SUPPORTING INFORMATION

Solvent-Controlled Switch of Selectivity between sp^2 and sp^3 C-H Bond Activation by Platinum (II)

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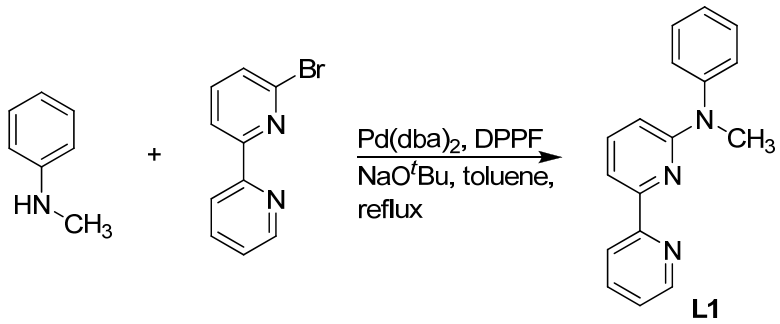
Synthesis

General: All manipulations were conducted under a dry nitrogen atmosphere and anhydrous conditions. Tetrahydrofuran (THF) was distilled from sodium and benzophenone. All other anhydrous solvents used were purchased from Sigma-Aldrich with Sure Seal. All other chemicals were also purchased from Sigma-Aldrich. All catalysts and reagents were purchased from Sigma-Aldrich, with the exception of K_2PtCl_4 which was purchased from Strem Chemicals. Commercial reagent grade solvents and chemicals were used as obtained unless otherwise noted. 6-Bromo-2,2'-bipyridine was prepared following the literature procedure.[1] Preparative chromatography was performed on silica gel 60 (0.063-0.200 mm) purchased from EMD chemicals. Thin layer chromatography was performed with silica gel 60 F_{254} plates, purchased from EMD chemicals. Compounds were visualized under UV lamp at 254 or 365 nm. ^1H and ^{13}C NMR spectra were recorded on Varian 500 MHz and 300 MHz spectrometers at 298K. Chemical shifts were reported relative to TMS (0.0 ppm for ^1H), dichloromethane-d_2 (53.8 ppm for ^{13}C), chloroform-d (77.0 ppm for ^{13}C), DMSO-d_6 (39.5 ppm for ^{13}C) and coupling constants are in Hertz. Elemental analyses were performed in Analytical Microlabs, Norcross, GA.

Preparation of Ligands

*N-Methyl-N-phenyl-2,2'-bipyridin-6-amine (**L1**)*

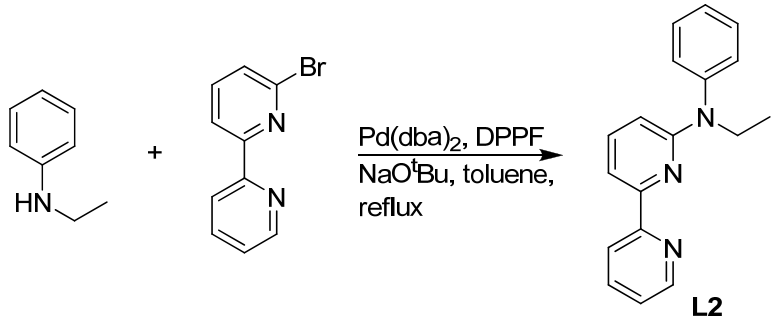


General Procedure A: To a 50 mL dry, three necked flask were added N-methylaniline (0.16 mL, 1.5 mmol), 6-bromo-2,2'-bipyridine (235 mg, 1.0 mmol), $Pd(dba)_2$ (23 mg, 0.04 mmol), DPPF (22 mg, 0.04 mmol), sodium *tert*-butoxide (115 mg, 1.2 mmol), and toluene (15 mL). The reaction mixture was refluxed under nitrogen for 1 hour. After cooling to room

