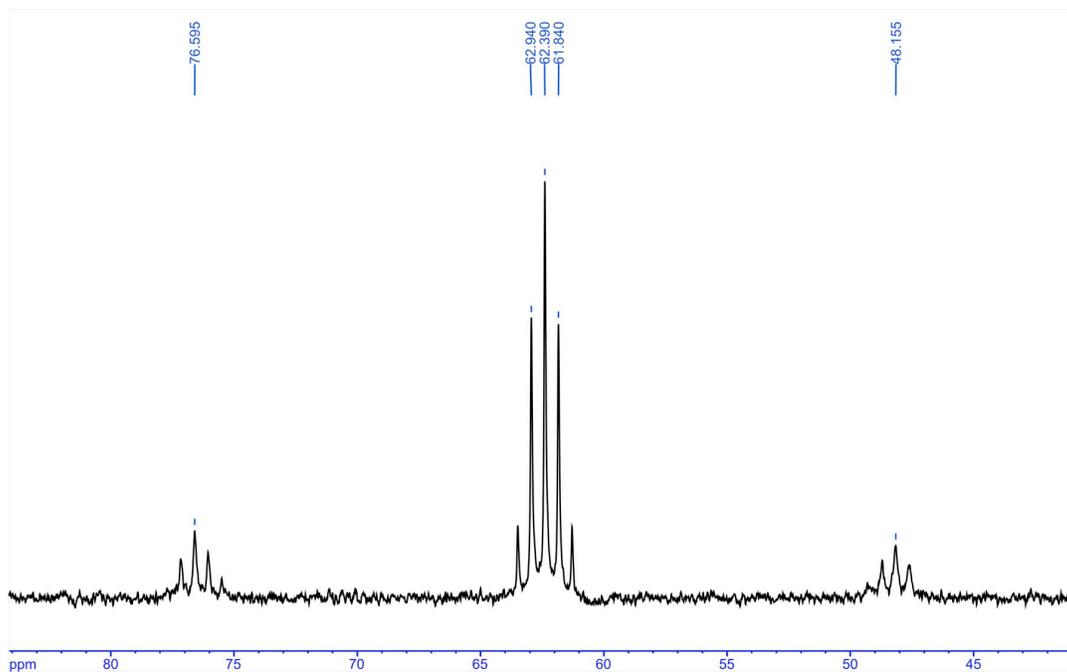
**Sapphire NMR Assembly Design:** We have designed several modified metal valves. Our latest design (see **Figure S-a**) is similar to that in reference #5, with the exception that the tube/valve seal is made by pressing the sapphire tube end directly into a Kel-F washer. This is done to eliminate contact of the tube contents with the epoxy seal. In our work with superacidic/oxidizing solutions, it is very important to make the entire assembly as corrosion-resistant as possible. We have therefore constructed our valve from **Inconel 686**, which is one of the best nonmagnetic corrosion-resistant alloys available (similar to Hastelloy C-276; see [www.specialmetals.com](http://www.specialmetals.com) for technical information about chemically-resistant alloys).

