

**Supporting Information**  
**for**  
**Proton Catalyzed Oxo-Alkene Coupling: 2-Platinaoxetane Formation**

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**General Procedures.** All experiments were done in a dinitrogen atmosphere in a Vacuum Atmosphere Corporation drybox unless otherwise noted. Solvents were dried under standard techniques and were stored in the drybox, over 4Å molecular sieves or sodium metal. Reagents and deuterated solvents were purchased from the following companies: 2-norbornene from TCI America, pvp (polyvinyl pyridine crosslinked with 2% DVB, ca. 60 mesh) and CD<sub>3</sub>NO<sub>2</sub> from Acros, HBF<sub>4</sub>·Et<sub>2</sub>O, NMe<sub>4</sub>OH·5H<sub>2</sub>O, KOH and polymer bound NEt<sub>2</sub> (~NEt<sub>2</sub>, 100-200 mesh, 1% cross linked, typical loading 1.0-1.5 mmol/g) from Aldrich and CD<sub>2</sub>Cl<sub>2</sub> from Cambridge Isotope Laboratories. All commercial reagents were used as received. Pt(COD)Cl<sub>2</sub>,<sup>1</sup> Pt(COD)(OTf)<sub>2</sub>,<sup>2</sup> and [Pt<sub>4</sub>(COD)<sub>4</sub>(μ<sup>3</sup>-O)<sub>2</sub>Cl<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (**1-BF<sub>4</sub>**)<sup>3</sup> were synthesized according to literature procedures. NMR spectra were recorded on Bruker AMX-300 or -500 spectrometers at ambient temperatures except where noted. All chemical shifts (δ) for the NMR data are reported in ppm with coupling constants in Hz. <sup>1</sup>H NMR chemical shifts are relative to residual protio solvent signals referenced to TMS (0 ppm). <sup>13</sup>C NMR chemical shifts are relative to internal solvent signals referenced to TMS (0 ppm). <sup>195</sup>Pt NMR chemical shifts are relative to external K<sub>2</sub>PtCl<sub>4</sub>/D<sub>2</sub>O (-1624 ppm). Elemental analyses were carried out by Columbia Analytical Services, Inc. (Desert Analytics Lab).

### Syntheses and Reactions

**[Pt(COD)(μ-OH)]<sub>4</sub>(OTf)<sub>4</sub> (5-OTf):** A. Pt(COD)(OTf)<sub>2</sub> (52.7 mg, 0.0876 mmol) was placed in an NMR tube. The tube was taken outside the drybox and placed in an ice/salt bath (-10 °C). The tube was removed from the bath and 1 mL of THF was injected into the opened tube and mixed to give a dark yellow solution. The tube was resealed and replaced in the ice-bath and freshly prepared KOH(aq) (6.0 μL, 29 M) was added to the cold Pt(COD)(OTf)<sub>2</sub> solution. The contents were mixed by agitation. After ~5 minutes, brown particles and a white precipitate appeared. Precipitation was allowed to continue for the next 24 h in the ice bath. The tube was then returned to the drybox and the contents were transferred to a vial. The volatiles were removed in vacuo. The residue was dissolved in 4 mL CH<sub>2</sub>Cl<sub>2</sub> and filtered. The resulting clear dark yellow solution was reduced to ~ 2.5 mL in vacuo. Ether

<sup>1</sup> McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, 98, 6521-6528.

<sup>2</sup> Karshtedt, D.; Bell, A. T.; Tilley, T.D. *Organometallics*, **2004**, 23 (18), 4169–4171.

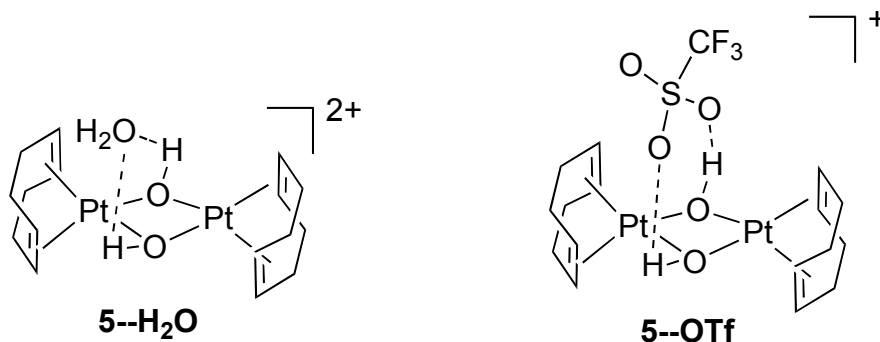
<sup>3</sup> Shan, H.; James, A.; Sharp, P. R. *Inorg. Chem.* **1998**, 37, 5727-5732.

was added until there was no further precipitation of white **5-OTf**. The product was separated by decantation, washed with ether and hexane, and then dried in vacuo. Yield: 25 mg (61%).

**B.** Pt(COD)Cl<sub>2</sub> (21.2 mg, 0.0566 mmol) and NMe<sub>4</sub>OH.5H<sub>2</sub>O (20.6 mg, 0.110 mmol) were added to a 20 mL vial followed by 1 mL of CH<sub>2</sub>Cl<sub>2</sub>. To the resulting yellow solution and brown solid was added an agitated mixture of AgOTf (29.3 mg, 0.114 mmol) and 0.8 mL CH<sub>2</sub>Cl<sub>2</sub>. A white precipitate of AgCl formed. The AgCl was removed by filtration through diatomaceous earth. The clear filtrate was reduced to half its volume in vacuo. Ether was added until there was no further precipitation of white **5-OTf**. The product was separated by decantation, washed with ether and hexane, and then dried in vacuo. Yield: 15 mg (56 %). Crystals of **5-OTf** for X-ray crystallography were obtained by slow evaporation (at room temperature) of a CH<sub>2</sub>Cl<sub>2</sub> solution of the compound. Anal. Calcd (found) for C<sub>9</sub>H<sub>13</sub>F<sub>3</sub>O<sub>4</sub>PtS: C, 23.62 (23.03); H, 2.37 (2.79).

<sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 7.25 (br s, 1H, OH), 5.67 (s, J<sub>Pt-H</sub> = 67 Hz, 4H COD CH), 2.75, 2.25 (br m's, 8H total, COD CH<sub>2</sub>). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>NO<sub>2</sub>): 5.66 (s, J<sub>Pt-H</sub> = 67 Hz, 4H COD CH), 2.83, 2.34 (br m's, 8H total, COD CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 98.3 (COD CH), 30.5 (COD CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CD<sub>3</sub>NO<sub>2</sub>): 99.9 (COD CH), 31.1 (COD CH<sub>2</sub>). <sup>195</sup>Pt{<sup>1</sup>H} NMR (64 MHz, CD<sub>2</sub>Cl<sub>2</sub>): -2761. <sup>195</sup>Pt{<sup>1</sup>H} NMR (64 MHz, CD<sub>3</sub>NO<sub>2</sub>): -2787.

Low temperature NMR spectra (see Fig S1-S4 and data below) reveal the presence of another species of reduced symmetry and with a much sharper OH signal in equilibrium with **5**. We believe this is a hydrogen-bonded adduct either of water (**5--H<sub>2</sub>O**) or the triflate anion (**5--OTf**). The proportion of the adduct increases with decreasing temperature consistent with an entropically disfavored process.



At 0 °C: <sup>195</sup>Pt{<sup>1</sup>H} NMR (64 MHz, CD<sub>2</sub>Cl<sub>2</sub>): -2776, -2965 (adduct). At -20 °C: <sup>195</sup>Pt{<sup>1</sup>H} NMR (64 MHz, CD<sub>2</sub>Cl<sub>2</sub>): -2791, -2973 (adduct).

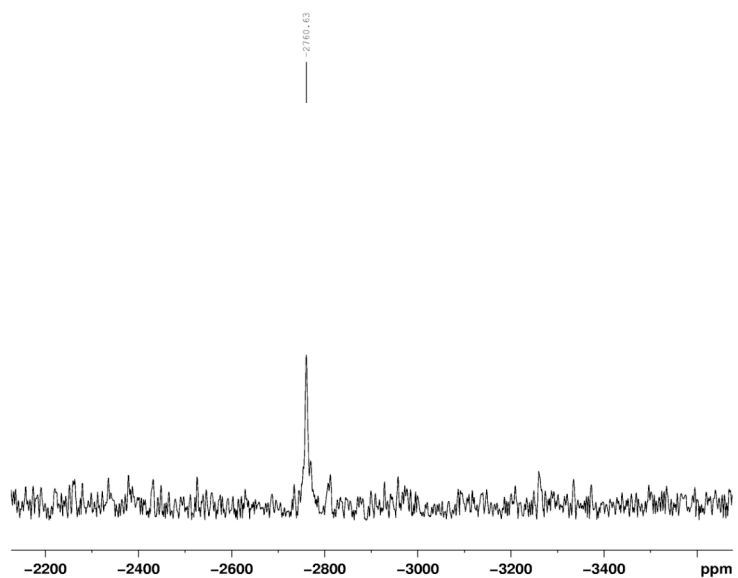


Figure S1.  $^{195}\text{Pt}\{^1\text{H}\}$  NMR spectrum of **5** ( $\text{CD}_2\text{Cl}_2$ , 25 °C).

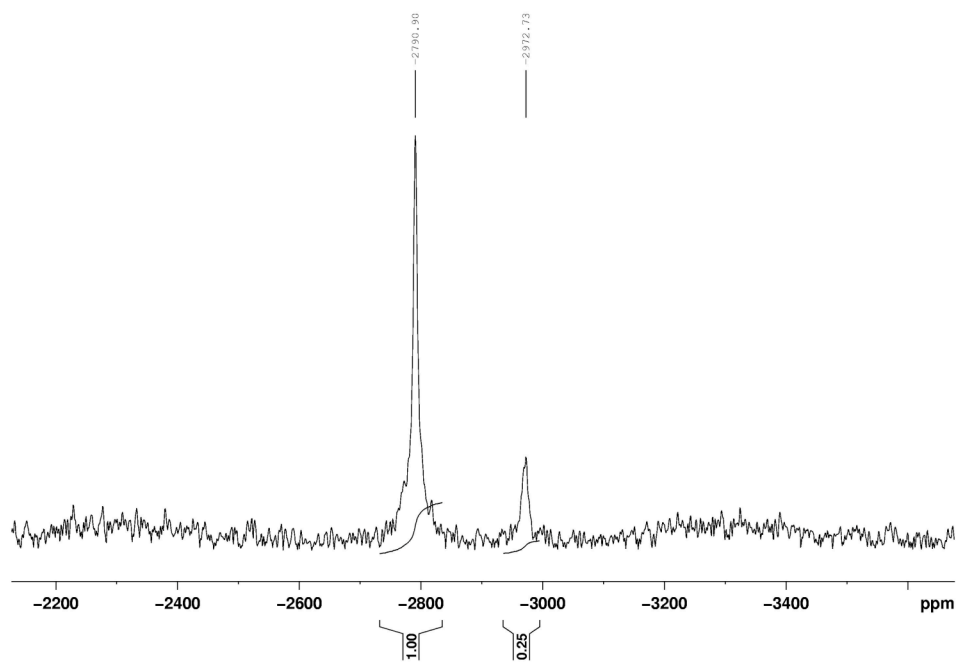


Figure S2.  $^{195}\text{Pt}\{^1\text{H}\}$  NMR spectrum of **5** ( $\text{CD}_2\text{Cl}_2$ , -20 °C).

