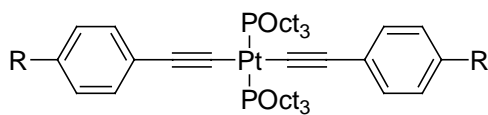


## **Supporting Information**

To accompany “Glass-forming liquid platinum acetylides” by Thomas M. Cooper, Benjamin C. Hall, Aaron R. Burke, Joy E. Rogers, Daniel G. McLean, Jonathan E. Slagle and Paul A. Fleitz.

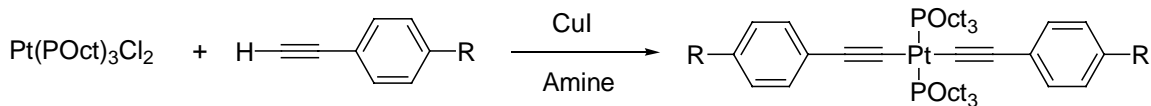
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13. Figure S11. Triplet state absorption spectra of compound **3** and *trans*- $\text{Pt}(\text{PBU}_3)_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_5)_2$
14. Figure S12. Phosphorescence spectrum of compound **3** in a glassy state compared with phosphorescence spectrum of  $\text{Pt}(\text{PBU}_3)_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_5)_2$  dissolved in a MeTHF glass.



**Figure S1.** Chemical formula of compounds prepared.

**Table S1 List of compounds prepared**

Compound	Number
PtCl <sub>2</sub> (POct <sub>3</sub> ) <sub>2</sub>	<b>1</b>
Pt(C≡CPh) <sub>2</sub> (POct <sub>3</sub> ) <sub>2</sub>	<b>2</b>
Pt(C≡CC <sub>6</sub> H <sub>4</sub> C≡CPh) <sub>2</sub> (POct <sub>3</sub> ) <sub>2</sub>	<b>3</b>
Pt(C≡CC <sub>6</sub> H <sub>4</sub> Ph) <sub>2</sub> (POct <sub>3</sub> ) <sub>2</sub>	<b>4</b>
Pt(C≡CC <sub>6</sub> H <sub>4</sub> Br) <sub>2</sub> (POct <sub>3</sub> ) <sub>2</sub>	<b>5</b>
Pt(C≡CC <sub>6</sub> H <sub>4</sub> C≡CC <sub>6</sub> H <sub>4</sub> C(CH <sub>3</sub> ) <sub>3</sub> ) <sub>2</sub> (POct <sub>3</sub> ) <sub>2</sub>	<b>6</b>
Pt(C≡CC <sub>6</sub> H <sub>4</sub> C≡CH) <sub>2</sub> (POct <sub>3</sub> ) <sub>2</sub>	<b>7</b>



**Figure S2. Reaction scheme.**

## EXPERIMENTAL

### GENERAL CONDITIONS

All reactions were carried out using dry, distilled solvents and under dry high purity nitrogen. Alumina column refers to a support of  $\text{Al}_2\text{O}_3$  (Activated, neutral, Brockman grade I, standard grade,  $\sim 150$  mesh,  $58 \text{ \AA}$ ). Silica column refers to a support of Silica (for column chromatography, mesh 70-230 mesh,  $60 \text{ \AA}$ ).

### INSTRUMENTATION

Infrared spectra were obtained on a Perkin-Elmer 2000 FT IR spectrometer. Thin film spectra were obtained from samples mounted between NaCl or KBr discs. NMR spectra were recorded on an Inova 300 ( $^1\text{H}$  at 299.79 MHz,  $^{13}\text{C}$  at 75.38 MHz,  $^{31}\text{P}$  at 121.36 MHz) spectrometer. Samples were dissolved in  $\text{CDCl}_3$  (Aldrich) and spectra were recorded using 5mm sample tubes. Electron impact mass spectra (EI MS) were obtained from samples dissolved initially in  $\text{CH}_2\text{Cl}_2$  and diluted with MeOH. Electrospray mass spectra (ES MS) were obtained from samples dissolved initially in  $\text{CH}_2\text{Cl}_2$  and diluted with MeOH. Chemical aids to ionisation were used where indicated. Differential scanning calorimetry (DSC) measurements were obtained from an Instruments TA DSC 2920 differential scanning calorimeter. DSC measurements were performed by equilibrating a weighed sample at  $15^\circ\text{C}$ , cooling at  $4^\circ\text{C}/\text{min}$  to  $-120^\circ\text{C}$ , followed by equilibration at  $-120^\circ\text{C}$  and heating at  $4^\circ\text{C}/\text{min}$  to  $15^\circ\text{C}$ . The glass transition temperature in  $^\circ\text{C}$  was measured from the overshoot peak temperature of the heating portion of the thermogram.

### REAGENTS

$\text{POct}_3$ ,  $\text{K}_2[\text{PtCl}_4]$ ,  $\text{HC}\equiv\text{CPh}$ ,  $\text{HC}\equiv\text{CPh-Ph}$  and  $\text{CuI}$  were purchased from Aldrich Chemical and used without further purification.

$\text{HC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CBr}$   $\text{HC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CPh}$ ,  $\text{HC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4\text{C}(\text{CH}_3)_3$  were prepared from reported literature methods (Rogers, J.E.; Cooper, T.M.; Fleitz, P.A.; Glass, D.J.; McLean D.G. J. Phys Chem A **106**: 10108-10115(2002)).

