Reversible Insertion/De-insertion of Carbon Dioxide into Pt(II)-Hydroxo Bonds

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Supporting Information

List of figures for supporting information:

Table S2. Data collection and refinement data for 1 **1-Me**.　　　　　　**S19**

General considerations.

An argon filled glove box was employed for manipulation and storage of all oxygen and moisture sensitive compounds. All reactions were performed on a double manifold high vacuum line using standard techniques.[1] Residual oxygen and moisture were removed from the argon stream by passage through an OxisorBW scrubber from Matheson Gas Products. Toluene, tetrahydrofuran, and hexanes solvents were dried and purified using the Grubbs/Dow purification system and stored in evacuated 500 mL bombs over sodium- tetraglyme/benzophenone ketyl. Pentane and dichloromethane were dried, distilled, and stored in an evacuated 500 mL bombs over sodium-tetraglyme/benzophenone ketyl (pentane) and calcium hydride (dichloromethane). All solvents were distilled prior to use. Water and deuterium oxide were degassed by 3 freeze-pump-thaw cycles and stored in a glovebox designated for water usage, or in a sealed glass bomb. d_6-benzene and d_2-methylene chloride were dried over and distilled from CaH_2, and was stored in glass bombs in a glove box. ^1H, and ^{13}C chemical shifts were referenced to residual proton, and naturally abundant ^{13}C resonance of the deuterated solvent, respectively. Assignments of chemical shifts are based on ^1H, ^2H, ^{13}C, DQF-COSY, $^1H,^{13}C$-HMQC, and NOESY NMR spectra performed on Bruker RDQ-400, DRY-400, UGI-400 and CFI-600 spectrometers. NMR spectra were processed and analyzed with MestReNova (v7.0.2-8636). High-resolution mass spectra were obtained using a Bruker Esquire 3000 spectrometer operating in electrospray ionization (ESI) mode. X-ray crystallographic analyses were performed on suitable crystals coated in Paratone 8277 oil (Exxon) and mounted on a glass fibre. Measurements were collected on a Nonius KappaCCD diffractometer by Dr. Masood Parvez of this department; full details can be found in the independently deposited crystallography information files (cif). Elemental analyses were performed using a Perkin-Elmer model 2400 series II analyzer by Johnson Li of this department. Absolute ethanol and Silver(1) oxide were purchased from Aldrich and used as received. Carbon dioxide, bone-dry grade 3.0, and $^{13}CO_2$ (99% ^{13}C) were obtained from Praxair and Cambridge Isotopes and used as received. All NMR solvents were purchased from Cambridge Isotope Laboratories Inc. and dried according

to the procedures outlined above or used as received. All air-sensitive compounds were stored in the glove box. *trans*-[Pt(SMe$_2$)$_2$(CH$_3$)Cl][2] was synthesized according to reported procedures. Compound **1**, **2**, and **L** have been reported elsewhere.[3,4] The IR of **3** was done as a THF film sandwiched between two NaCl plates and sealed from air in the glovebox by sealing the outer edges of the plates with black electrical tape.
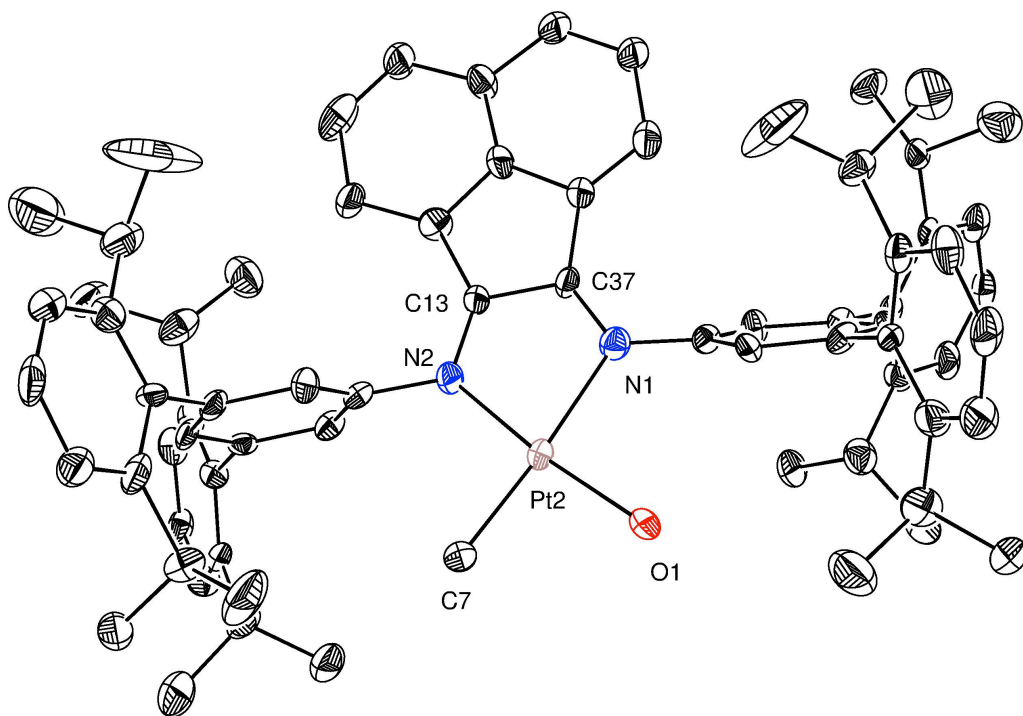
Figure S1. X-ray molecular structure of **1-Me** (R factor 11.81%). Ellipsoids are shown at 30% probability and hydrogen atoms have been omitted for clarity. Due to low quality of data, structure is just used to show connectivity.
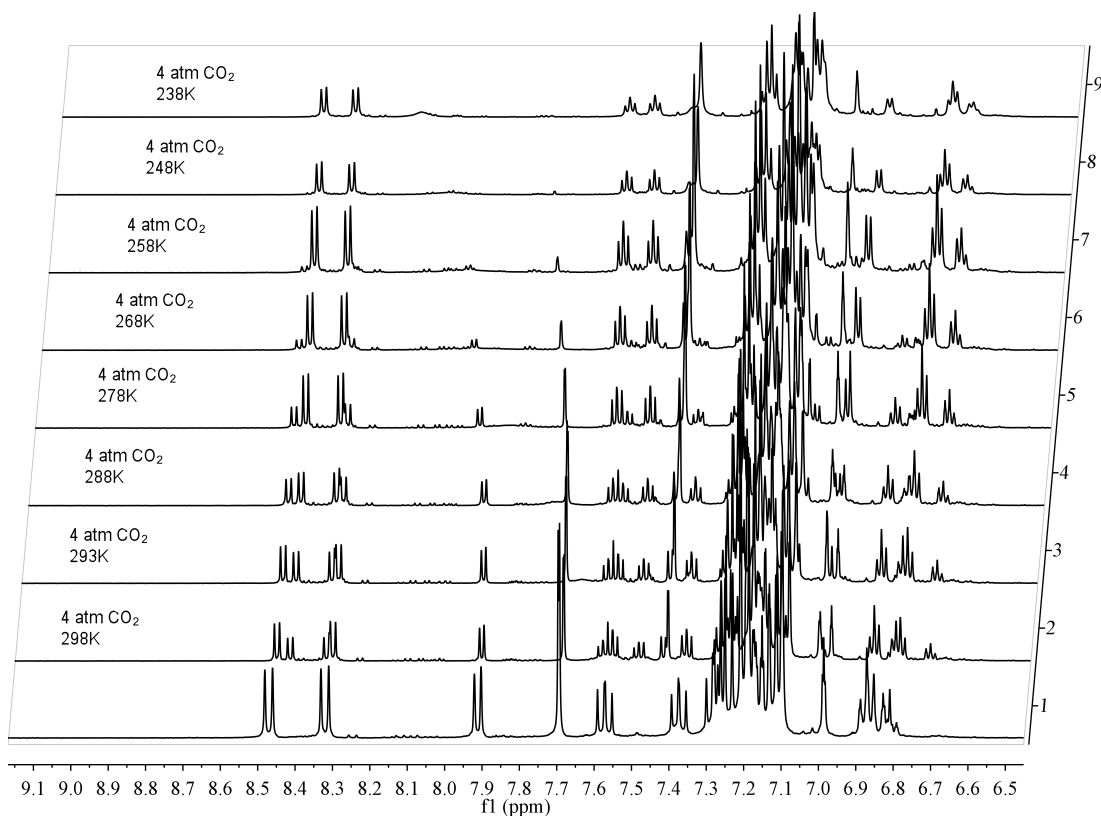
Figure S2. Variable Temperature [^1]H NMR plot of the aromatic region of **1-Ph** and **4-Ph** under 4 atm $^{13}CO_2$.