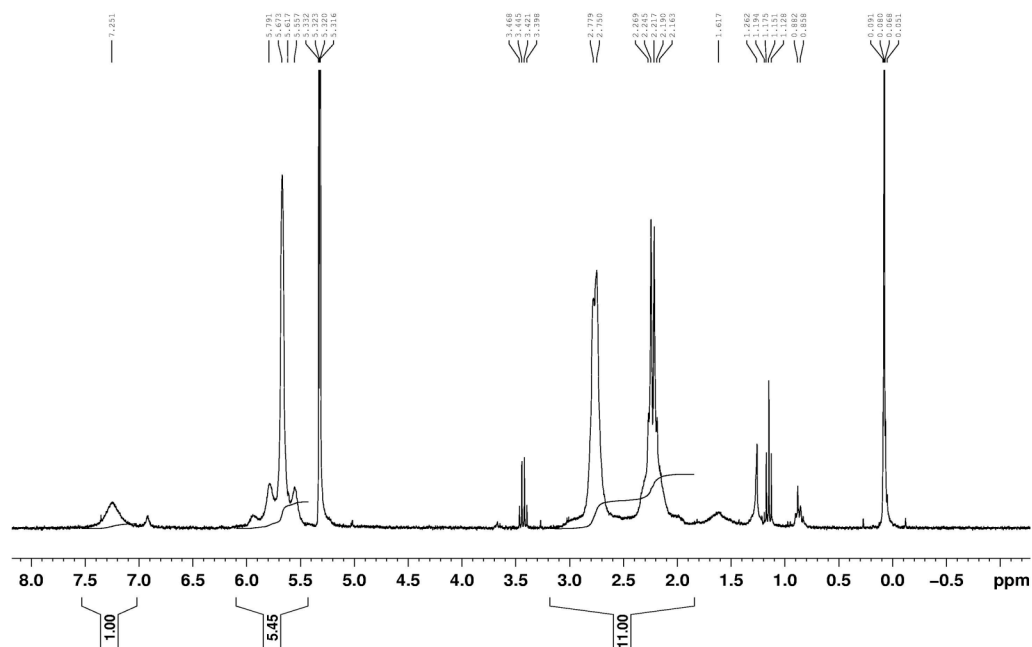


Figure S3.  $^1\text{H}$  NMR spectrum of **5** ( $\text{CD}_2\text{Cl}_2$ ,  $25^\circ\text{C}$ ).

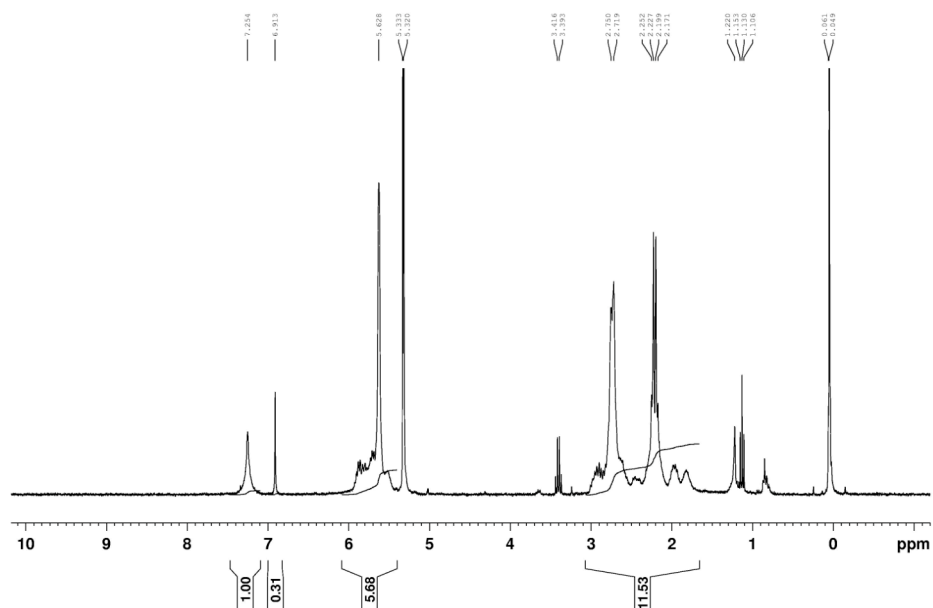


Figure S4.  $^1\text{H}$  NMR spectrum of **5** ( $\text{CD}_2\text{Cl}_2$ ,  $-20\text{ }^\circ\text{C}$ ).

**Formation of  $[\text{Pt}(\text{COD})(\text{C}_7\text{H}_{10}\text{OH})]^+$  (**7**).** **A. Excess NB:** Solid norbornene (NB, 12.6 mg, 0.139 mmol) was added to a solution of **5-OTf** (6.3 mg, 0.0067 mmol) in 0.55 mL  $\text{CD}_2\text{Cl}_2$  and the mixture was agitated. Product **7** formed immediately but could not be isolated (see main text) and was characterized by NMR spectroscopy. **B. Stoichiometric NB:** A  $\text{CD}_2\text{Cl}_2$  solution of NB (7.6  $\mu\text{L}$ , 1.2 M) was added a solution of **5-OTf** (4.3 mg, 0.0046 mmol) in 0.50 mL  $\text{CD}_2\text{Cl}_2$ , and the mixture was agitated.  $^1\text{H}$  and  $^{195}\text{Pt}$  NMR spectra showed partial conversion to **7** with remaining **5** ( $K_{\text{eq}} \approx 40$ , with  $n = 2$ ).

$^{195}\text{Pt}$  NMR (64 MHz,  $\text{CH}_2\text{Cl}_2$ ): -3071.