## SYNTHESIS PROCEDURES AND ANALYTICAL DATA.

### $\text{PtCl}_2(\text{POct}_3)_2$ **1**

To a solution of  $\text{K}_2[\text{PtCl}_4]$  (2000 mg, 4.84 mmol) in water (50 ml) trioctylphosphine (4313  $\mu\text{l}$ , 9.68 mmol) was added and the resulting solution left to stir at room temperature for 2 days giving a yellow sticky solid. Dichloromethane (30 ml) was added and the organic layer separated. Removal of the solvent gave a yellow liquid, which crystallises upon cooling. Identified as a mixture of *cis*- and *trans*-  $\text{PtCl}_2(\text{POct}_3)_2$  **1** (3000 mg, 62%). MA: found C, 57.54; H, 10.08.  $\text{C}_{48}\text{H}_{102}\text{Cl}_2\text{P}_2\text{Pt}$ . requires C, 57.24; H, 10.21 %.  $M_w = 1005$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.88 (m, 9H,  $\text{CH}_3$ ), 1.25 (m, 24H,  $\text{CH}_2$ ), 1.38 (m, 6H,  $\text{CH}_2$ ), 1.52 (m, 6H,  $\text{CH}_2$ ), 1.95 (m, 6H,  $\text{CH}_2$ ) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  14.30 (s,  $\text{CH}_3$ ), 22.85 (s,  $\text{CH}_2$ ), 24.38 (t,  $J(\text{CP}) = 17$  Hz,  $\text{CH}_2$ ), 24.70 (s,  $\text{CH}_2$ ), 29.41 (s,  $\text{CH}_2$ ), 29.45 (s,  $\text{CH}_2$ ), 31.30 (t,  $J(\text{CP}) = 7$  Hz,  $\text{CH}_2$ ), 32.05 (s,  $\text{CH}_2$ ) ppm.  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.08 (s,  $J(\text{PPt}) = 3515$  Hz, *cis*- $\text{POct}_3$ ), 5.75 (s,  $J(\text{PPt}) = 2378$  Hz, *trans*- $\text{POct}_3$ ) ppm. EI MS: ( $m/z$ ) 1005,  $[\text{M}]^+$ ; 935,  $[\text{M}-2\text{Cl}]^+$ ; 407,  $[\text{Cl.P}(\text{C}_8\text{H}_{17})_3]^+$ ; 371,  $[\text{H.P}(\text{C}_8\text{H}_{17})_3]^+$ ; 258,  $[\text{H.P}(\text{C}_8\text{H}_{17})_2]^+$ .

### $\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{POct}_3)_2$ **2**

To a microwave cell, **1** (500 mg, 0.50 mmol),  $\text{HC}\equiv\text{CPh}$  (137  $\mu\text{l}$ , 1.24 mmol), CuI (19 mg, 0.1 mmol) and  $\text{NH}_2\text{Et}_2$  (10 ml) were added and heated for 10 minutes at 150 W [ $\sim 48$  PSI]. After this time the solution was pale green and the white precipitate of  $\text{NH}_2\text{Et}_2\text{Cl}$  was seen. Solvent was removed, residue dissolved in  $\text{CH}_2\text{Cl}_2$  and purified on alumina, elution with hexane gave a pale yellow fraction, which gave an oil upon removal of solvent. Identified as  $\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{POct}_3)_2$  **2** (512 mg, 90%). MA: found C, 67.58; H, 9.96.  $\text{C}_{64}\text{H}_{112}\text{P}_2\text{Pt}$  requires C, 67.51; H, 9.91 %.  $M_w = 1137.79$ ; IR(thin film):  $2103\text{ cm}^{-1}$  ( $\text{Pt-C}\equiv\text{C}$  stretch);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.89 (m, 9H,  $\text{CH}_3$ ), 1.27 (m, 24H,  $\text{CH}_2$ ), 1.42 (m, 6H,  $\text{CH}_2$ ), 1.60 (m, 6H,  $\text{CH}_2$ ), 2.16 (m, 6H,  $\text{CH}_2$ ), 7.10 – 7.29 (m, 5H, ArH) ppm.  $^{13}\text{C}$

NMR (CDCl<sub>3</sub>):  $\delta$  14.38 (s, CH<sub>3</sub>), 22.94 (s, CH<sub>2</sub>), 24.38 (t,  $J(\text{CP}) = 17$  Hz, CH<sub>2</sub>), 24.48 (s, CH<sub>2</sub>), 29.51 (s, CH<sub>2</sub>), 31.59 (t,  $J(\text{CP}) = 7$  Hz, CH<sub>2</sub>), 32.16 (s, CH<sub>2</sub>), 108.28 (t,  $J(\text{CP}) = 15$  Hz, Pt-C $\equiv$ C), 109.20 (s, Pt-C $\equiv$ C), 124.98 (s, ArH), 128.01 (s, ArH), 129.35 (s, Ar), 131.06 (s, ArH) ppm. <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  4.41 (s,  $J(\text{PPt}) = 2355$  Hz, POct<sub>3</sub>) ppm. EI MS: ( $m/z$ ) 1138, [M]<sup>+</sup>; 1024, [M-C<sub>8</sub>H<sub>17</sub>]<sup>+</sup>; 558, [Pt(PC<sub>8</sub>H<sub>15</sub>)<sub>2</sub>]<sup>+</sup>; 471, [PhC $\equiv$ C.P(C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>]<sup>+</sup>; 371, [H.P(C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>]<sup>+</sup>. ES MS: (added NaOMe,  $m/z$ ) 1160, [M+Na]<sup>+</sup>.