Method for determination of [CO₂] at different temperatures in THF[5,6]:

The equilibrium concentration of carbon dioxide, $[CO_2]_{equil}$, as derived from two simultaneous equations:

$$(\text{mol } CO_2)_{tot} = \frac{p(V1)}{RT} + [CO_2]_{equil}(V2)$$

$$[CO_2]_{equil} = \frac{p([CO_2]_{std})}{1 \text{ atm}}$$

where p is the pressure of CO_2 above the solution, *V1* is the volume of gas space above the solution, *R* is the gas constant, *T* is the temperature, *V2* is the volume of the solution, and $[CO_2]_{std}$ is the concentration of CO_2, in THF at temperature *T* when the pressure of CO_2 is 4 atm. The expression for $[CO_2]_{equil}$ is thus:

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$$[CO_2]_{equil} = \frac{(total\ mol\ CO_2)([CO_2]_{std}RT)}{V1\ +\ V2([CO_2]_{std}RT}$$

where (total mol CO_2) is the original amount of CO_2 placed into the system. Exposure to CO_2 occurred at -196C, thus the assumption was made that the amount of CO_2 in the solution phase was zero, and the calculated (using the ideal gas law) total amount of CO_2 was made from the volume of gas space above the solution.

$[CO_2]_{std}$ was calculated by a combination of Henry's Law to determine the mol fraction solubility of CO_2 in THF at under 4 atm of CO_2 at temperature T, with adjustments for the partial pressure changes of CO_2 and THF at different temperatures.

There is only data for the change in THF partial pressure at temperatures above room temp, but not below. To solve this, known data[7] was graphed and extrapolated to find the partial pressures at low temperature:

Figure S3: Plot of Partial pressure of THF at temperatures above 288K.[7]

$$y = 1E\text{-}22x^{9.45}$$
$$R^2 = 0.99109$$
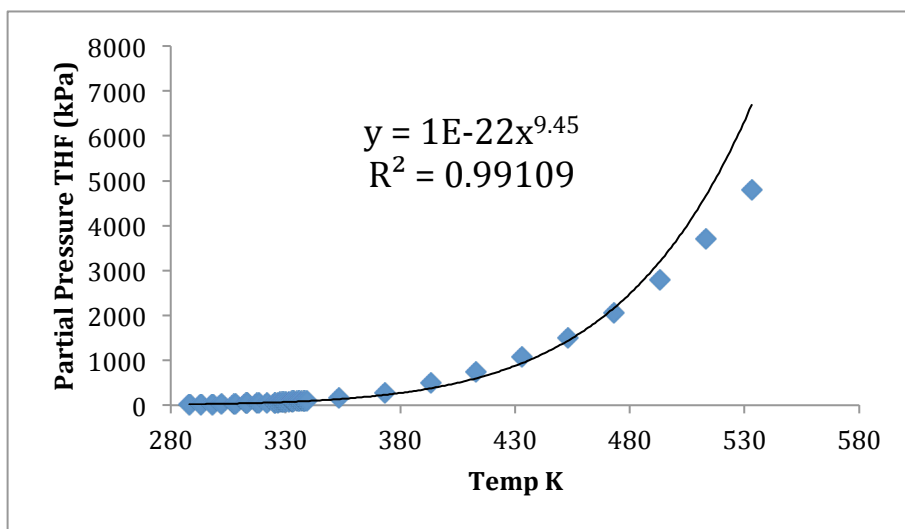
Henry's Law constants were found for CO_2 in THF at different temperatures from IUPAC solubility data series[8] for Temperatures of 273K, 248K, 223K, and 198K with corresponding mol fraction in solution values (x):

Table S1. Henry's Law Constants

T	kPa	X (in sol't)	KH
273.2	101.3	0.04	25
248.2	101.3	0.0689	14.5137881
223.2	101.3	0.205	4.87804878
198	101.3	0.547	1.828153565

$$y = 1\text{E-}19x^{8.3597}$$
$$R^2 = 0.99073$$
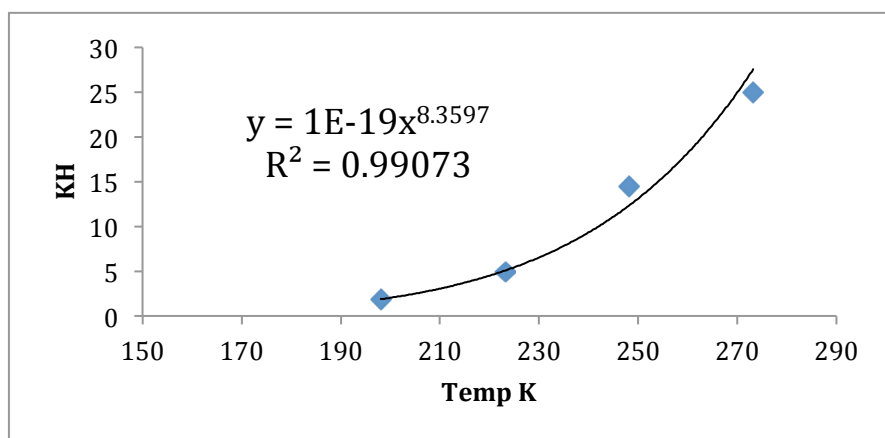
Figure S4. Plot of Henry's Constant (KH) dependence on temperature (for 101.3 kPa).[8]

Plotting the relationship between Henry's Constant and Temperature (while maintaining constant pressure) gives the above graph. Using the above equation allowed for the determination of Henry's constants at all of the different temperatures of the experiment. Applying Henry's Law at each temperature to determine the mol fraction of CO_2 in solution, and knowing the total moles of CO_2 in the system, $[CO_2]std$ was then determined. Plugging this back into the equation at the beginning, $[CO_2]_{equil}$ can be found for every temperature:

T	$[CO_2]_{equil}$ Mol/L
298	2.700
288	2.704
278	2.709
268	2.712
258	2.714
248	2.716
293	2.702

PtPhOH

Temp	[CO2]eq	Keq	1/T K-1x 1000	lnKeq
298	2.6996	0.370425248	3.355704698	0.993103614
293	2.702	0.47742413	3.412969283	0.739350021
288	2.705	0.665434381	3.472222222	0.407315247
278	2.709	1.476559616	3.597122302	0.389714798
268	2.712	3.10840708	3.731343284	1.134110402
258	2.714	7.332350774	3.875968992	1.99229617
248	2.716	19.88217968	4.032258065	2.989823837