**Figure S-A.** Design schematic for corrosion-resistant Sapphire NMR tube valve

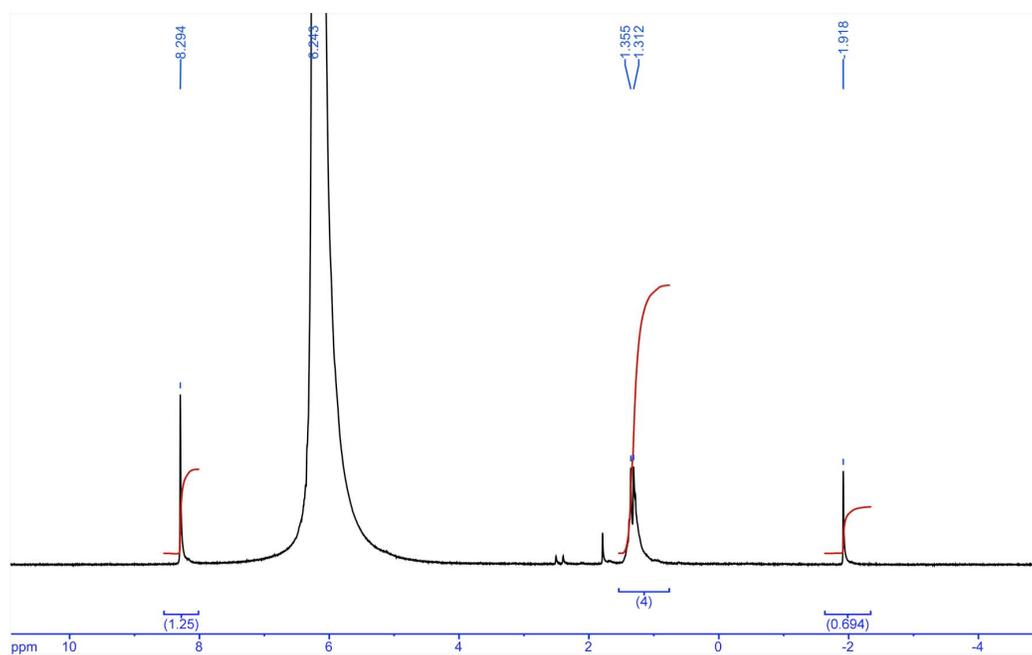


## NMR Spectra.

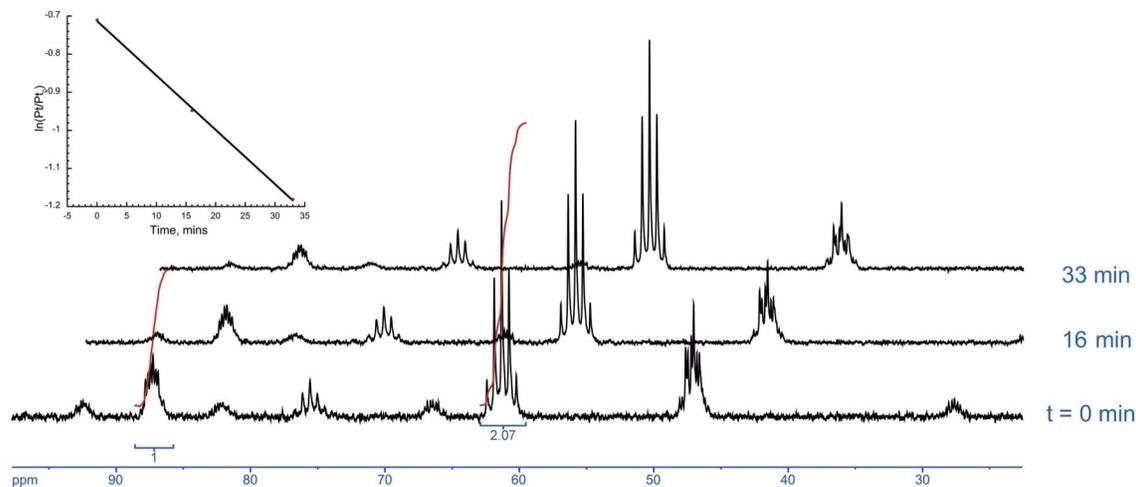
**Figure S1.**  $^{31}\text{P}$  (161.97 MHz) NMR spectrum of  $(\text{dfepe})\text{Pt}^{2+}$  (**2**) generated from  $(\text{dfepe})\text{Pt}(\text{Me})_2$  dissolved in 10 mol%  $\text{SbF}_5\text{-HF}$  at 25 °C.