### Pt(C $\equiv$ CC<sub>6</sub>H<sub>4</sub>C $\equiv$ CPh)<sub>2</sub>(POct<sub>3</sub>)<sub>2</sub> **3**

To a solution of **1** (200 mg, 0.20 mmol) and HC $\equiv$ CC<sub>6</sub>H<sub>4</sub>C $\equiv$ CPh (100 mg, 0.50 mmol) in a mixture of piperidine (5 ml) and toluene (10 ml), CuI (4 mg, 0.02 mmol) was added and stirred at room temperature for 16 hours. Solvent was removed and the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and purified on alumina, elution with hexane gave an orange-yellow fraction, which gave an orange - yellow oil upon removal of solvent. Identified as Pt(C $\equiv$ CC<sub>6</sub>H<sub>4</sub>C $\equiv$ CPh)<sub>2</sub>(POct<sub>3</sub>)<sub>2</sub> **3** (454 mg, 85%). MA: found C, 71.78; H, 8.80. C<sub>80</sub>H<sub>120</sub>P<sub>2</sub>Pt requires C, 71.77; H, 9.03 %. M<sub>w</sub> = 1337.85; IR(thin film): 2098 cm<sup>-1</sup>(Pt-C $\equiv$ C stretch); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.90 (m, 9H, CH<sub>3</sub>), 1.28 (m, 24H, CH<sub>2</sub>), 1.43 (m, 6H, CH<sub>2</sub>), 1.65 (m, 6H, CH<sub>2</sub>), 2.15 (m, 6H, CH<sub>2</sub>), 7.24 – 7.55 (m, 9H, ArH) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  14.41 (s, CH<sub>3</sub>), 22.97 (s, CH<sub>2</sub>), 24.38 (t,  $J(\text{CP}) = 17$  Hz, CH<sub>2</sub>), 24.50 (s, CH<sub>2</sub>), 29.53 (s, CH<sub>2</sub>), 31.60 (t,  $J(\text{CP}) = 7$  Hz, CH<sub>2</sub>), 32.18 (s, CH<sub>2</sub>), 89.98 (s, C $\equiv$ C), 90.33 (s, C $\equiv$ C), 109.66 (s, Pt-C $\equiv$ C), 112.04 (t,  $J(\text{CP}) = 15$  Hz, Pt-C $\equiv$ C), 123.86 – 132.69 (m, Ar and ArH) ppm. <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  4.51 (s,  $J(\text{PPt}) = 2342$  Hz, POct<sub>3</sub>) ppm. EI MS: ( $m/z$ ) 1338, [M]<sup>+</sup>; 935, [Pt(P(C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>)<sub>2</sub>]<sup>+</sup>; 573, [PhC $\equiv$ CC<sub>6</sub>H<sub>4</sub>C $\equiv$ C.P(C<sub>8</sub>H<sub>17</sub>)<sub>3</sub> + 2H]<sup>+</sup>; 571, [PhC $\equiv$ CC<sub>6</sub>H<sub>4</sub>C $\equiv$ C.P(C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>]<sup>+</sup>; 369, [P(C<sub>8</sub>H<sub>17</sub>)<sub>3</sub> - H]<sup>+</sup>; 327, [C<sub>5</sub>H<sub>10</sub>P(C<sub>8</sub>H<sub>17</sub>)<sub>2</sub>]<sup>+</sup>; 285, [C<sub>2</sub>H<sub>5</sub>P(C<sub>8</sub>H<sub>17</sub>)<sub>2</sub>]<sup>+</sup>; 228, HP(C<sub>8</sub>H<sub>17</sub>)<sub>2</sub><sup>+</sup>. ES MS: (added NaOMe,  $m/z$ ) 1360, [M+Na]<sup>+</sup>.

### Pt(C $\equiv$ CC<sub>6</sub>H<sub>4</sub>Ph)<sub>2</sub>(POct<sub>3</sub>)<sub>2</sub> **4**

To a microwave cell, **1** (500 mg, 0.50 mmol), HC≡CC<sub>6</sub>H<sub>4</sub>Ph (196 mg, 1.10 mmol), CuI (10 mg, 0.05 mmol) and NH<sub>4</sub>Et<sub>2</sub> (15 ml) were added and heated for 30 minutes at 150 W [~ 48 PSI]. After this time the solution was pale green and the white precipitate of NH<sub>4</sub>Et<sub>2</sub>Cl was seen. Solvent was removed, residue dissolved in CH<sub>2</sub>Cl<sub>2</sub> and purified on alumina, elution with hexane gave a pale yellow fraction, which gave a yellow oil upon removal of solvent. Identified as Pt(C≡CC<sub>6</sub>H<sub>4</sub>Ph)<sub>2</sub>(POct<sub>3</sub>)<sub>2</sub> **4** (305 mg, 48%). MA: found C, 70.77; H, 9.42. C<sub>76</sub>H<sub>120</sub>P<sub>2</sub>Pt requires C, 70.72; H, 9.37 %. M<sub>w</sub> = 1289.85; IR(thin film): 2101 cm<sup>-1</sup>(Pt-C≡C stretch); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.88 (m, 9H, CH<sub>3</sub>), 1.28 (m, 24H, CH<sub>2</sub>), 1.46 (m, 6H, CH<sub>2</sub>), 1.67 (m, 6H, CH<sub>2</sub>), 2.17 (m, 6H, CH<sub>2</sub>), 7.35 – 7.62 (m, 9H, ArH) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 14.39 (s, CH<sub>3</sub>), 22.95 (s, CH<sub>2</sub>), 24.45 (t, J(CP) = 17 Hz, CH<sub>2</sub>), 24.53 (s, CH<sub>2</sub>), 29.55 (s, CH<sub>2</sub>), 31.64 (t, J(CP) = 7 Hz, CH<sub>2</sub>), 31.87 (s, CH<sub>2</sub>), 32.19 (s, CH<sub>2</sub>), 109.18 (s, Pt-C≡C), 109.71 (t, J(CP) = 15 Hz, Pt-C≡C), 126.76 (s, ArH), 126.99 (s, ArH), 127.09 (s, Ar), 128.93 (s, ArH), 131.44 (s, ArH), 137.64 (s, Ar), 141.42 (s, Ar) ppm. <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ 4.50 (s, J(PPt) = 2353 Hz, POct<sub>3</sub>) ppm. ES MS: (added NaOMe, *m/z*) 1313, [M + Na]<sup>+</sup>; 1290, [M]<sup>+</sup>.