PtMeOH

Temp	[CO2]eq	Keq	1/T K-1x 1000	lnKeq
298	2.6996	1.055711957	3.355704698	0.05421538
288	2.7047	2.255333309	3.472222222	0.813297771
278	2.709	6.34551495	3.597122302	1.847748256
268	2.712	15.36873156	3.731343284	2.732335027

Thermodynamic Parameters:

From **1-Ph** to **4-Ph**:   From **1-Me** to **4-Me**:

$\Delta H^o = -11.8(4)$ Kcalmol^{-1} $\Delta H^o = -14(2)$ Kcalmol^{-1}

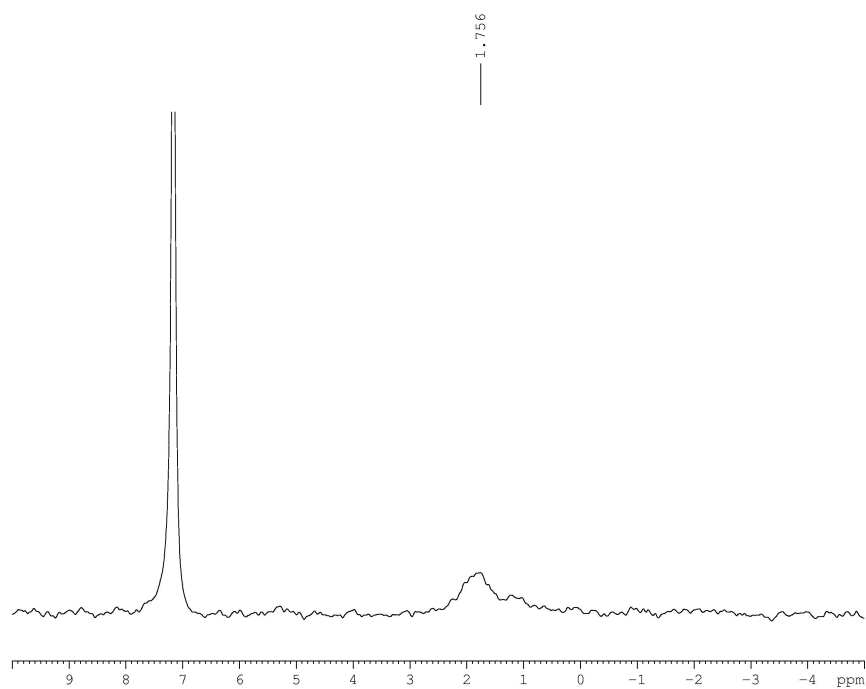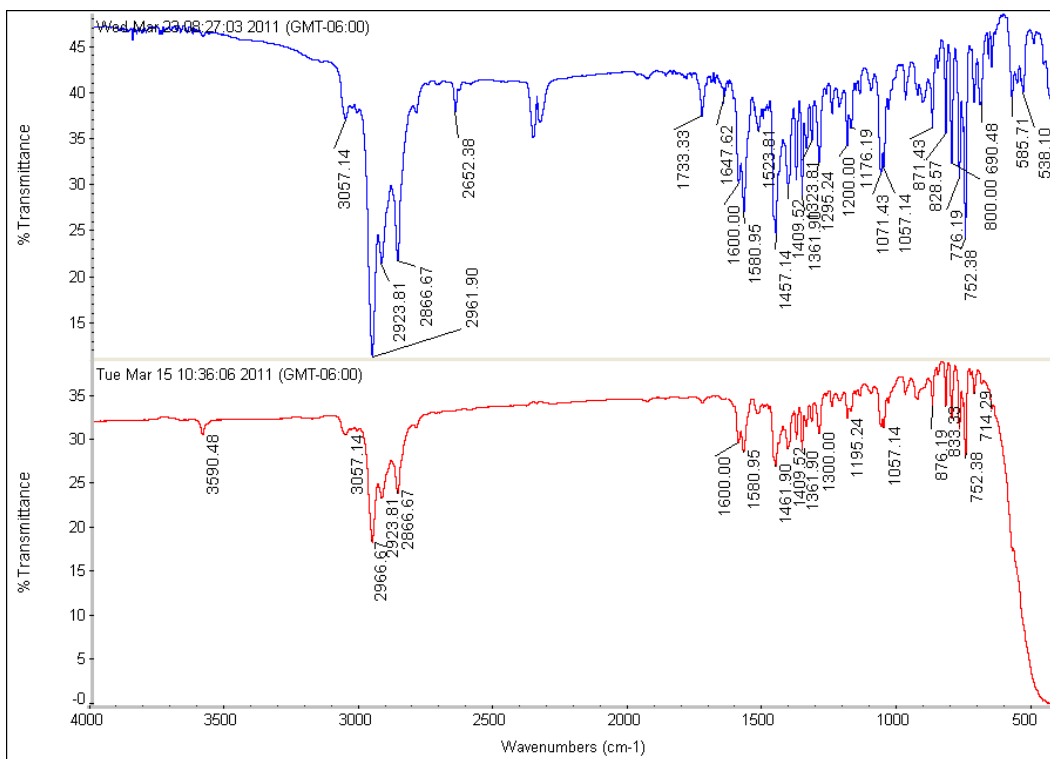$\Delta S^o = -41(1)$ e.u. $\Delta S^o = -48(7)$ e.u.