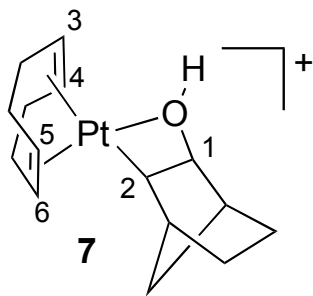


Table S1.  $^1\text{H}$  and  $^{13}\text{C}$  NMR data for protonated 2-platinaoxetane  $[\text{Pt}(\text{COD})(\text{C}_7\text{H}_{10}\text{OH})]^+$  (**7**)

H or C assignment <sup>a,c</sup>	$^1\text{H}$ NMR (300 MHz, $\text{CD}_2\text{Cl}_2$ )	$^{13}\text{C}$ NMR (500 MHz, $\text{CD}_2\text{Cl}_2$ )
OH	8.86 (d with satellites, $J_{\text{H-H}} = 3.3$ Hz, $J_{\text{Pt-H}} = 25$ Hz)	-
1	6.38 (br m with satellites, $J_{\text{Pt-H}} = 27$ Hz)	104.0
2 <sup>b</sup>	1.42 (br, patially overlapping with NB peaks)	20.4
3,4	4.84 (td with satellites, $J_{\text{H-H}} = 11.1, 3.3$ Hz, $J_{\text{Pt-H}} = 84$ Hz) 4.65 (br m with satellites, $J_{\text{Pt-H}} = 87$ Hz )	82.7 82.5
5,6	5.67 & 5.58 (br overlapping m's)	117.5 & 117.0
COD $\text{CH}_2$ 's	2.49, 2.50, 2.75	31.5, 30.0

a) Assignments based on  $^1\text{H}$ - $^1\text{H}$  COSY,  $^{13}\text{C}$  DEPT and  $^1\text{H}$ - $^{13}\text{C}$  HMQC studies.

b) Similar shift to analogous platinaoxetanes.

c) Other platinaoxetane-NB peaks could not be assigned as they were overlapping with free NB peaks.

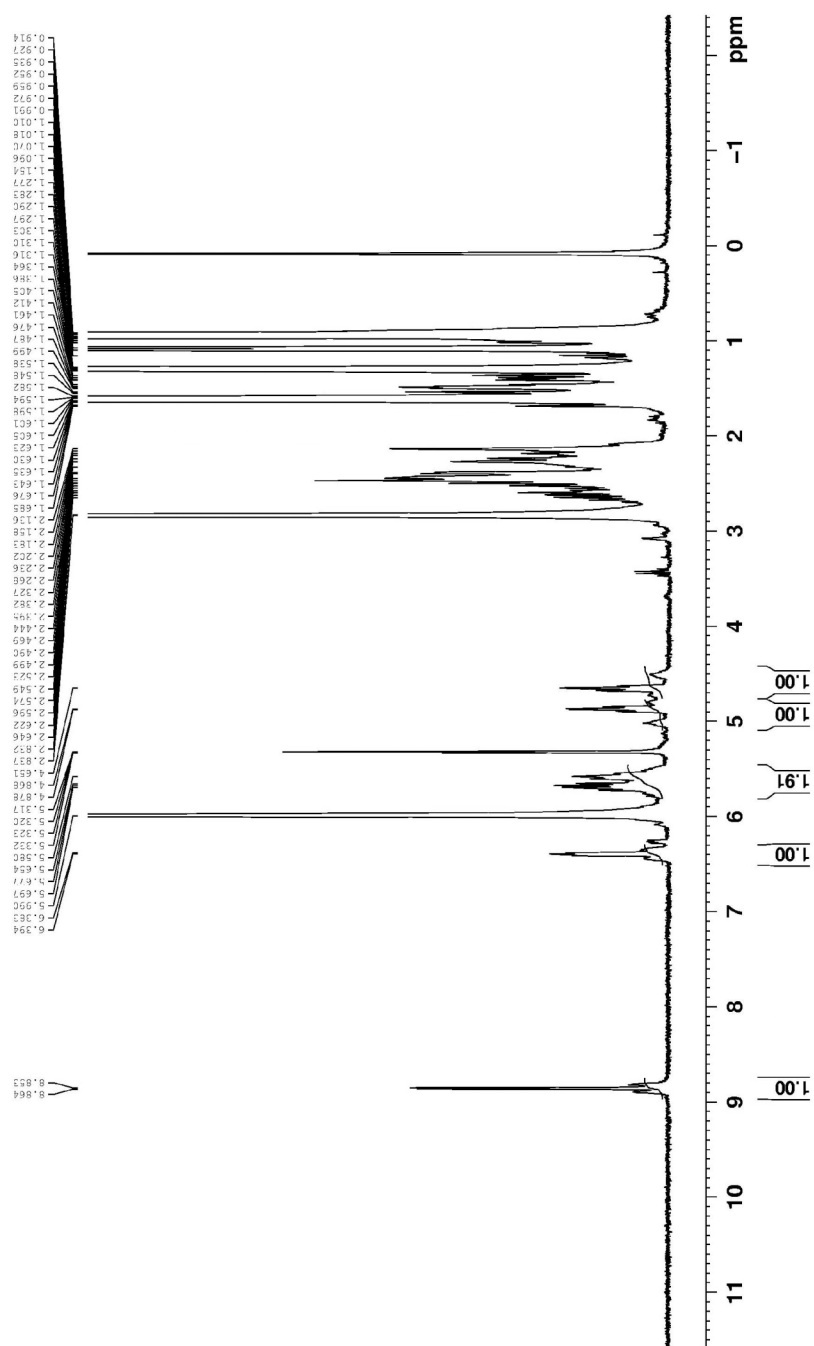


Figure S5.  $^1\text{H}$  NMR spectrum of  $[\text{Pt}(\text{COD})(\text{C}_7\text{H}_{10}\text{OH})]^+$  (7) (From excess NB).