#### Pt(C≡CC<sub>6</sub>H<sub>4</sub>Br)<sub>2</sub>(POct<sub>3</sub>)<sub>2</sub> **5**

To a microwave cell, **1** (500 mg, 0.50 mmol), HC≡CC<sub>6</sub>H<sub>4</sub>Br (223 mg, 1.24 mmol), CuI (19 mg, 0.1 mmol) and NH<sub>4</sub>Et<sub>2</sub> (10 ml) were added and heated for 20 minutes at 150 W [~ 48 PSI]. After this time the solution was pale green and the white precipitate of NH<sub>4</sub>Et<sub>2</sub>Cl was seen. Solvent was removed, residue dissolved in CH<sub>2</sub>Cl<sub>2</sub> and purified on alumina, elution with hexane gave a pale yellow fraction, which gave an oil upon removal of solvent. Identified as Pt(C≡CC<sub>6</sub>H<sub>4</sub>Br)<sub>2</sub>(POct<sub>3</sub>)<sub>2</sub> **5** (530 mg, 82%). MA: found C, 59.65; H, 8.46. C<sub>64</sub>H<sub>110</sub>Br<sub>2</sub>P<sub>2</sub>Pt requires C, 59.29; H, 8.55 %. M<sub>w</sub> = 1293; IR(thin film): 2103 cm<sup>-1</sup>(Pt-C≡C stretch); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.88 (m, 9H, CH<sub>3</sub>), 1.27 (m, 24H, CH<sub>2</sub>), 1.39 (m, 6H, CH<sub>2</sub>), 1.60 (m, 6H, CH<sub>2</sub>), 2.09 (m, 6H, CH<sub>2</sub>), 7.09 – 7.32 (m, 4H, ArH) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 14.36 (s, CH<sub>3</sub>), 22.93 (s, CH<sub>2</sub>), 24.46 (t, J(CP) = 17 Hz, CH<sub>2</sub>), 29.49 (s, CH<sub>2</sub>), 31.56 (t, J(CP) = 7 Hz, CH<sub>2</sub>), 31.85 (s, CH<sub>2</sub>), 32.15 (s, CH<sub>2</sub>), 108.28 (s, Pt-C≡C), 110.13 (t, J(CP) = 15 Hz, Pt-C≡C), 118.57 (s, ArBr), 131.15 (s,

ArH), 132.47 (s, ArH), 133.78 (s, Ar) ppm.  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  4.49 (s,  $J(\text{PPt}) = 2344$  Hz,  $\text{POct}_3$ ) ppm. ES MS: (added, NaOMe,  $m/z$ ) 1319,  $[\text{M} + \text{Na}]^+$ ; 1296,  $[\text{M}]^+$ .

$\text{Pt}(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4\text{CMe}_3)_2(\text{POct}_3)_2$  **6**