Spectra of New Compounds:
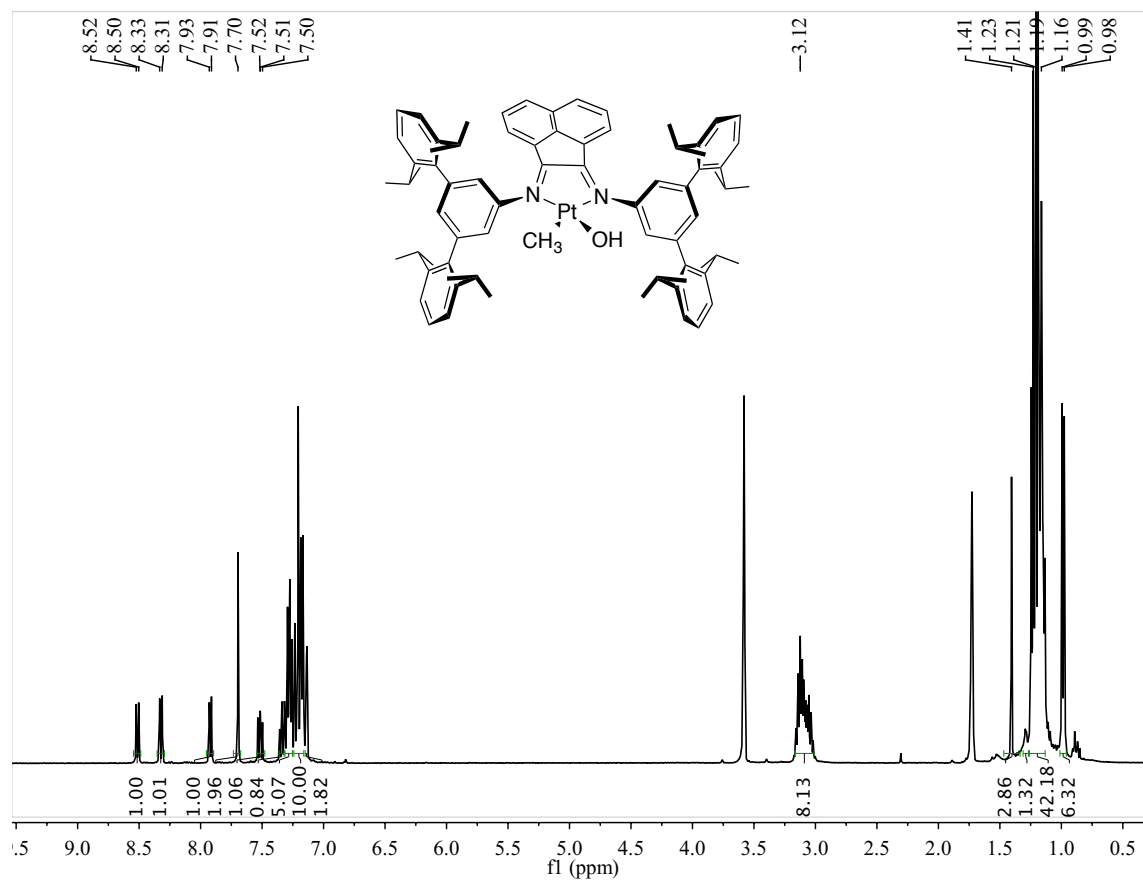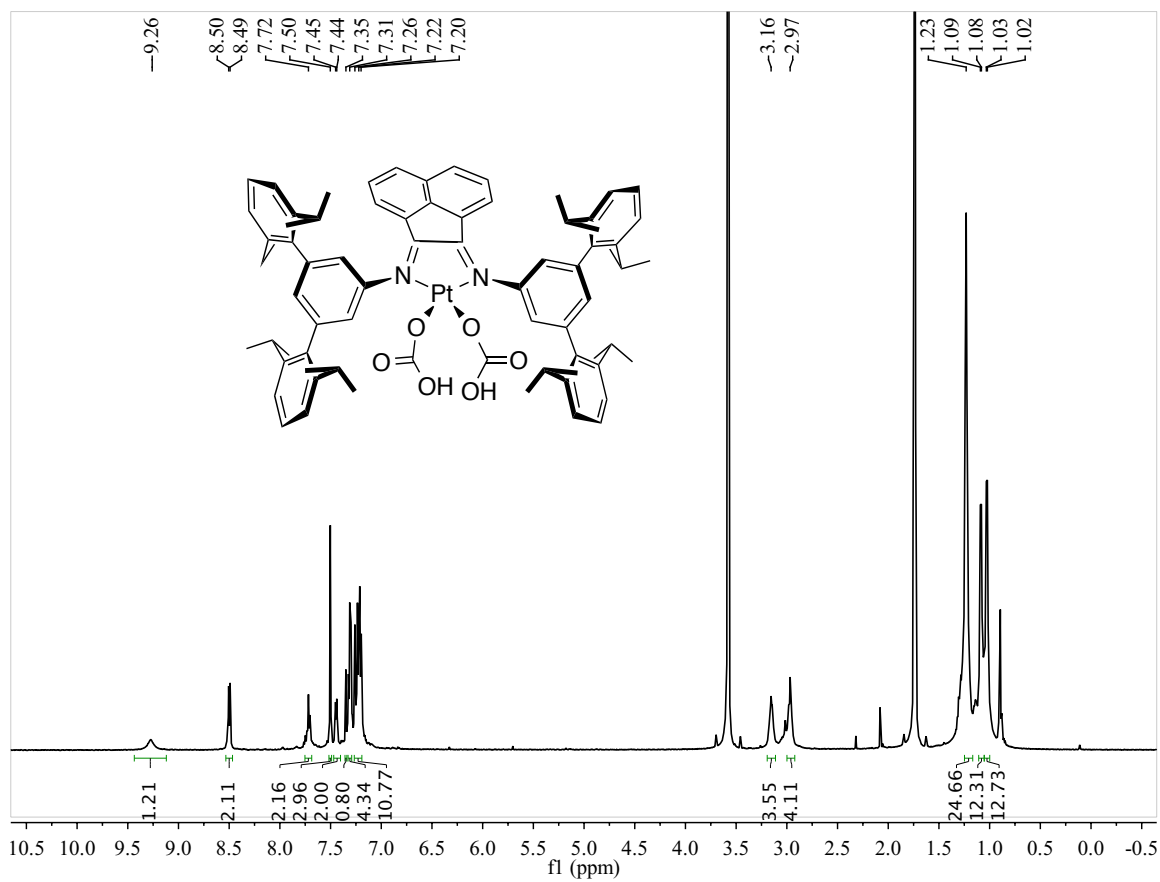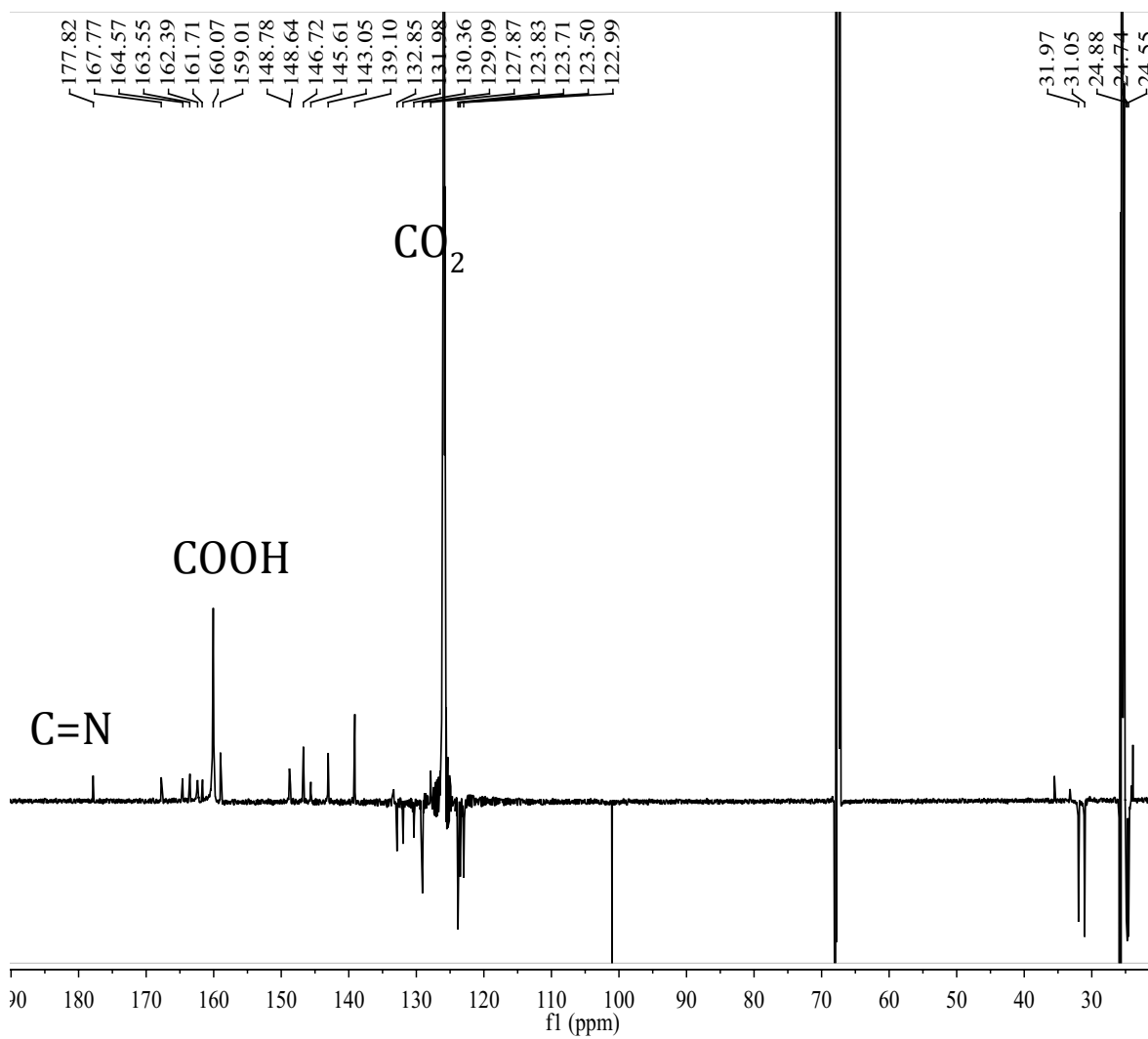
Figure S5. ^{1}H NMR Spectrum of **1-Me** in thf-d8 (298K)