[1] Y.-Q. Fang and G. S. Hana,; *Synlett*, 2003, 852–854

temperature, the reaction mixture was quenched with water and extracted with ethyl acetate (3 x 50 mL). The combined organic phases were washed with water (50 mL), brine (50 mL), dried over $MgSO_4$, filtered, and evaporated. The crude product was purified by column chromatography on silica gel with dichloromethane and ethyl acetate (v/v: 40:1 to 20:1) to give a white colored solid, 206 mg, 79%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65 (d, *J* = 4.5 Hz, 1H), 8.43 (d, *J* = 9.0 Hz, 1H), 7.79-7.76 (m, 2H), 7.47-7.39 (m, 3H), 7.32-7.30 (m, 2H), 7.27-7.20 (m, 2H), 6.59 (d, *J* = 9.0 Hz, 1H), 3.60 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.2, 156.9, 153.8, 148.9, 146.9, 137.5, 136.6, 129.6 (2C), 126.3 (2C), 125.3, 123.2, 120.9, 110.4, 109.4, 38.2. Anal. Calcd for $C_{17}H_{15}N_3$: C, 78.13; H, 5.79; N, 16.08. Found: C, 77.93; H, 5.70; N, 15.95.

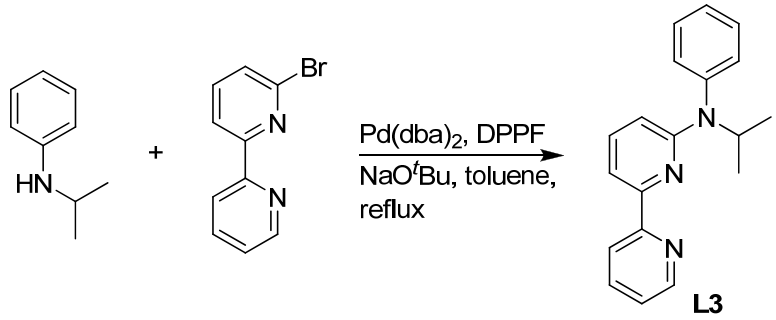
N-Ethyl-N-phenyl-2,2'-bipyridin-6-amine (***L2)***



L2

This compound was prepared according to the **General Procedure A**. The crude product was purified by column chromatography on silica gel with dichloromethane and ethyl acetate (v/v: 3:1) then hexane and ethyl acetate (v/v: 5:1) to give a light yellow colored solid, yield 89%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65 (d, *J* = 4.5 Hz, 1H), 8.42 (d, *J* = 8.5 Hz, 1H), 7.80 (dt, *J* = 7.8, 2.0Hz, 1H), 7.74 (d, *J* = 7.0 Hz, 1H), 7.44-7.40 (m, 3H), 7.30-7.24 (m, 4H), 6.42 (d, *J* = 8.5 Hz, 1H), 4.15 (q, *J* = 7.0 Hz, 2H), 1.31 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) 157.9, 157.2, 153.8, 149.0, 145.7, 137.7, 136.9, 129.9 (2C), 127.9 (2C), 126.0, 123.4, 121.1, 110.3, 109.8, 45.3, 13.3. Anal. Calcd for $C_{18}H_{17}N_3$: C, 78.52; H, 6.22; N, 15.26. Found: C, 78.24; H, 6.18; N, 15.31.

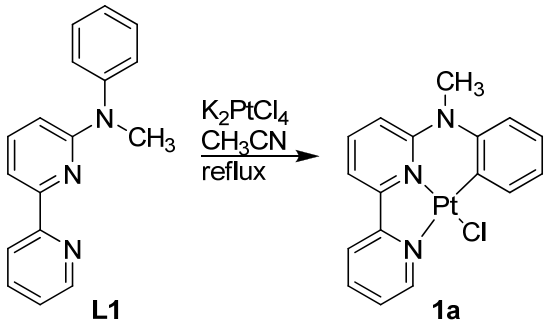
N-Isopropyl-N-phenyl-2,2'-bipyridin-6-amine (***L3)***



This compound was prepared according to the **General Procedure A**. The crude product was purified by column chromatography on silica gel with a mixture of dichloromethane and hexane (v/v: 1:1) to give a white solid, yield 55%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.65 (d, *J* = 4.5 Hz, 1H), 8.44 (d, *J* = 9.5 Hz, 1H), 7.81 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.69 (d, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.38-7.33 (m, 2H), 7.28-7.25 (m, 1H), 7.21-7.19 (m, 2H), 6.00 (d, *J* = 8.0 Hz, 1H), 5.47-5.39 (m, 1H), 1.22 (d, *J* = 7 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ (ppm): 158.4, 157.1, 153.2, 148.7, 141.5, 137.4, 136.8, 131.5 (2C), 129.6 (2C), 127.2, 123.1, 120.9, 109.7, 109.4, 46.4, 21.1 (2C). Anal. Calcd for $C_{19}H_{19}N_3$: C, 78.86; H, 6.62; N, 14.52. Found: C, 78.59; H, 6.55; N, 14.42.