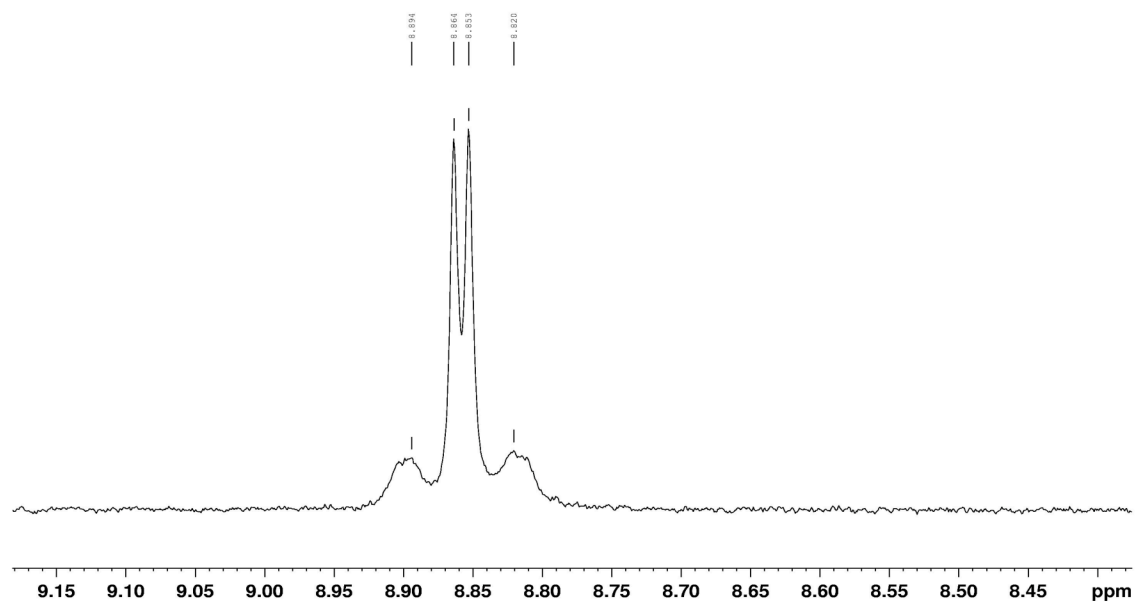


Figure S6.  $^1\text{H}$  NMR spectrum of  $[\text{Pt}(\text{COD})(\text{C}_7\text{H}_{10}\text{OH})]^+$  (7). Expansion of the OH peak region showing coupling to H1 and  $^{195}\text{Pt}$  satellites.

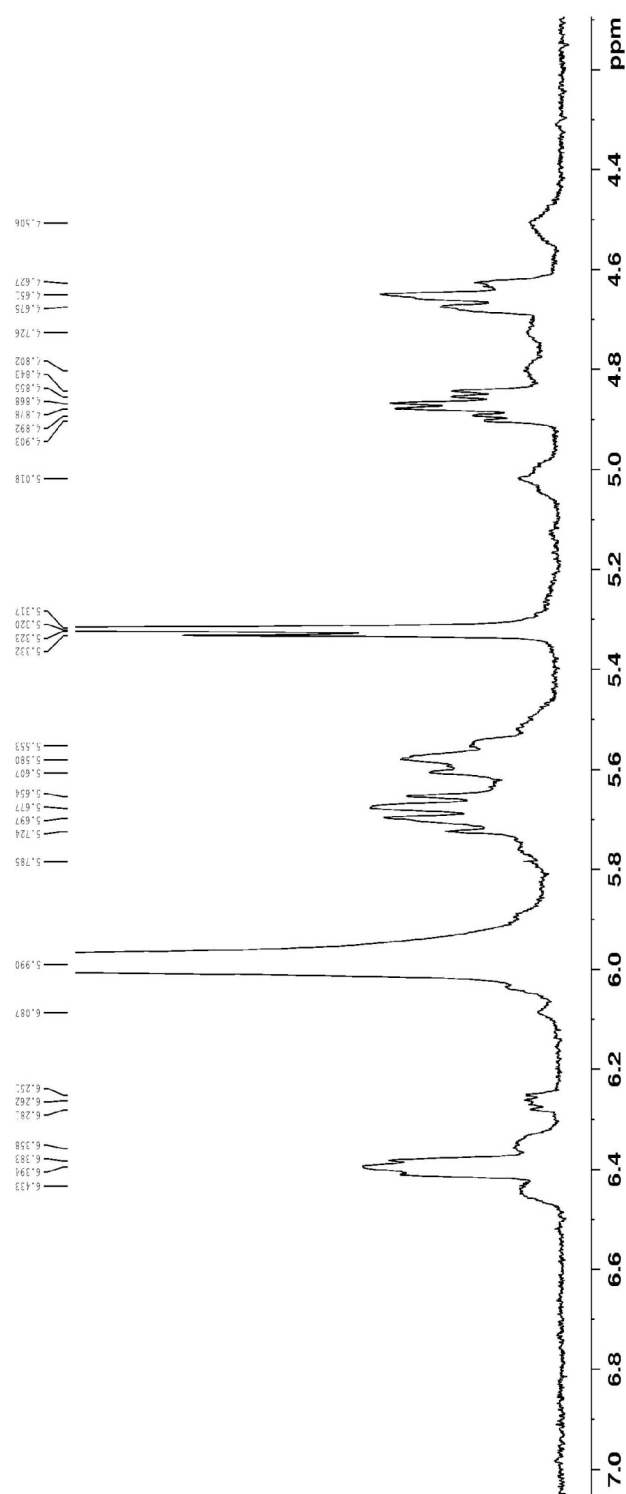


Figure S7.  $^1\text{H}$  NMR spectrum of  $[\text{Pt}(\text{COD})(\text{C}_7\text{H}_{10}\text{OH})]^+$  (7). Expansion of olefinic and H1 region.