Figure S6. ^{2}H NMR Spectrum of **1-Me-OD** in C$_6$H$_6$ (298K)
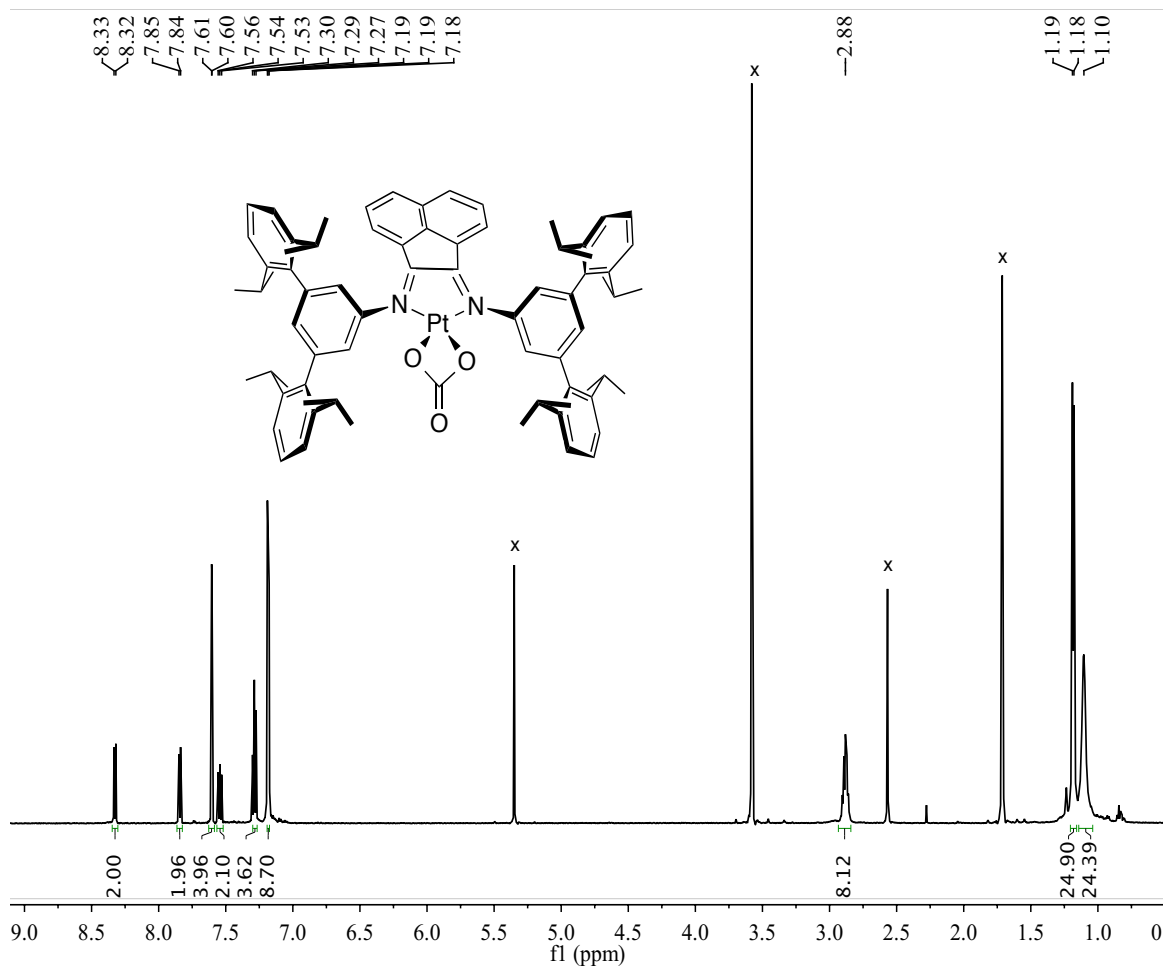

Figure S7. IR Spectra of **1-Me-OD** (top) and **1-Me-OH** (Bottom)

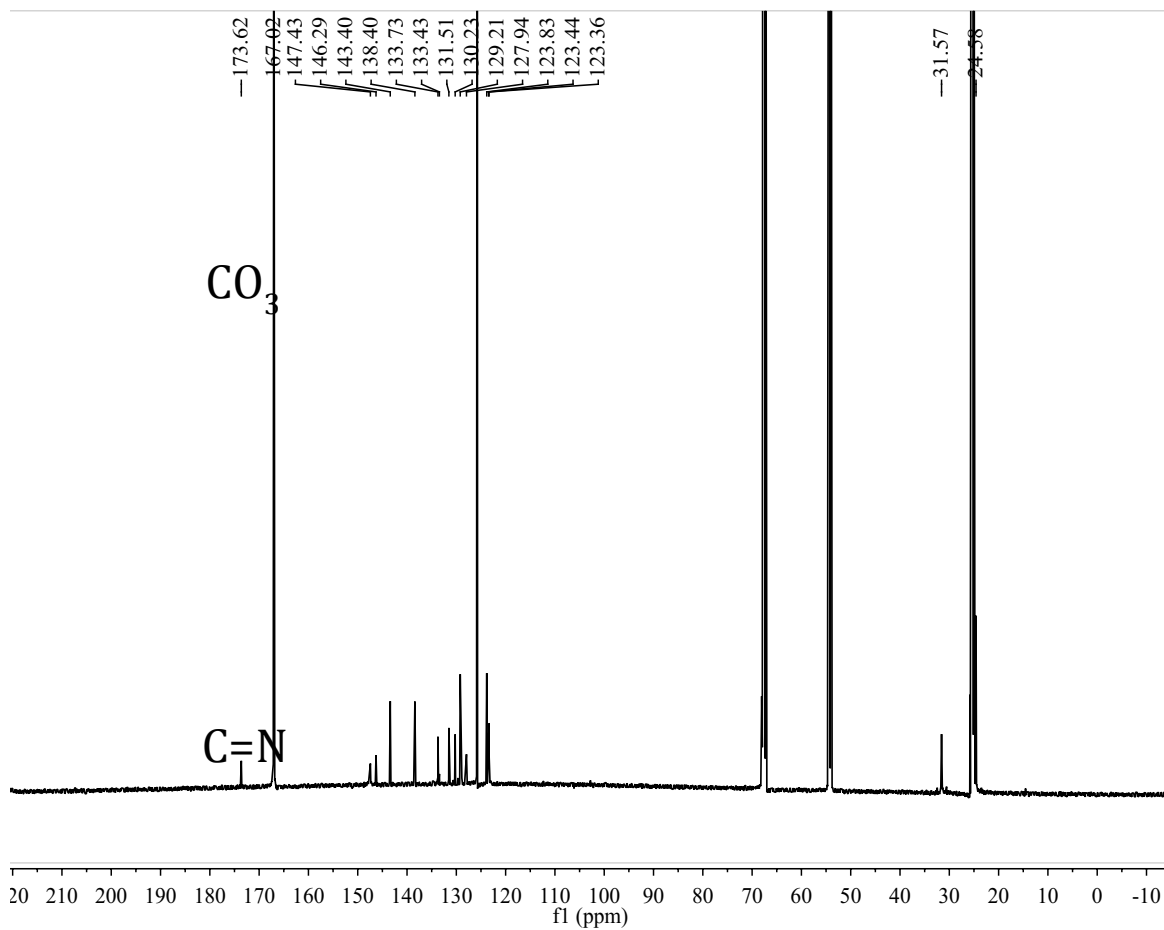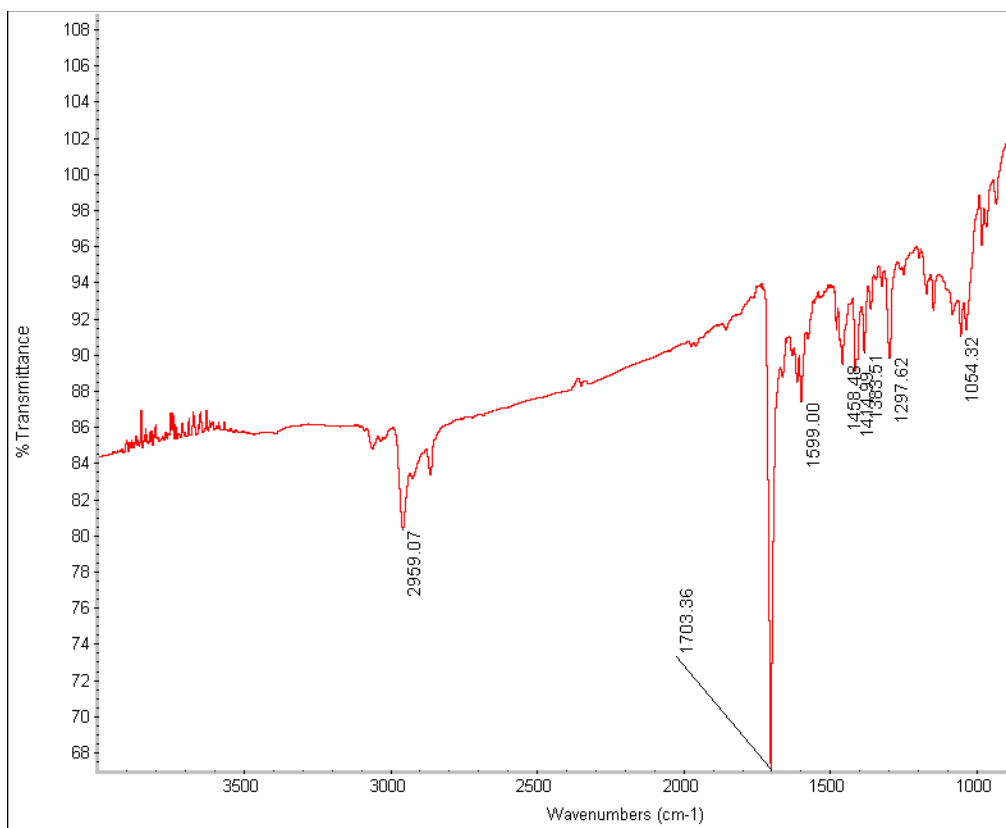**Figure S8**. ^{1}H NMR Spectrum of **3** in thf-d8 (205K)