Reaction of L1-L3 with K_2PtCl_4

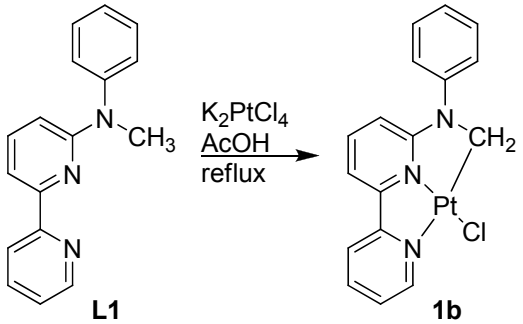
*Complex **1a***



To a dry 50 mL three necked flask were added **L1** (118 mg, 0.45 mmol), K_2PtCl_4 (187 mg, 0.45 mmol), and acetonitrile (20 mL). The reaction mixture was refluxed for 4 days then cooled to room temperature. The solvent was removed by a rotavapor, and the crude product was purified by column chromatography on silica gel with a mixture of dichloromethane and ethyl acetate (v/v: 50:1, 25:1) to give an orange solid (**1a**), 161 mg, 73%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.78 (d, *J* = 5.0 Hz, 1H), 8.44 (dd, *J* = 7.5, 1.5 Hz, $^3J_{Pt-H}$ = 27.3 Hz, 1H), 8.04-8.00 (m, 2H), 7.95 (t, *J* = 8.5 Hz, 1H), 7.60 (dt, *J* = 6.0, 2.5 Hz, 1H), 7.51 (d, J = 7.5 Hz, 1H), 7.22-7.18 (m, 1H), 7.14-

7.11 (m, 1H), 7.08 (d, J = 8.0 Hz, 1H), 6.98 (t, J = 7.0 Hz, 1H), 3.74 (s, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 156.5, 155.1, 151.6, 148.5, 141.0, 139.5, 138.5, 136.5, 126.2, 124.4, 122.3, 122.0, 119.0, 116.9, 115.5, 114.7 (J_{Pt-C} = 14.6 Hz), 42.3. Anal. Calcd for $C_{17}H_{14}ClN_3Pt$: C, 41.60; H, 2.87; N, 8.56. Found: C, 41.70; H, 2.78; N, 8.63.