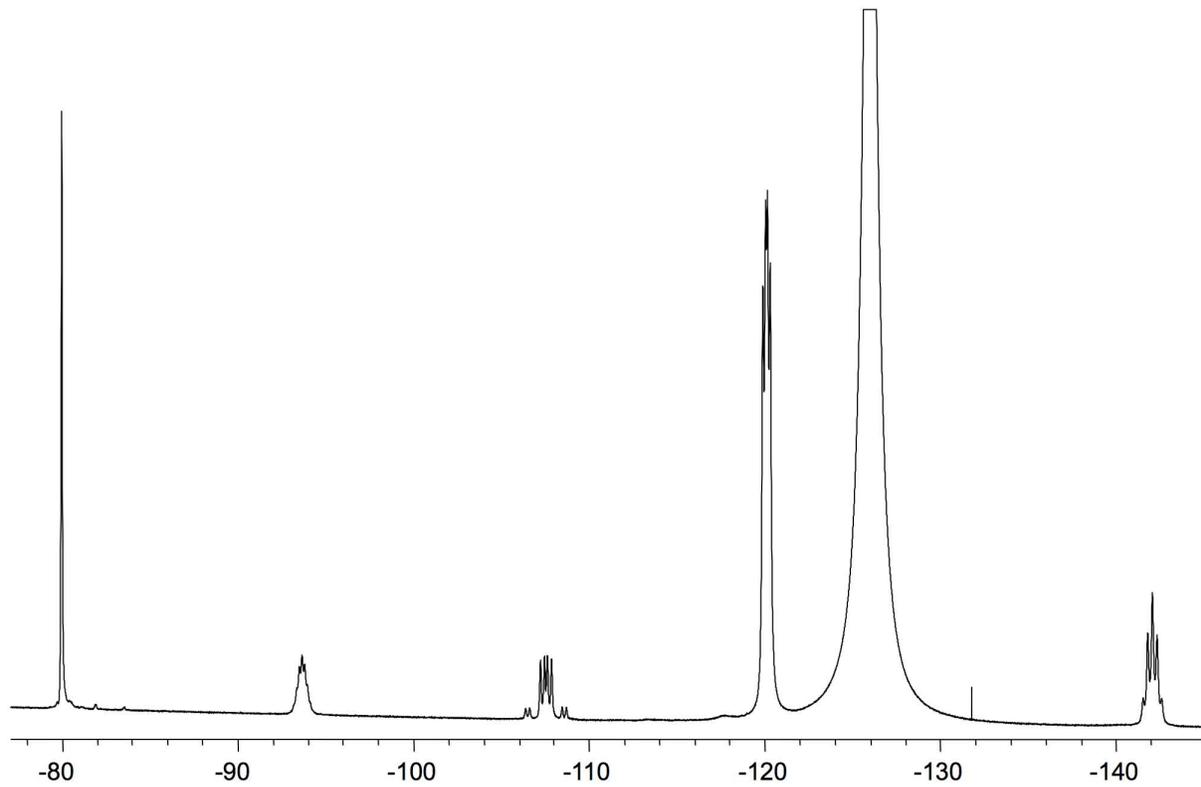
**Figure S2.**  $^1\text{H}$  (400.13 MHz) NMR spectrum of  $(\text{dfepe})\text{Pt}^{2+}$  (**2**) generated from  $(\text{dfepe})\text{Pt}(\text{Me})_2$  dissolved in 10 mol%  $\text{SbF}_5\text{-HF}$  at 25 °C.



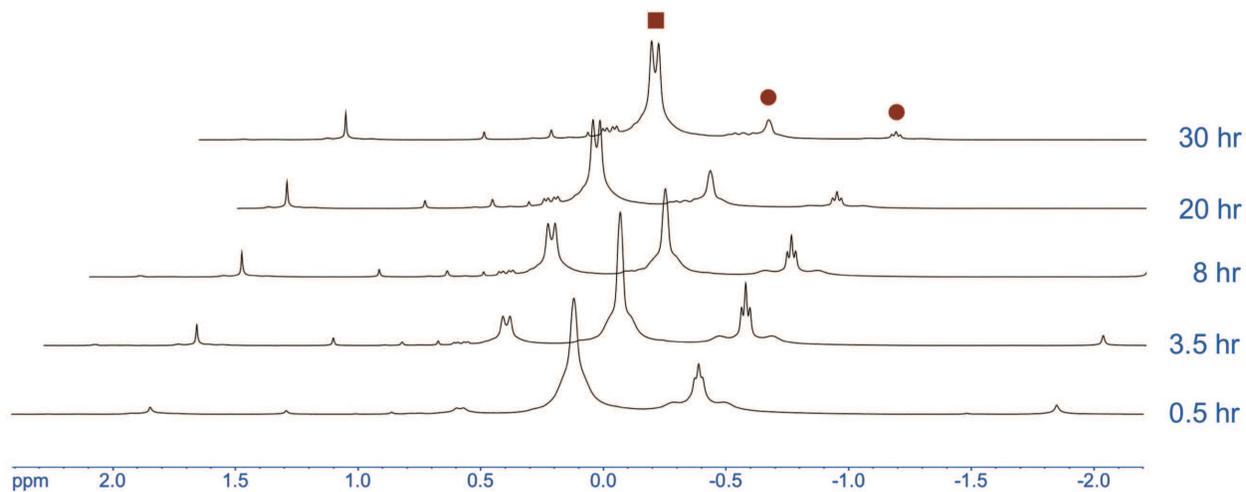
**Figure S3.**  $^{31}\text{P}$  (161.97 MHz) NMR spectrum of  $(\text{dfepe})\text{Pt}(\text{Me})_2$  product in 10 mol%  $\text{SbF}_5\text{-HF}$  at  $-20\text{ }^\circ\text{C}$  as a function of time, with 1<sup>st</sup> order inset plot