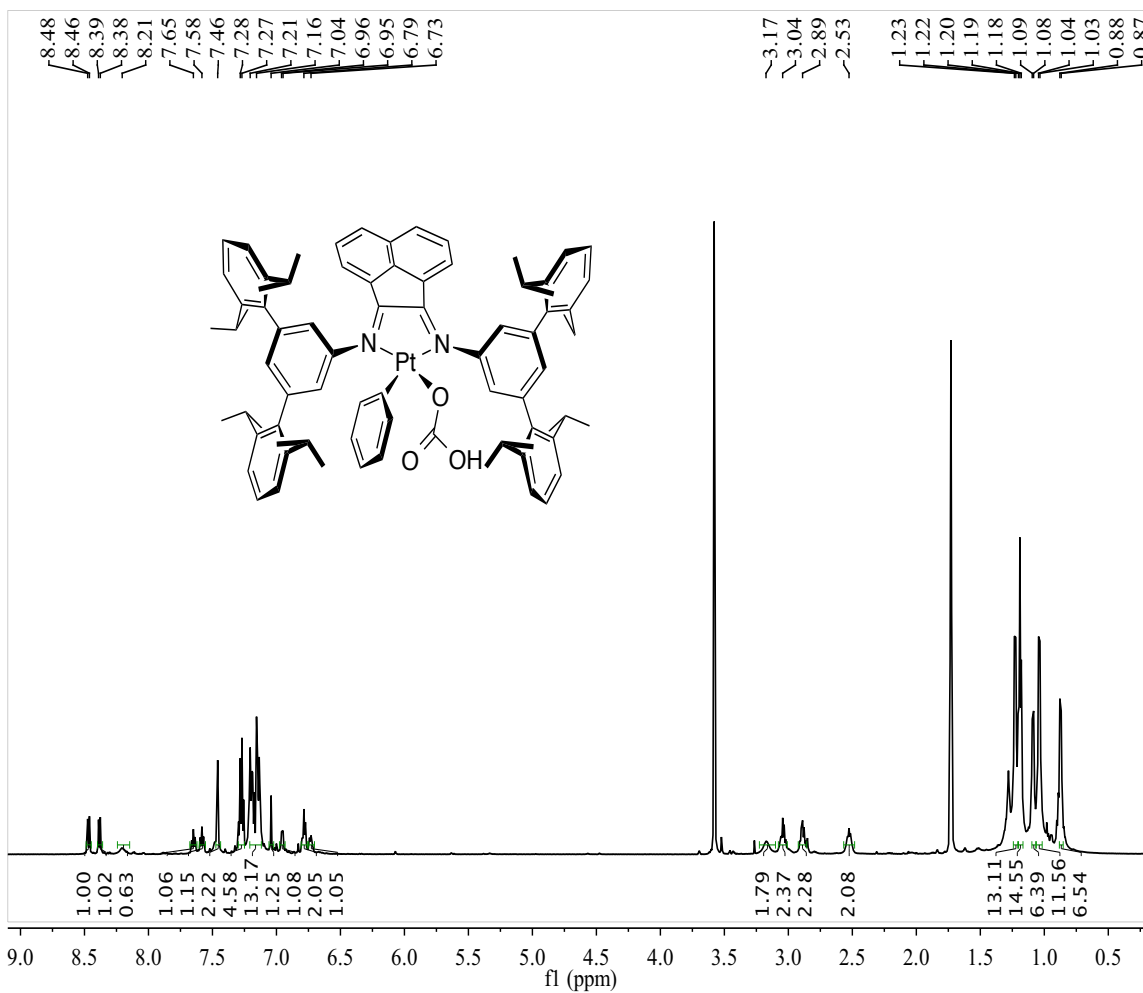**Figure S9**. DEPT-Q ^{13}C NMR of **3** in thf-d8 (205K)