**Formation of Pt ene-yl complex (6) from 7 and NB.** A solution of **7** with excess NB was prepared as described above. After a few h NMR peaks for **6** began to grow in along with another unidentified Pt complex **X**. After 2 days only peaks for **6** and the unknown complex remained. With stoichiometric NB (mixture of **5** and **7**, see above), peaks for **6** do not appear until after ~16 h.

Data for **X**:  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ): 5.07 (br, overlapped with **6**), 4.57 (d,  $J_{\text{H-H}} = 11$  Hz), 4.31 (s), 3.78 (d,  $J_{\text{H-H}} = 7$  Hz), 3.65 (s), 3.35 (m, br)  $^{195}\text{Pt}$  NMR (64 MHz,  $\text{CD}_2\text{Cl}_2$ ): -3777.

**Reaction of  $[\text{Pt}(\text{COD})(\text{C}_7\text{H}_{10}\text{OH})]^+$  (**7**) and  $[\text{Pt}_4(\text{COD})_4(\mu^3\text{-O})_2\text{Cl}_2](\text{BF}_4)_2$  (**1-BF<sub>4</sub>**): Formation of **2** and **5**.** A solution of **7** in a screw-cap NMR tube was prepared by adding solid NB (13.1 mg, 0.139 mmol) to **5-OTf** (6.3 mg, 0.0067 mmol) in 0.5 mL  $\text{CD}_2\text{Cl}_2$ . A  $^1\text{H}$  NMR spectrum established complete conversion of **5** to **7**. The tube was then cooled in a dry ice/acetone bath. The screw-cap was removed and solid Pt oxo complex **1-BF<sub>4</sub>** (10.0 mg, 0.00672 mmol) was added. The vial that contained **1** was washed with 0.2 mL  $\text{CD}_2\text{Cl}_2$  and the washings were also added. The tube was shaken and immediately placed in the pre-cooled ( $-20^\circ\text{C}$ ) NMR probe.  $^1\text{H}$  and  $^{195}\text{Pt}$  NMR data indicated the formation of **2** and **5**. Characteristic peaks for **2**:  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ): 6.22 (m, 1H), 4.61 (m with Pt satellites  $J_{\text{Pt-H}} = 80.4$  Hz, 1H), 4.51 (m with Pt satellites,  $J_{\text{Pt-H}} = 80.4$  Hz, 1H);  $^{195}\text{Pt}$  NMR (64 MHz,  $\text{CH}_2\text{Cl}_2$ ): -2975 (Pt1), -3109 (Pt2). Characteristic peak for **5**:  $^{195}\text{Pt}$  NMR (64 MHz,  $\text{CH}_2\text{Cl}_2$ ): -2793.

### Kinetic Studies

**$[\text{Pt}_4(\text{COD})_4(\mu^3\text{-O})_2\text{Cl}_2]^{2+}$  (**1**) + NB.** In a typical reaction a solution of **1-BF<sub>4</sub>** (10.0 mg, 0.00672 mmol) in 0.45 mL  $\text{CD}_3\text{NO}_2$  was prepared in a screw-cap NMR tube and removed from the drybox. The sample was cooled in a dry ice/acetone bath and a solution of NB (13.5 mg, 0.143 mmol) in 0.2 mL of  $\text{CD}_3\text{NO}_2$  was added via syringe through the rubber septum cap. The contents were mixed and immediately the NMR tube was placed in the NMR probe (300 MHz). The reaction was monitored by  $^1\text{H}$  NMR spectroscopy.

Table S2. Kinetic data (25 °C) for the reaction of **1** and NB with excess **1** ( $[1]_0 = 74.3$  mM,  $[NB]_0 = 9.91$  mM).

t /min	integration NB	[NB]	ln[NB]
3	69.9	9.91	2.29
5	66.8	9.48	2.25
7	63.6	9.03	2.20
10	61.4	8.71	2.16
13	58.6	8.31	2.12
20	52.1	7.39	2.00
30	45.8	6.49	1.87
40	39.2	5.56	1.72
55	31.1	4.41	1.48
65	26.6	3.77	1.33
83	20.5	2.91	1.07
90	18.6	2.64	0.97
100	15.7	2.23	0.80
117	12.3	1.75	0.56

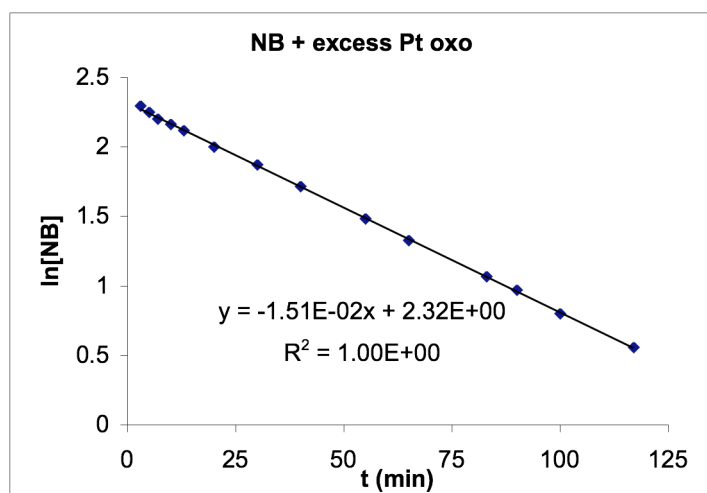


Figure S8. First order plot for the reaction of **1** and NB with excess **1** ( $[1]_0 = 74.3$  mM,  $[NB]_0 = 9.91$  mM) at 25 °C.