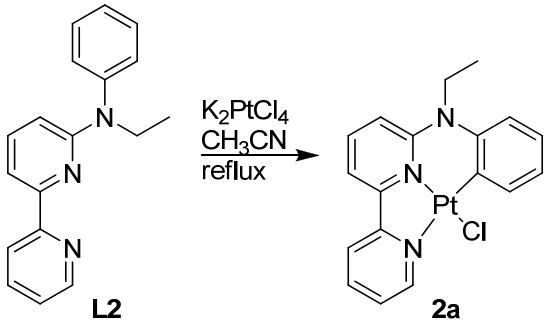
*Complex **1b***



L1 **1b**

To a dry 50 mL three necked flask were added **L1** (117 mg, 0.45 mmol), K_2PtCl_4 (186 mg, 0.45 mmol), and glacial acetic acid (20 mL). The reaction mixture was refluxed for 24h then cooled to room temperature. The solvent was removed by a rotavapor and the crude product was purified by column chromatography on silica gel with a mixture of dichloromethane and ethyl acetate (v/v: 10:1) to give an orange solid that contains small amount of **1a**. The solid was dissolved in dichloromethane and pure **1b** was precipitated by addition of methanol, 160 mg, 73%. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 9.10 (dd, J = 5.5, 1.0 Hz, 1H), 8.10 (dt, J = 8.0, 1.5 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.68-7.65 (m, 1H), 7.60 (t, J = 8.3 Hz, 1H), 7.49-7.45 (m, 2H), 7.40-7.38 (m, 2H), 7.33 (t, J = 7.5 Hz, 1H), 7.13 (d, J = 8.0 Hz, 1H) 6.51 (d, J = 9.0 Hz, 1H), 5.42 (s, $^2J_{Pt-H}$ = 40.5 Hz, 2H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 159.8, 157.3, 151.5, 147.9, 144.1, 138.5, 135.9, 130.2 (2C), 127.2, 127.1, 125.5 (2C), 122.2, 111.1, 110.0, 36.4 (J_{Pt-C} = 416.2 Hz). Anal. Calcd for $C_{17}H_{14}ClN_3Pt$: C, 41.60; H, 2.87; N, 8.56. Found: C, 41.35; H, 2.79; N, 8.47.

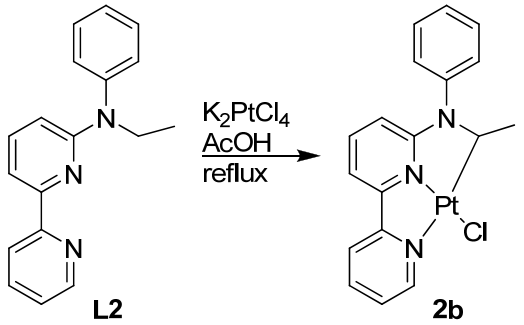
*Complex **2a***



L2 **2a**

To a dry 50 mL three necked flask were added **L2** (137 mg, 0.5 mmol), K_2PtCl_4 (208 mg, 0.5 mmol), and acetonitrile (20 mL). The reaction mixture was refluxed for 2 days then cooled to room temperature. The solvent was removed by rotavapor and the crude product was purified by column chromatography on silica gel with a mixture of dichloromethane and ethyl acetate (v/v=100:1) to give an orange solid, 174 mg. Further purification was done by dissolving the solid in dichloromethane followed by the addition of methanol, The precipitates were collected and dried in air, 164 mg, 70%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.79 (d, J = 4.5 Hz, 1H), 8.43 (d, J = 8.0 Hz, $^3J_{Pt\text{-}H}$ = 27.3 Hz, 1H), 8.05-8.00 (m, 2H), 7.93 (t, J = 8.0 Hz, 1H), 7.62-7.59 (m, 1H), 7.51 (d, J = 7.5 Hz, 1H), 7.30 (d, J = 9.0 Hz, 1H), 7.15-7.08 (m, 2H), 6.98 (t, J = 8.0 Hz, 1H), 4.25 (q, J = 7.0 Hz, 2H), 1.44 (t, J = 6.5 Hz, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 155.7, 154.1, 150.5, 147.2, 139.3, 139.1, 138.9, 137.0, 126.4, 123.7, 122.9, 120.9, 119.9, 118.4, 116.4, 115.7, 47.5, 14.1. Anal. Calcd for $C_{18}H_{16}ClN_3Pt$: C, 42.82; H, 3.19; N, 8.32. Found: C, 42.33; H, 2.97; N, 8.17.

*Complex **2b***

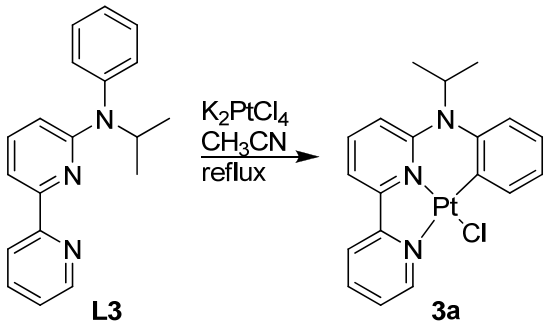


L2 **2b**

To a dry 50 mL three necked flask were added **L2** (180.0 mg, 0.65 mmol), K_2PtCl_4 (270 mg, 0.6 mmol), and glacial acetic acid (20 mL). The reaction mixture was refluxed for 3 days then cooled to room temperature. It was then quenched by water and extracted with dichloromethane (3 x 75 mL). The combined organic phases were washed with water (100 mL),