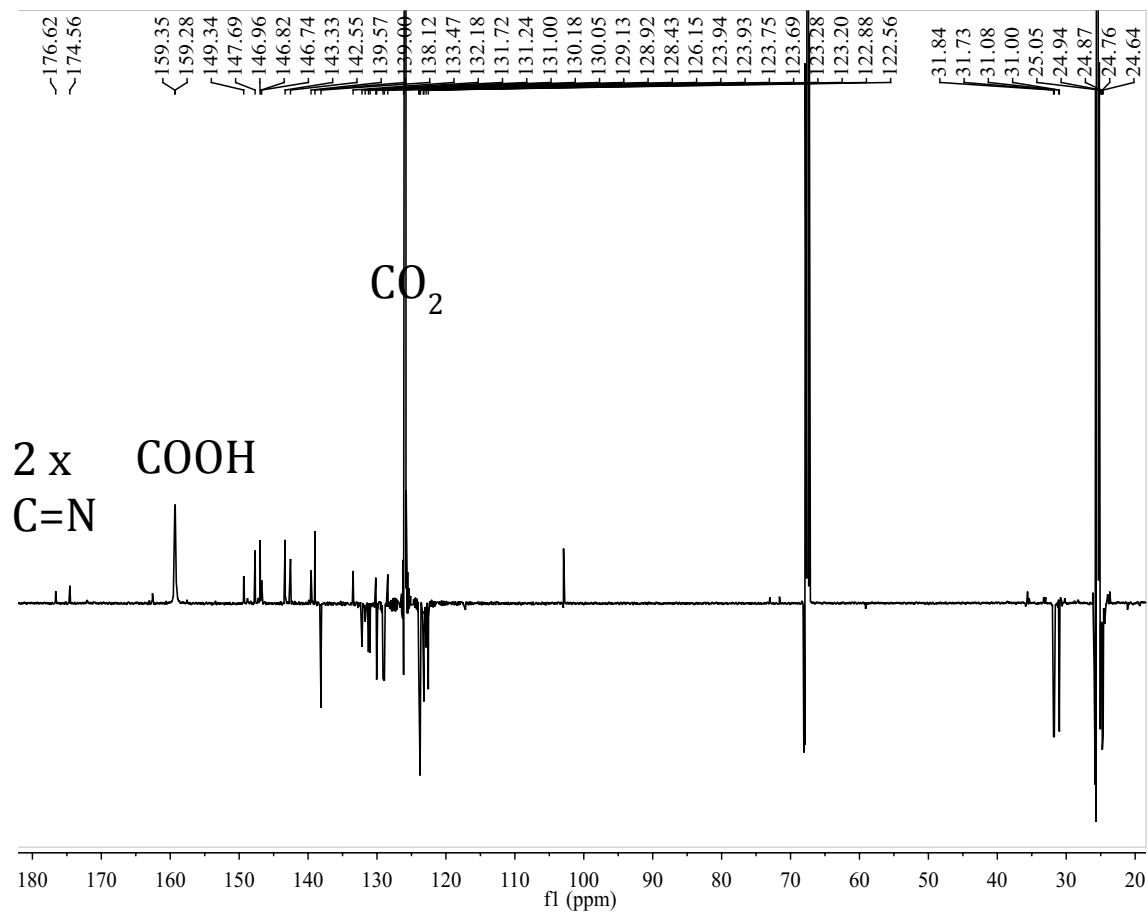**Figure S10**. ^{1}H NMR Spectrum of **2** in 50:50 thf-d8:CD$_2$Cl$_2$ (wet in air, 298K, x = solvent)

Figure S11. ^{13}C NMR of **2** in 50:50 thf-d8:CD$_2$Cl$_2$ (wet in air, 298K)

Figure S12. IR Spectrum of **2** (NaCl plates)

Figure S13. ^{1}H NMR Spectrum of **4-Ph** in thf-d8 (238K)