Table S3. Kinetic data (15 °C) for the reaction of **1** and NB with excess NB ( $[1]_0 = 10.3$  mM,  $[NB]_0 = 221$  mM). (See text for data plot.)

time/mins	Integration	[2]
5	0.10	3.4
15	0.16	5.4
25	0.19	6.4
35	0.21	7.1
45	0.25	8.4
55	0.27	9.1
65	0.31	10.5
75	0.36	12.2

85	0.38	12.8
95	0.43	14.5
105	0.47	15.9
115	0.49	16.5
125	0.50	16.9
135	0.55	18.6
145	0.58	19.6
155	0.60	20.3

**[Pt<sub>4</sub>(COD)<sub>4</sub>(μ<sup>3</sup>-O)<sub>2</sub>Cl<sub>2</sub>]<sup>2+</sup> (1) + NB + additives.** **A. HBF<sub>4</sub>.** A solution of **1-BF<sub>4</sub>** (10.0 mg, 0.00672 mmol) in 0.45 mL CD<sub>3</sub>NO<sub>2</sub> was prepared in a screw-cap NMR tube and 1.86 μL of a freshly prepared 0.67 M stock solution of HBF<sub>4</sub>·Et<sub>2</sub>O in CD<sub>3</sub>NO<sub>2</sub> was added. The tube was removed from the drybox and cooled in a dry ice/acetone bath. A solution of NB (13.5 mg, 0.143 mmol) in 0.2 mL was then added by syringe through the rubber septum. The contents were mixed and immediately the NMR tube was placed in the pre-cooled (15.0 °C) NMR probe (300 MHz). The formation of **2** was monitored by <sup>1</sup>H NMR spectroscopy. **B. BF<sub>3</sub>·Et<sub>2</sub>O and Pt(COD)(OTf)<sub>2</sub>.** A similar procedure was followed for these additives. In the case of BF<sub>3</sub>·Et<sub>2</sub>O, 2.8 μL of a 0.24 M stock solution of BF<sub>3</sub>·Et<sub>2</sub>O in CD<sub>3</sub>NO<sub>2</sub> was added. For Pt(COD)(OTf)<sub>2</sub>, 4.0 μL of a 0.17 M stock solution of Pt(COD)(OTf)<sub>2</sub> in CD<sub>3</sub>NO<sub>2</sub> was added. **C. PVP (Polyvinylpyridine).** PVP (~ 2 mg) was added to a room temperature solution of **1-BF<sub>4</sub>** (10.0 mg, 0.00672 mmol) in 0.45 mL CD<sub>3</sub>NO<sub>2</sub>, in a screw-cap NMR tube. After ~45 minutes the tube was removed from the dry box and placed in a dry ice/acetone bath. NB was added and the reaction monitored as described above. **D. [Pt(COD)(OH)]<sub>n</sub><sup>n+</sup> (5).** A CD<sub>3</sub>NO<sub>2</sub> solution of **5-OTf** (28.0 μL, 0.0479 M, n = 2) was added to a solution of **1-BF<sub>4</sub>** (10.0 mg, 0.00672 mmol) in 0.45 mL CD<sub>3</sub>NO<sub>2</sub>, in a screw-cap NMR tube. The tube was placed in a dry ice/acetone bath. NB was added and the reaction monitored as described above.

Table S4. Kinetic data (15 °C) for the reaction of **1** and NB with excess NB ([**1**]<sub>0</sub> = 10.3 mM, [NB]<sub>0</sub> = 221 mM) with added HBF<sub>4</sub>. (See text for data plot.)

<i>time/mins</i>	<i>Integration</i>	<i>[2]</i>
6	0.27	6.7
16	0.46	11.4
26	0.64	15.9
36	0.77	19.1

Table S5. Kinetic data (15 °C) for the reaction of **1** and NB with excess NB ( $[1]_0 = 10.3$  mM,  $[NB]_0 = 221$  mM) in the presence of PVP. (See text for data plot.)

<u>time/min</u>	<u>Integration</u>	<u>[2]</u>
4	0.15	3.43
9	0.12	2.75
14	0.14	3.20
19	0.11	2.52
24	0.15	3.43
29	0.17	3.89
34	0.21	4.81
39	0.19	4.35
44	0.18	4.12
49	0.18	4.12
54	0.2	4.58

$[Pt(COD)(OH)_2]^{2+}$  (**5**,  $n = 2$ ) + NB. A solution of **5-OTf** (10.0 mg, 0.0107 mmol,  $n = 2$ ) in 1.00 mL  $CD_2Cl_2$ , was prepared in a screw-cap NMR tube and removed from the drybox. The sample was cooled in a dry ice/acetone bath and a solution of NB (20.0 mg, 0.212 mmol) in 0.20 mL of  $CD_2Cl_2$  was added via syringe through the rubber septum. The tube was shaken and immediately placed in the pre-cooled (-10 °C) NMR probe (300 MHz). The formation of  $[Pt(COD)(C_7H_{10}OH)]^+$  (**7**) was monitored by  $^1H$  NMR spectroscopy. A similar procedure was followed with 40.0 mg (0.434 mmol) of NB in 0.20 mL of  $CD_2Cl_2$ . No correction was made for volume changes from the solutes or temperature differences.

Table S6. Kinetic data ( $T = -10$  °C) for the reaction of **5**,  $n = 2$  (8.9 mM) with NB (362 mM).