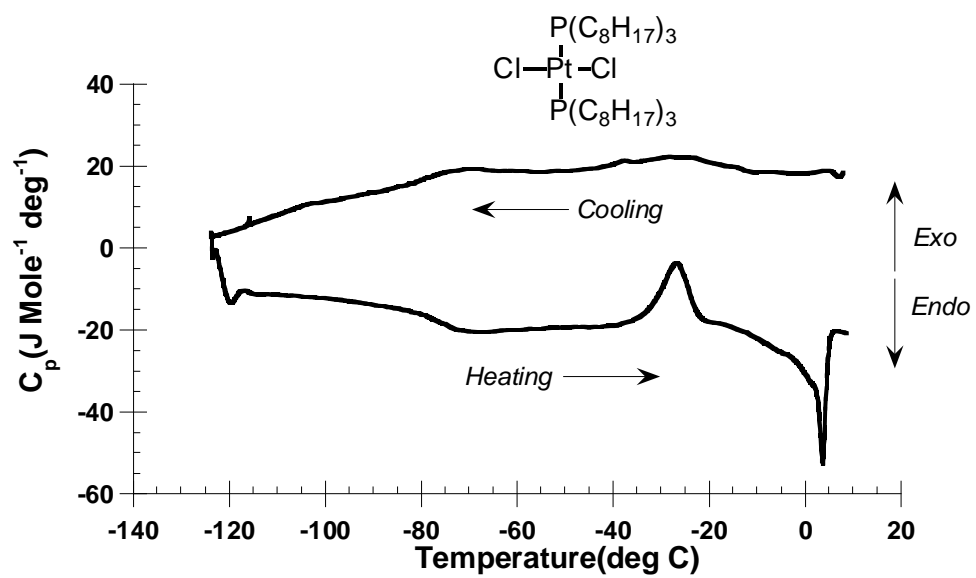
To a solution of **1** (1065 mg, 1.06 mmol) and  $\text{HC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4\text{CMe}_3$  (684 mg, 2.65 mmol) in diethylamine (35 ml), CuI (19 mg, 0.1 mmol) was heated in a microwave for 30 minutes. Solvent was removed and the residue was dissolved in  $\text{CH}_2\text{Cl}_2$  and purified on alumina, elution with hexane gave a yellow-orange fraction, which gave a yellow - orange oil upon removal of solvent. Identified as  $\text{Pt}(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4\text{CMe}_3)_2(\text{POct}_3)_2$  **6** (1152 mg, 75%). MA: found C, 71.68; H, 9.31.  $\text{C}_{88}\text{H}_{136}\text{P}_2\text{Pt}(0.33\text{CH}_2\text{Cl}_2)$  requires C, 71.72; H, 9.31 %.  $M_w = 1449.98$ ; IR(thin film):  $2099\text{ cm}^{-1}$  (Pt-C $\equiv$ C stretch);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.95 (t, 9H,  $\text{CH}_3$ ), 1.31 (m, 6H,  $\text{CH}_2$ ), 1.36 (s, 9H,  $\text{CMe}_3$ ), 1.45 (m, 24H,  $\text{CH}_2$ ), 1.66 (m, 6H,  $\text{CH}_2$ ), 2.16 (m, 6H,  $\text{CH}_2$ ), 7.17 – 7.52 (m, 8H, ArH) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  14.04 (s,  $\text{CH}_3$ ), 22.95 (s,  $\text{CH}_2$ ), 22.99 (s,  $\text{CMe}_3$ ), 24.52 (t,  $J(\text{CP}) = 17$  Hz,  $\text{CH}_2$ ), 29.55 (s,  $\text{CH}_2$ ), 31.53 (t,  $J(\text{CP}) = 7$  Hz,  $\text{CH}_2$ ), 31.70 (s,  $\text{CH}_2$ ), 31.89 (s,  $\text{CH}_2$ ), 32.21 (s,  $\text{CH}_2$ ), 34.99 (s,  $\text{CMe}_3$ ), 89.66 (s, C $\equiv$ C), 90.11 (s, C $\equiv$ C), 109.69 (s, Pt-C $\equiv$ C), 111.76 (t,  $J(\text{CP}) = 15$  Hz, Pt-C $\equiv$ C), 119.79 (s, Ar), 120.89 (s, Ar), 125.54 (s, ArH), 131.39 (s, ArH), 131.46 (s, ArH), 132.52 (s, Ar), 151.44 (s, Ar) ppm.  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  4.58 (s,  $J(\text{PPt}) = 2346$  Hz,  $\text{POct}_3$ ) ppm. ES MS: (added NaOMe,  $m/z$ ) 1449,  $[\text{M}]^+$ .

$\text{Pt}(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CH})_2(\text{POct}_3)_2$  **7**

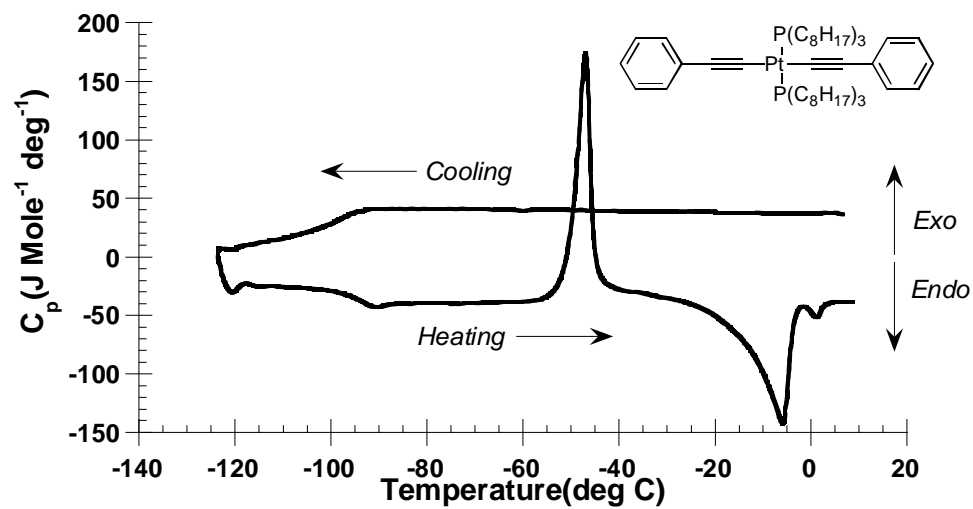
To a solution of **1** (500 mg, 0.50 mmol) and  $\text{HC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CH}$  (138 mg, 1.1 mmol) in a mixture of piperidine (5 ml) and toluene (10 ml), CuI (10 mg, 0.05 mmol) was added and stirred at room temperature for 16 hours. Solvent was removed and the residue was dissolved in  $\text{CH}_2\text{Cl}_2$  and purified on alumina, elution with hexane gave a pale yellow fraction, which gave a yellow - orange oil upon removal of solvent. Identified as  $\text{Pt}(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CH})_2(\text{POct}_3)_2$  **7** (550 mg, 93%). MA: found C, 65.25; H, 9.18.  $\text{C}_{68}\text{H}_{112}\text{P}_2\text{Pt} \cdot \text{CH}_2\text{Cl}_2$  requires C, 65.17; H, 9.04 %.  $M_w = 1185.79$ ; IR(thin film):  $2098\text{ cm}^{-1}$  (Pt-C $\equiv$ C stretch),  $3318\text{ cm}^{-1}$  (C $\equiv$ C-H stretch);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.88 (m, 9H,  $\text{CH}_3$ ), 1.25 (m, 24H,  $\text{CH}_2$ ), 1.38 (m, 6H,  $\text{CH}_2$ ), 1.57 (m, 6H,  $\text{CH}_2$ ), 2.23 (m, 6H,  $\text{CH}_2$ ),