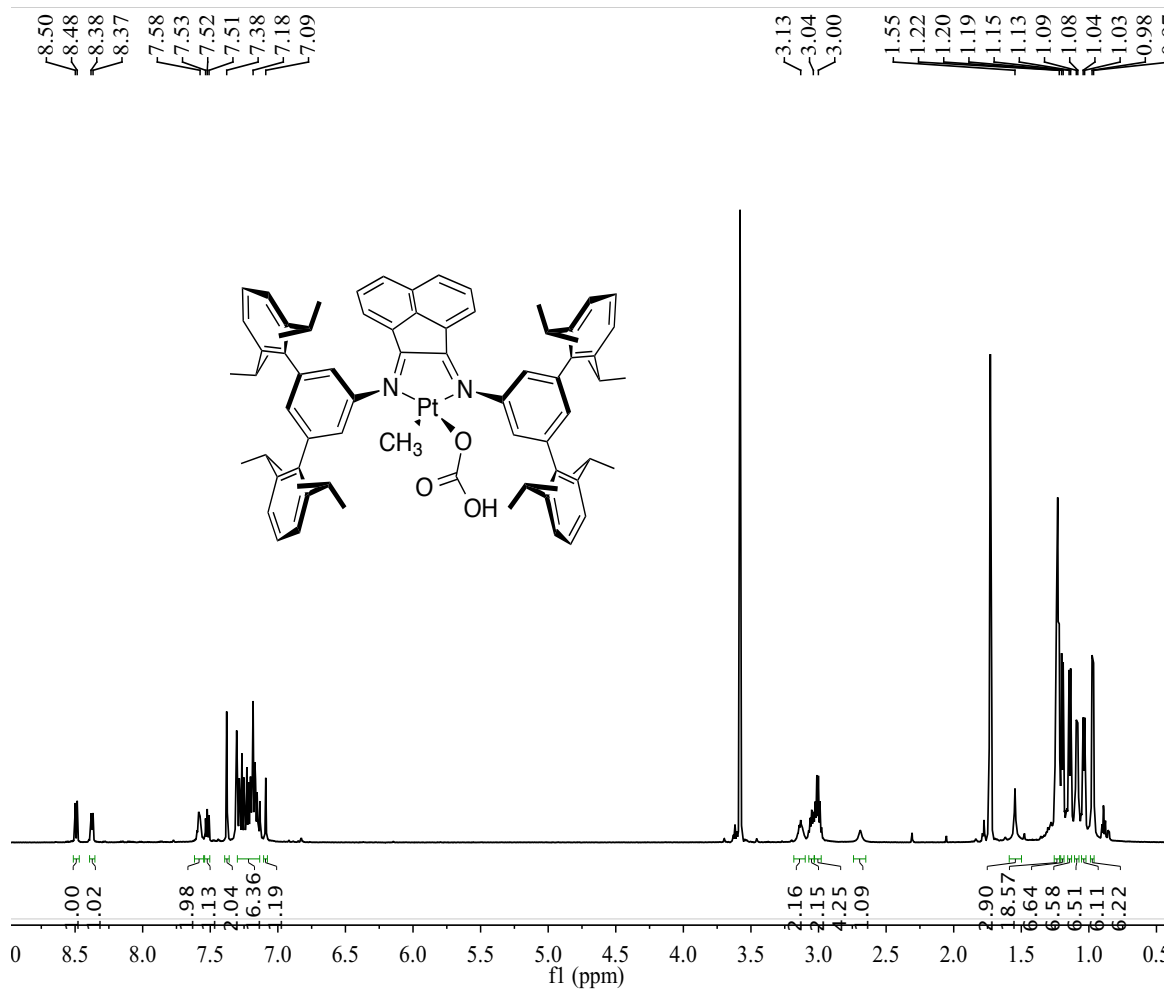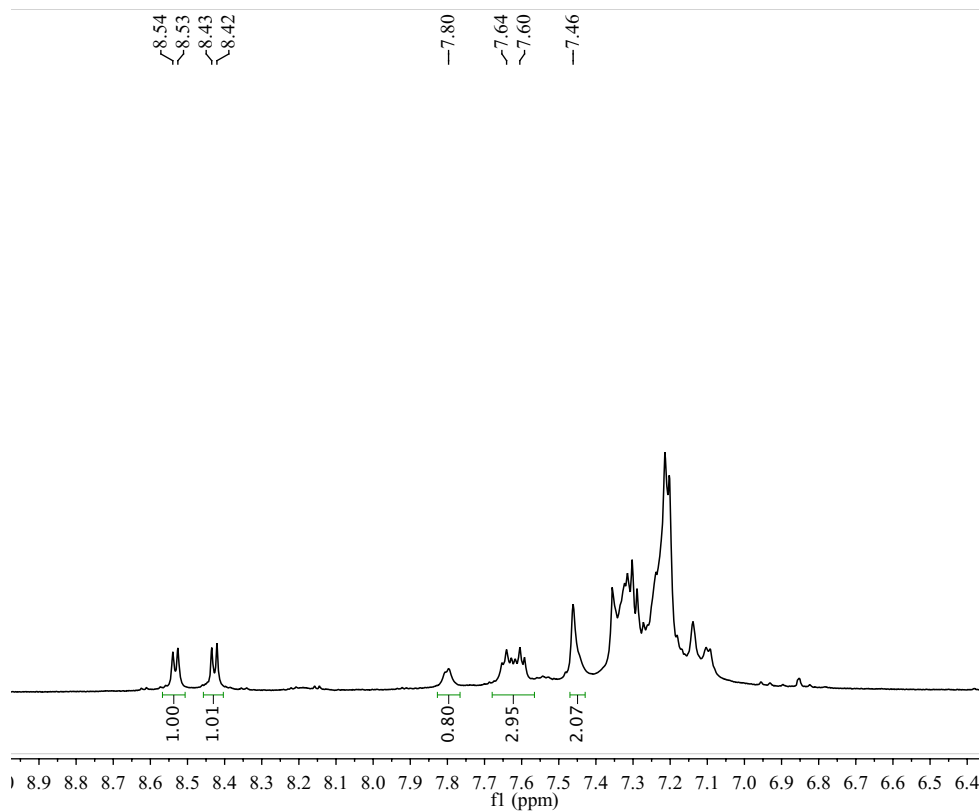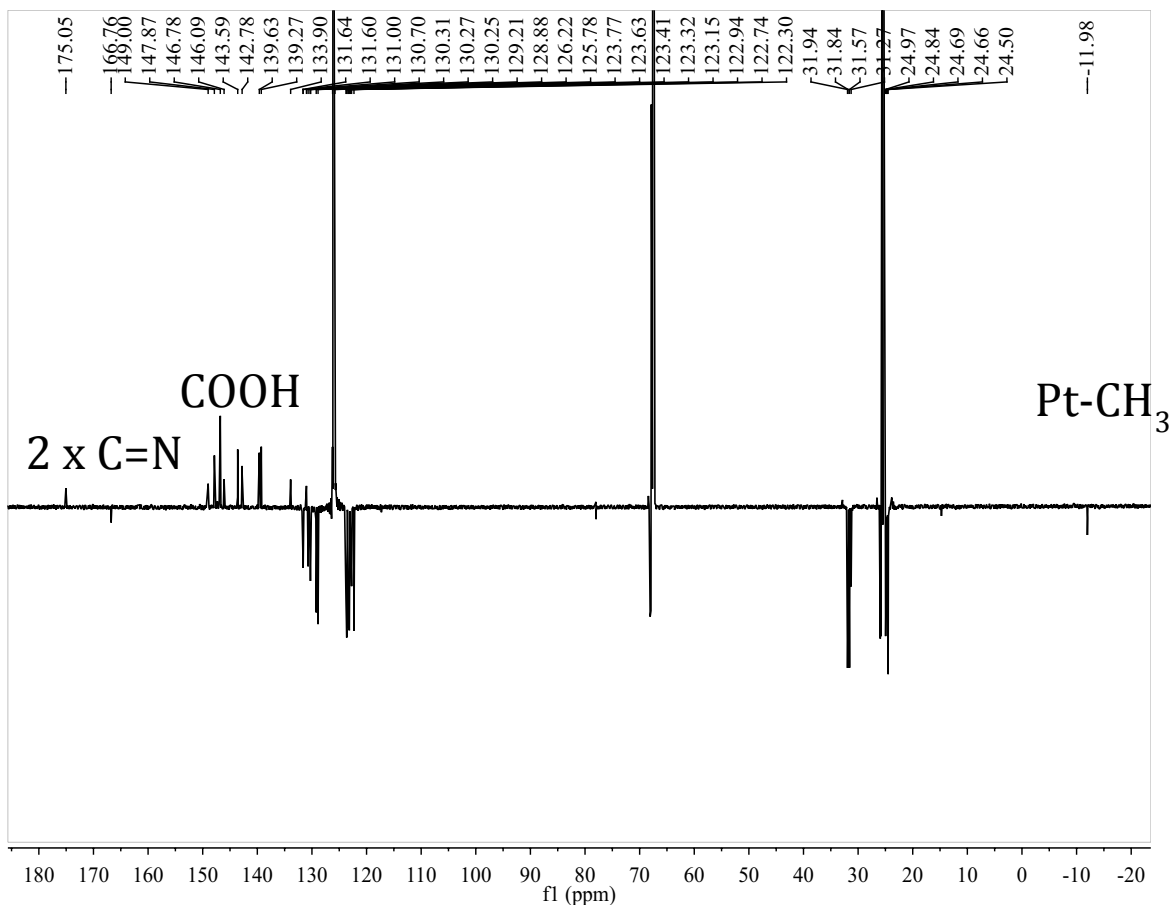**Figure S14.** DEPT-Q ^{13}C NMR of **4-Ph** in thf-d8 (238K)

Figure S15. ^{1}H NMR Spectrum of **4-Me** in thf-d8 (263K)

Figure S16. ^{1}H NMR Spectrum of the aromatic region of **4-Me** in thf-d8 (228K)

Figure S17. DEPT-Q ^{13}C NMR of **4-Me** in thf-d8 (268K)

Table S2. Data Collection and Structure Refinement Details for **1-Me**

	1-Me
formula	$C_{73}H_{83}N_2OPt$
fw	1199.50
crystal system	triclinic
space group	P-1
a, Å	10.442(2)
b, Å	12.460(3)
c, Å	32.990(7)
α, deg	96.55(3)
β, deg	91.94(3)
γ, deg	111.94(3)
V, Å^3	3941.8(17)
Z	2
T, K	293

λ, Å	0.71073
ρ_{calc}, g/cm^3	0.96
F(000)	1100.0
μ, mm^{-1}	1.813
Data Completeness	0.734
Number of reflections	10262
θ range, deg	3.2-25.05
R_1 (I > 2σ(I))	0.1181
wR_2 (all data)	0.3164

References for Supporting Information:

1. Burger, B. J.; Bercaw, J. E. *Experimental Organometallic Chemistry*; American Chemical Society: Washington, D.C., 1987.

2. Hill, G.S.; Irwin, M.J; Levy, C.J.; Rendina, L.M.; Puddephatt, R.J. *Inorganic Syntheses*, **1998**, *32*, 151.

3. Lohr, T.L.; Piers, W.E.; Parvez, M. *Inorganic Chemistry,* **2012**, *51*, 4900-4902.

4. Lohr, T.L.; Piers, W.E.; Parvez, M. *Chemical Science,* **2013**, *4*, 770-775.

5.Thompson, M.E, Baxter, S.E., Bulls, A.B., Burger, B.J., Nolan, M.C., Santarsiero, B.D., Schaefer, W.P., Bercaw, J.E. *J. Am. Chem. Soc.,* **1987**, *109*, 203-219.

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7. Partial Pressure of THF at different temperatures: The UNIFAC Consortium:
http://www.ddbst.com/en/EED/PCP/VAP_C159.php

8. IUPAC Solubility Data Series, Volume 50, Carbon dioxide in non-aqueous solvents at pressures less than 200 KPa. (pg 237-238).