brine (100 mL), dried over $MgSO_4$, and filtered. The solvents were removed by rotavapor and the crude product was purified by column chromatography on silica gel with a mixture of dichloromethane and ethyl acetate (v/v: 25:1) to give an orange solid, which was further purified by recrystallization from CH_2Cl_2-methanol, 224 mg, 63%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.19 (d, J = 6.0 Hz, 1H), 8.05 (dt, J = 8.0, 1.5 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.62-7.60 (m, 1H), 7.54-7.47 (m, 3H), 7.38-7.35 (m, 1H), 7.30-7.28 (m, 2H), 7.06 (d, J = 8.0 Hz, 1H), 6.29 (d, J = 9.0 Hz, 1H), 5.88 (q, J = 7.0 Hz, $^2J_{Pt\text{-}C}$ = 48.0 Hz, 1H), 1.40 (d, J = 7.0 Hz, $^3J_{Pt\text{-}H}$ 21.5 Hz, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 160.2, 157.2, 151.2, 148.3, 140.8, 138.5, 135.9, 134.3, 130.2, 127.9, 127.7, 126.9, 125.5, 122.1, 110.3, 109.7, 46.3 ($J_{Pt\text{-}C}$ = 436.9 Hz), 23.8. Anal. Calcd for $C_{18}H_{16}ClN_3Pt$•0.5 CH_2Cl_2: C, 41.17; H, 3.27; N, 7.58. Found: C, 40.76; H, 3.11; N, 7.68.

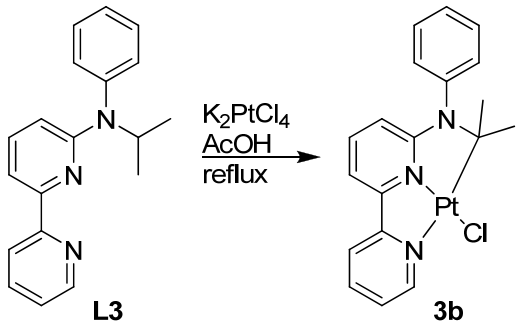
*Complex **3a***



L3 **3a**

To a dry 50 mL three necked flask were added **L3** (145 mg, 0.50 mmol), K_2PtCl_4 (214 mg, 0.51 mmol) and acetonitrile (20 mL). The reaction mixture was refluxed for 4 days then cooled to room temperature. The solvent was removed by rotavapor and the crude product was purified by column chromatography on silica gel with a mixture of dichloromethane and ethyl acetate (v/v=50:1) to give an orange solid that contains both **3a** and **3b**. Further purification by recrystallization from dichloromethane and hexane to give 97 mg pure **3a** as orange crystals, 36% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.64 (1H, d, J = 5.0 Hz), 8.20 (d, J = 7.5 Hz, $^3J_{Pt\text{-}H}$ 25.3 Hz, 1H), 8.06-8.02 (m, 2H), 7.95-7.92 (m, 1H), 7.63-7.56 (m, 2H), 7.46 (d, J = 8.0 Hz, 1H), 7.27 (d, J = 8.0 Hz, 1H), 7.05-7.02 (m, 1H), 6.90 (td, J = 1.5, 7.3 Hz, 1H), 4.43-4.34 (m, 1H), 1.61 (d, J = 6.5 Hz, 6H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 156.8, 155.4, 153.9, 148.3, 140.4, 139.3, 138.5, 136.3, 126.2, 123.9, 122.8, 122.1, 119.8, 119.2, 115.7, 114.6, 58.8, 23.7 (2C). Anal. Calcd for $C_{19}H_{18}ClN_3Pt$: C, 43.98; H, 3.50; N, 8.10. Found: C, 43.93; H, 3.43; N, 8.22.