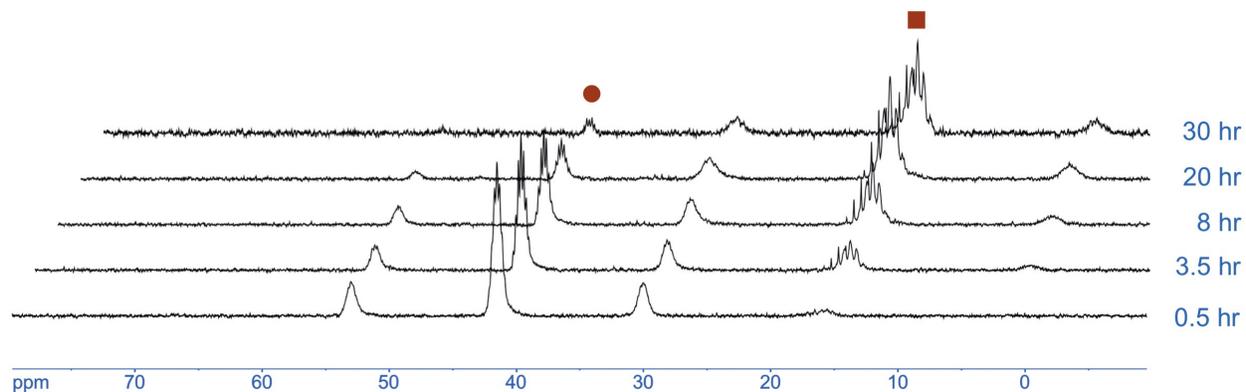
**Figure S4.**  $^{19}\text{F}$  (376.46 MHz) NMR spectrum of  $(\text{dfepe})\text{Pt}^{2+}$  (**2**) in 10 mol%  $\text{SbF}_5\text{-HF}$ , after cooling to  $-90\text{ }^\circ\text{C}$ . The resonances at  $-79.9$  and  $-107.5$  are due to  $\text{CF}_3$  and  $\text{CF}_2$  of the dfepe ligand, respectively, the resonances at  $-93.6$ ,  $-120$ , and  $-142$  are due to the  $\text{Sb}_2\text{F}_{11}^-$  anion, and the resonance at  $-125.9$  is due to the  $\text{SbF}_6^-$  anion. The signal due to HF at  $-184$  ppm is not shown.