3.08 (s, 1H, C≡CH), 7.12 – 7.48 (m, 4H, ArH) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  14.36 (s,  $\text{CH}_3$ ), 22.91 (s,  $\text{CH}_2$ ), 24.46 (m,  $\text{CH}_2$ ), 29.47 (m,  $\text{CH}_2$ ), 31.54 (t,  $J(\text{CP}) = 7$  Hz,  $\text{CH}_2$ ), 32.13 (s,  $\text{CH}_2$ ), 77.48 (s, C≡CH), 84.47 (s, C≡CH), 109.38 (s, Pt-C≡C), 112.15 (t,  $J(\text{CP}) = 15$  Hz, Pt-C≡C), 129.87 – 132.61 (m, Ar and ArH) ppm.  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  4.52 (s,  $J(\text{PPt}) = 2340$  Hz,  $\text{POct}_3$ ) ppm. EI MS: ( $m/z$ ) 1185,  $[\text{M}]^+$ ; 370,  $[\text{P}(\text{C}_8\text{H}_{17})_3]^+$ ; 327,  $[\text{P}(\text{C}_8\text{H}_{17})_2]^+$ ; 258,  $[\text{H.PC}_8\text{H}_{17} - \text{C}_2\text{H}_5]^+$ ; 126,  $[\text{HC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CH}]^+$ . ES MS: (added NaOMe,  $m/z$ ) 1208,  $[\text{M}+\text{Na}]^+$ .