Time/mins	Integration	$[Pt_2(OH)_2]$	$[Pt_2(OH)_2]^{1/2}$
7	1.0	8.2	2.9
15	3.4	6.6	2.6
20	4.5	5.9	2.4
25	5.1	5.5	2.4
30	6.0	4.9	2.2
35	7.0	4.2	2.1
40	7.7	3.8	1.9
45	8.5	3.3	1.8
50	9.2	2.8	1.7
55	9.9	2.4	1.5
60	10.3	2.1	1.4
65	10.9	1.7	1.3
70	11.3	1.4	1.2
75	11.7	1.2	1.1

Table S7. Kinetic data (T = -10 °C) for the reaction of **5** (8.9 mM) with NB (181 mM).

Time/mins	Integration	[Pt <sub>2</sub> (OH) <sub>2</sub> ]	[Pt <sub>2</sub> (OH) <sub>2</sub> ] <sup>1/2</sup>
10	1.0	8.3	2.9
15	1.5	8.1	2.8
20	2.2	7.7	2.8
25	2.8	7.4	2.7
30	3.3	7.1	2.7
35	3.8	6.8	2.6
40	4.4	6.6	2.6
45	4.9	6.3	2.5
50	5.4	6.0	2.5
55	5.8	5.8	2.4
60	6.4	5.5	2.3
65	6.9	5.2	2.3
70	7.4	5.0	2.2
75	7.8	4.8	2.2
80	8.2	4.5	2.1
85	8.7	4.3	2.1
90	9.1	4.1	2.0
95	9.6	3.8	2.0
100	10.1	3.6	1.9
105	10.3	3.4	1.9
110	10.7	3.3	1.8
115	11.1	3.0	1.7
120	11.5	2.8	1.7
125	11.9	2.6	1.6
130	12.1	2.5	1.6
135	12.5	2.3	1.5
140	12.8	2.1	1.5
145	13.1	2.0	1.4
150	13.5	1.8	1.3
155	13.8	1.7	1.3
160	14.0	1.5	1.2
165	14.4	1.3	1.2
170	14.6	1.2	1.1
175	14.8	1.1	1.1
180	14.9	1.1	1.0
185	15.2	0.9	1.0
190	15.4	0.8	0.9
195	15.5	0.7	0.9
200	15.6	0.7	0.8

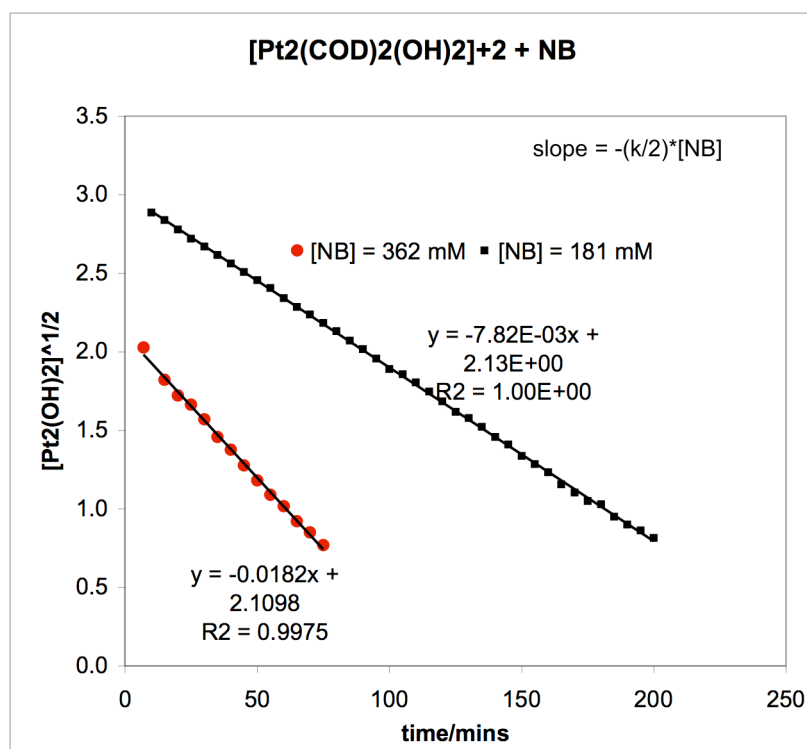


Figure S9. Half-order plots for the reaction of **5** with NB.

NB concentrations = 181 mM and 0.362 mM

$$\text{slope} = -(k/2) \cdot [NB]$$

$$k = -2(\text{slope}/[NB])$$

[NB]	k	
181 mM	8.64E-05	
362 mM	1.01E-04	
average	9.35E-05	min*(mM) <sup>-1/2</sup>

**Crystal Structure of 5-OTf (n = 4).** A crystal was mounted by transferring the crystals from the mother liquor into a pool of heavy oil. A suitable crystal was selected and removed from the oil with a glass fiber. With the oil covered crystal adhering to the end of the glass fiber the sample was transferred to an N<sub>2</sub> cold stream on the diffractometer and data were collected at −100 °C. Data reduction and processing followed routine procedures. The structure was solved by direct methods.

Siemens SMART CCD: The data collection nominally covered over a hemisphere of reciprocal space, by a combination of three sets of exposures; each set had a different  $\omega$  angle for the crystal and each exposure covered 0.3° in  $\omega$ . The crystal-to-detector distance was 5.00



cm. Coverage of the unique set is over 95% complete to at least  $26^\circ$  in  $\theta$ . Crystal decay was monitored by repeating the initial frames at the end of data collection and analyzing the duplicate reflections. No decay was detected. Data were corrected for absorption using the program SADABS based on the method of R.H. Blessing (Acta Cryst. A51, 33-38, 1995). Structures were solved by indirect methods. Refinement of  $F^2$  against all reflections. The weighted R-factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional R-factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\sigma(F^2)$  is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and R-factors based on ALL data will be even larger.

As detailed in the cif file the triflate anions are disordered and could not be well modeled. A drawing of the cationic portion is given below.