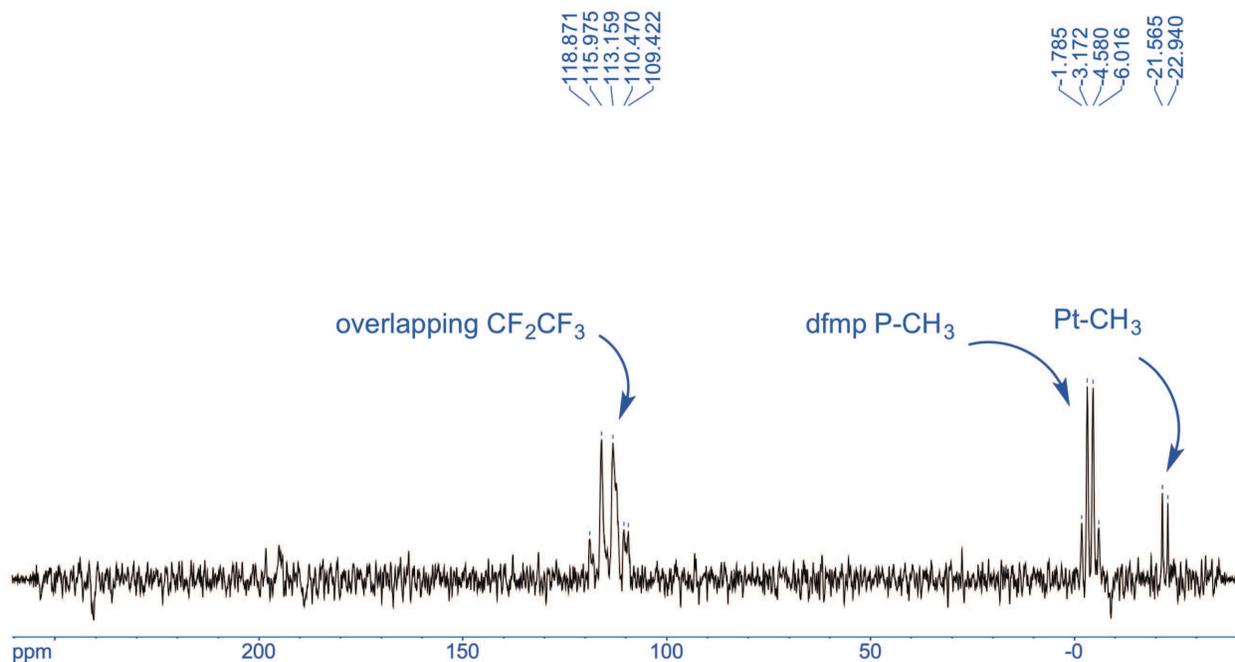
**Figure S5.**  $^1\text{H}$  (400.13 MHz) NMR spectra showing the thermal conversion of *trans*-(dfmp) $_2\text{Pt}(\text{Me})^+$  (**3**, labeled ●) to *cis*-(dfmp) $_2\text{Pt}^{2+}$  (**4**, labeled ■) in 50 mol%  $\text{SbF}_5\text{-HF}$  at 20 °C. The chemical shift scale is not referenced.



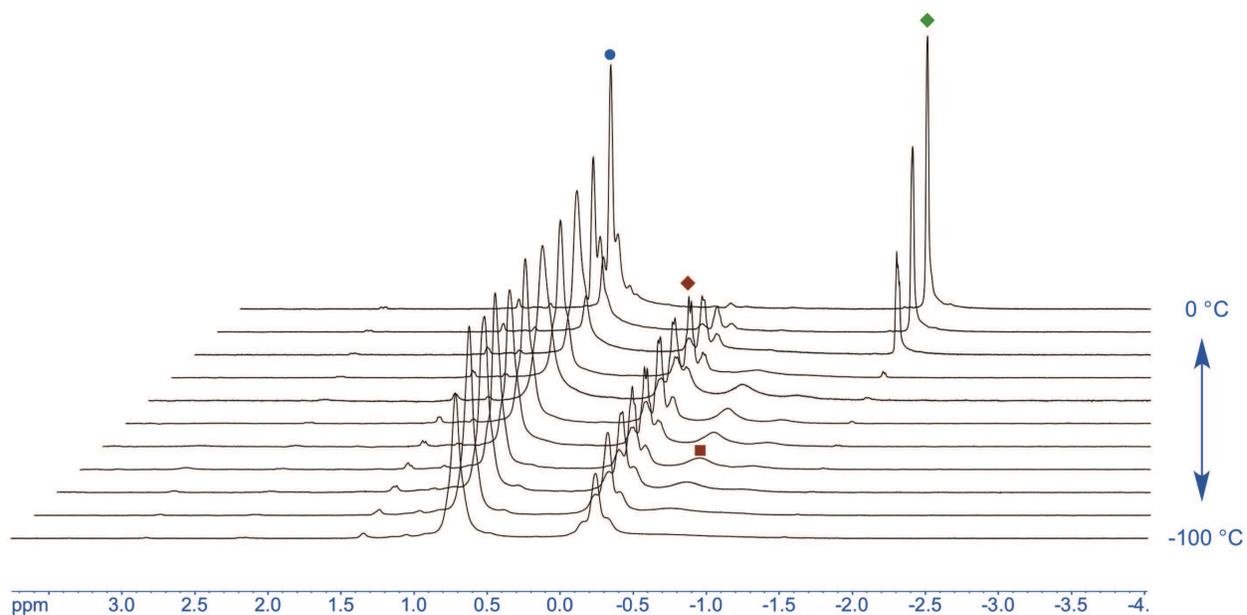
**Figure S6.**  $^{31}\text{P}$  (161.97 MHz) NMR spectra showing the thermal conversion of *trans*-(dfmp) $_2\text{Pt}(\text{Me})^+$  (**3**, labeled ●) to *cis*-(dfmp) $_2\text{Pt}^{2+}$  (**4**, labeled ■) in 50 mol%  $\text{SbF}_5\text{-HF}$  at 20 °C.