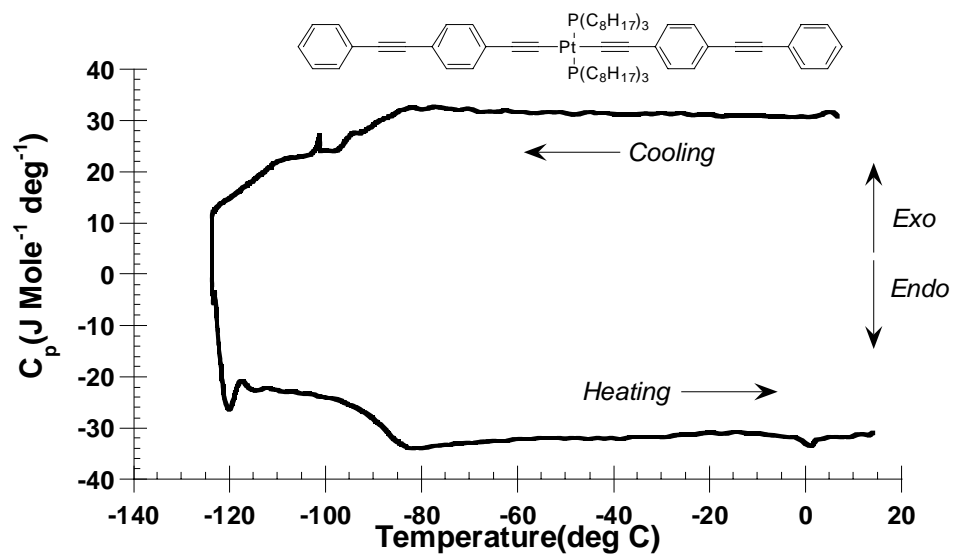




**Figure S3.** DSC plot for compound **1**.



**Figure S4.** DSC plot for compound 2.



**Figure S5.** DSC plot for compound **3**

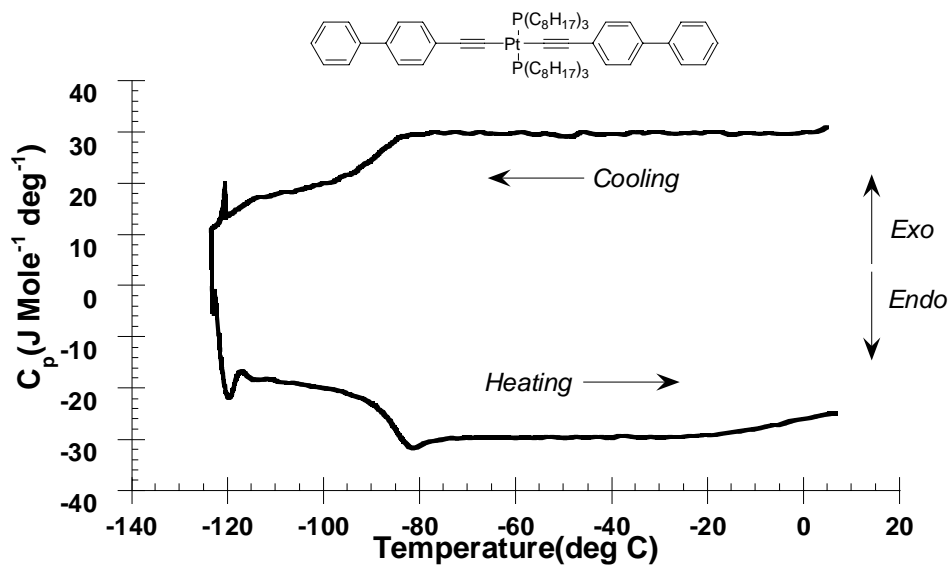
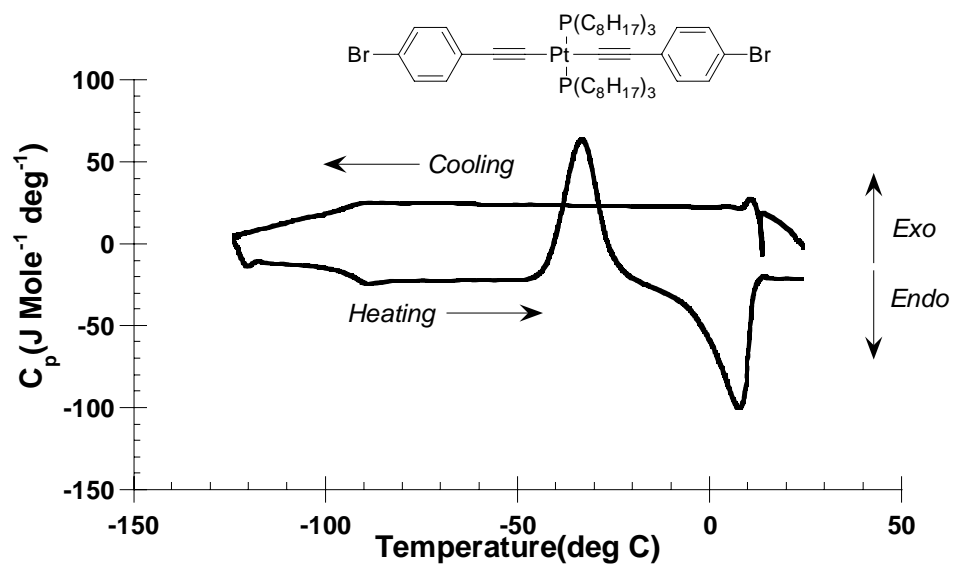
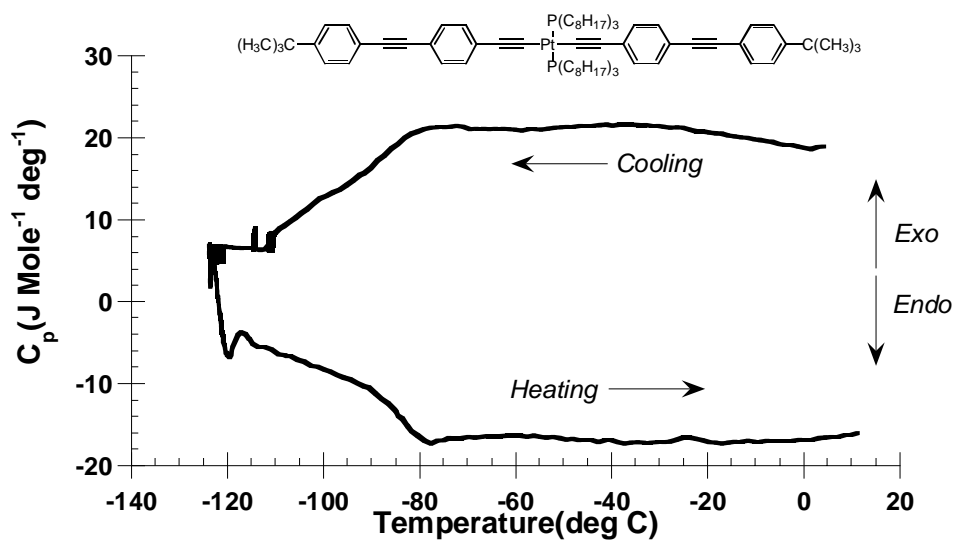


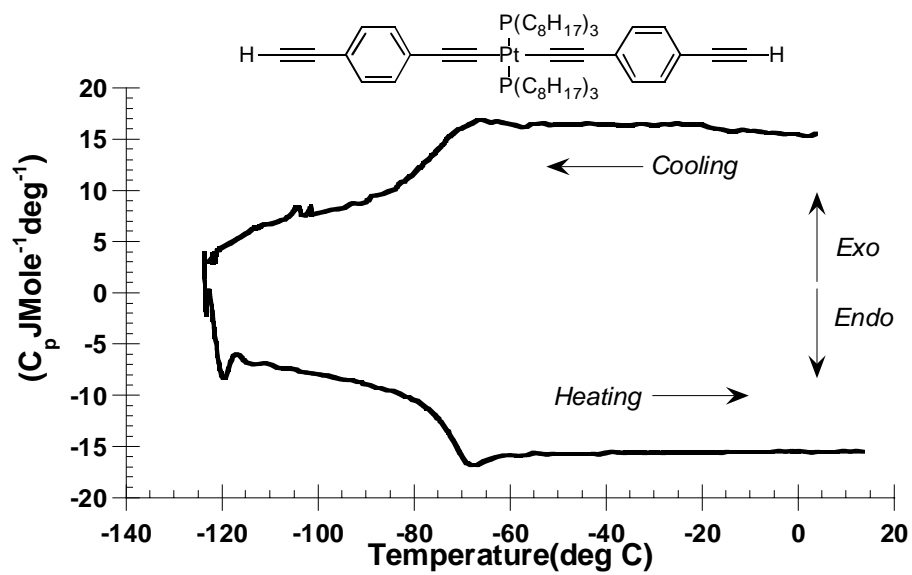
Figure S6. DSC plot for compound 4.