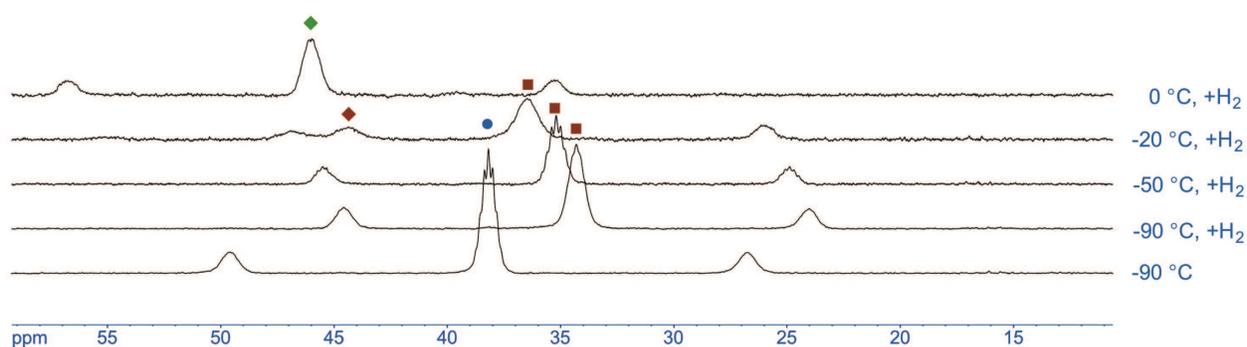
**Figure S7** Coupled  $^{13}\text{C}$  (100.62 MHz) NMR spectrum of  $(\text{dfmp})_2\text{Pt}(\text{Me})^+$  (**3**) in 10 mol%  $\text{SbF}_5\text{-HF}$  at  $-60\text{ }^\circ\text{C}$ .



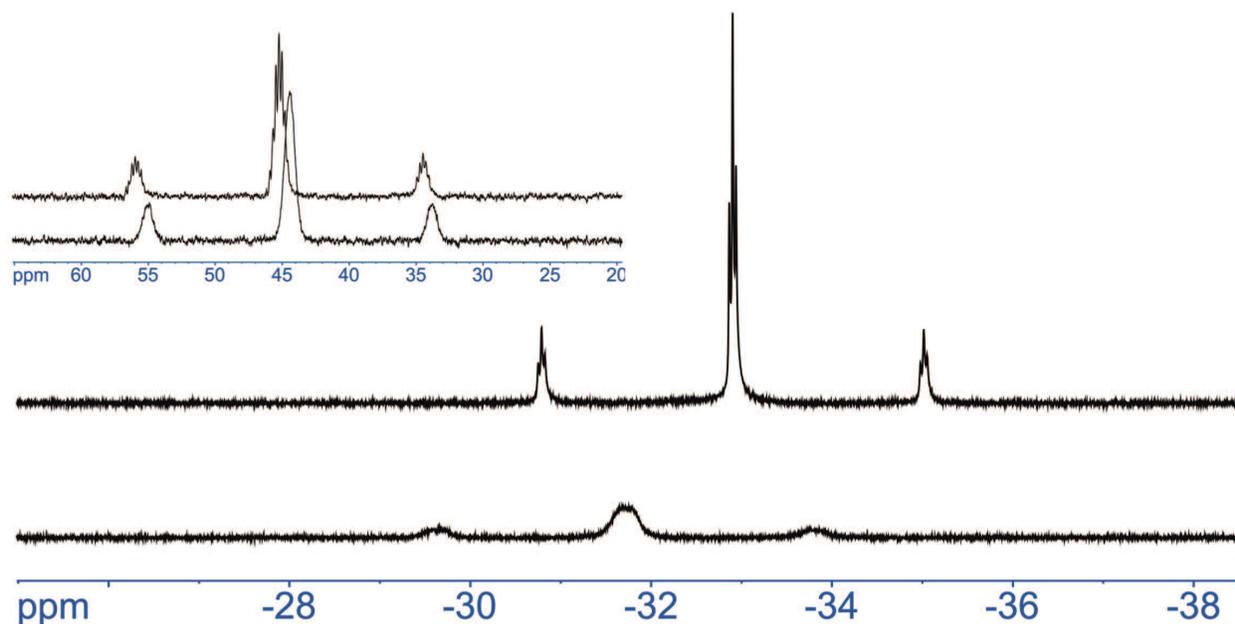
**Figure S8.**  $^1\text{H}$  (400.13 MHz) VT NMR spectra in 10 degree increments from  $-100$  to  $0\text{ }^\circ\text{C}$  showing the thermal stability of  $\text{trans}-(\text{dfmp})_2\text{Pt}(\text{Me})(\eta^2\text{-H}_2)^+$  (**5**) in 10 mol%  $\text{SbF}_5\text{-HF}$  under 200 psi  $\text{H}_2$ . The  $\text{Pt-CH}_3$  and  $\text{Pt-H}_2$  resonances are labeled by  $\blacklozenge$  and  $\blacksquare$ , respectively. The onset of  $\text{trans}-(\text{dfmp})_2\text{Pt}(\text{H})(\eta^2\text{-H}_2)^+$  (**6**) formation begins at  $-20\text{ }^\circ\text{C}$  with the appearance of free methane (labeled  $\blacklozenge$ ). Overlapping dfmp methyl resonances are indicated by  $\bullet$ .



**Figure S9.**  $^{31}\text{P}$  (161.97 MHz) VT NMR spectra showing the conversion of *trans*-(dfmp) $_2\text{Pt}(\text{Me})^+$  (**3**, labeled  $\bullet$ ) to *trans*-(dfmp) $_2\text{Pt}(\text{Me})(\eta^2\text{-H}_2)^+$  (**5**, labeled  $\blacksquare$ ) in 10 mol%  $\text{SbF}_5\text{-HF}$  under 200 psi  $\text{H}_2$ . *trans*-(dfmp) $_2\text{Pt}(\text{H})^+$  (**6**, labeled  $\blacklozenge$ ) begins to form at  $-20\text{ }^\circ\text{C}$  and is the sole species observed at  $0\text{ }^\circ\text{C}$ .



**Figure S10.**  $^1\text{H}$  (400.13 MHz) NMR spectra, hydride region, at  $20\text{ }^\circ\text{C}$  of *trans*-(dfmp) $_2\text{Pt}(\text{H})^+$  (**6**) in 10 mol%  $\text{SbF}_5\text{-HF}$  under 200 psi  $\text{H}_2$  (bottom spectrum) and after  $\text{H}_2$  removal (top spectrum). The inset shows the corresponding  $^{31}\text{P}$  NMR spectra.



**Figure S11.**  $^1\text{H}$  (400.13 MHz) VT NMR spectra of *trans*-(dfmp) $_2\text{Pt}(\text{CD}_3)(\eta^2\text{-H}_2)^+$  (**5-d<sub>3</sub>**) in 10 mol%  $\text{SbF}_5\text{-HF}$  under 200 psi  $\text{H}_2$ . The residual  $\text{Pt-CD}_x\text{H}_{3-x}$ , the  $\text{Pt-H}_2$ , and the free methane peaks are labeled  $\blacksquare$ ,  $\bullet$ , and  $\blacklozenge$ , respectively. The large unlabeled resonance is due to the dfmp methyl group. The chemical shift scale is not referenced.