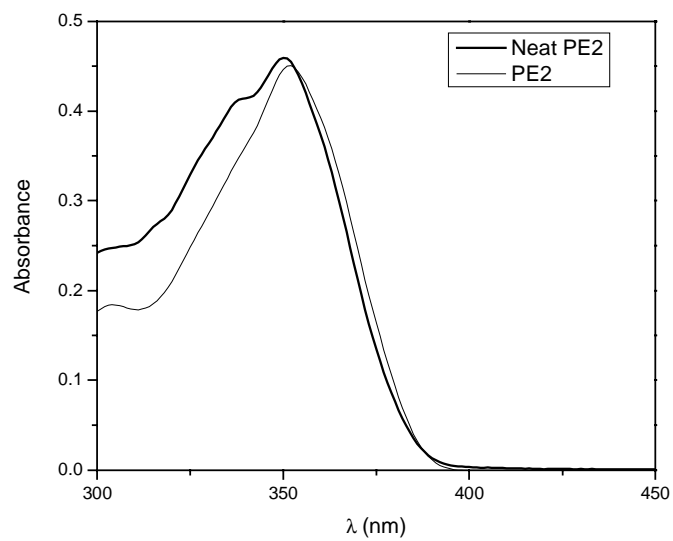
**Figure S7.** DSC plot for compound **5**.



**Figure S8.** DSC plot for compound 6.

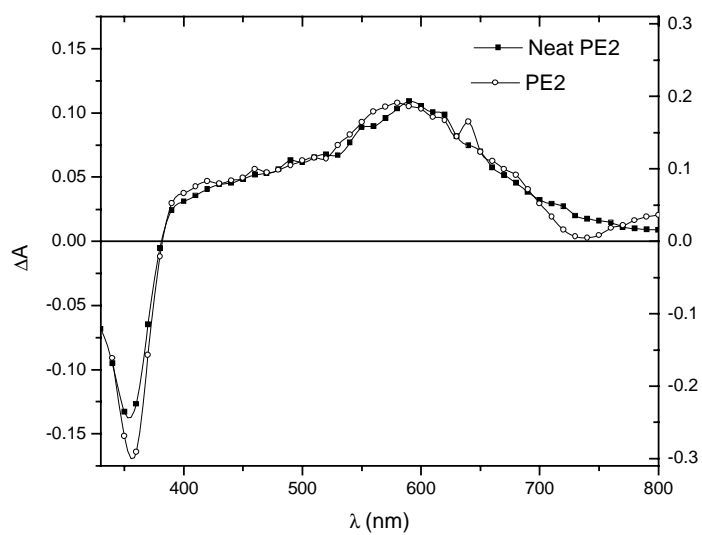


**Figure S9.** DSC plot for compound **7**.

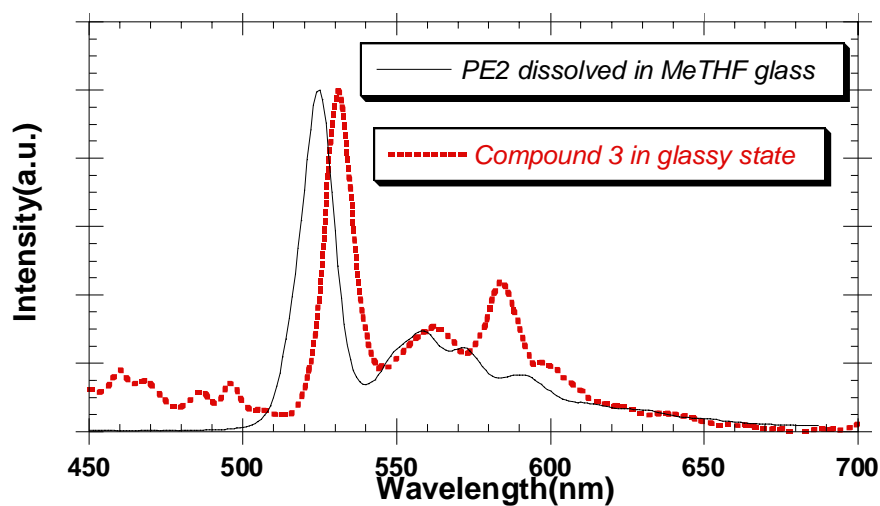


**Figure S10.** Ground state absorption spectra of compound **3** and *trans*-Pt(PBu<sub>3</sub>)<sub>2</sub>(C≡CC<sub>6</sub>H<sub>4</sub>C≡CC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>





**Figure S11.** Triplet state absorption spectra of compound **3** and *trans*-Pt(PBu<sub>3</sub>)<sub>2</sub>(C≡CC<sub>6</sub>H<sub>4</sub>C≡CC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>



**Figure S12.** Phosphorescence spectrum of compound **3** in a glassy state compared with phosphorescence spectrum of  $\text{Pt}(\text{PBu}_3)_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_5)_2$  dissolved in a MeTHF glass. Compound **3** or  $\text{Pt}(\text{PBu}_3)_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_5)_2$  dissolved in MeTHF was placed in a quartz capillary and cooled to 77 °K. Emission spectra were collected by exciting the sample at 350 nm. The spectrometer excitation and emission slit widths were set at 5 nm.