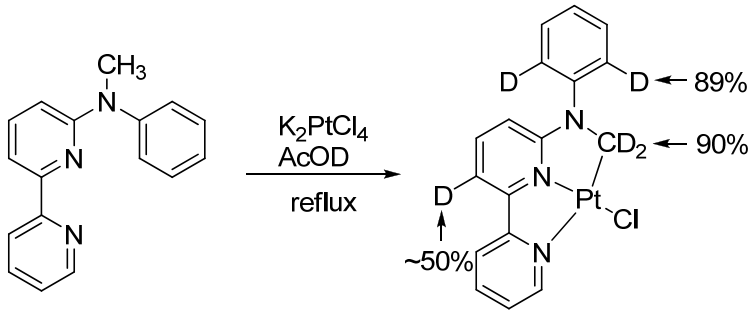
*Complex **3b***



L3 **3b**

To a dry 50 mL three necked flask were added **L3** (145 mg, 0.50 mmol), K_2PtCl_4 (210 mg, 0.51 mmol) and acetonitrile (20 mL). The reaction mixture was refluxed for 2 days then cooled to room temperature. The solvent was removed by rotavapor and the crude product was purified by column chromatography on silica gel with a mixture of dichloromethane and ethyl acetate (v/v=15:1) to give an orange solid, 99 mg, 38% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.09 (d, J = 5.5 Hz, 1H), 8.06 (td, J = 1.5, 8.0 Hz, 1H), 7.95 (d, J = 7.0 Hz, 1H), 7.62-7.60 (m, 1H), 7.53-7.46 (m, 4H), 7.22-7.20 (m, 2H), 7.08 (d, J = 7.0 Hz, 1H), 5.91 (d, J = 8.5, 1H), 1.49 (s, $^3J_{Pt\text{-}H}$ = 17.5 Hz, 6H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 160.8, 157.1, 150.7, 148.5, 138.5, 137.0, 135.9, 131.2 (2C), 130.2 (2C), 128.5, 126.8, 122.1, 110.0, 109.2, 55.3 ($J_{Pt\text{-}C}$ = 458.7 Hz), (2C) 31.6. Anal. Calcd for $C_{19}H_{18}ClN_3Pt$: C, 43.98; H, 3.50; N, 8.10. Found: C, 44.07; H, 3.34; N, 8.10.

Reaction of L1 with K_2PtCl_4 in AcOD

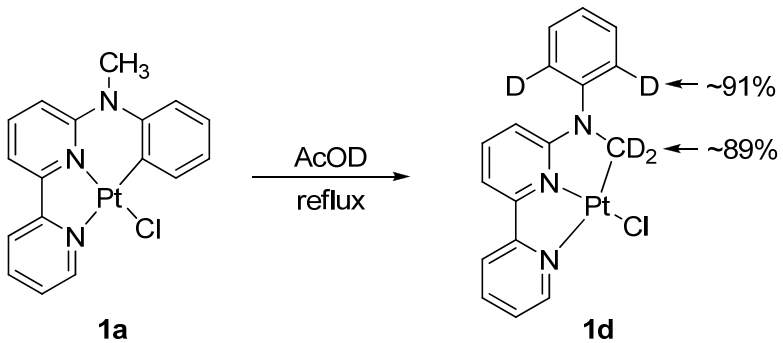


L1 **1c**

To a dry 50 mL three necked flask were added **L1** (131 mg, 0.50 mmol), K_2PtCl_4 (208 mg, 0.50 mmol), and deuterated glacial acetic acid (20 mL). The reaction mixture was refluxed for 24 h then cooled to room temperature. The solvent was removed by a rotavapor, and the

crude product analyzed by NMR to determine the level of H/D exchange. ^{1}H NMR of **1c** (500 MHz, $CDCl_3$) δ 9.20 (d, *J* = 4.0 Hz, 1H), 8.08 (t, *J* = 7.8 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.67-7.64 (m, 1H), 7.58-7.55 (m, this proton is partially deuterated with ~50% deuteration), 7.47-7.45 (m, 2H), 7.33 (t, *J* = 7.0 Hz, 1H), 7.07 (d, *J* = 7.0 Hz, 1H), 6.51 (d, *J* = 9.0 Hz, 1H).

Isomerization of 1a in AcOD



1a **1d**

To a dry 50 mL flask were added 11.2 mg of **1a** and deuterated glacial acetic acid (4.0 mL). The reaction was refluxed for 3 days then cooled to room temperature. The solvent was removed by rotavapor and the crude product analyzed by NMR to determine the level of H/D exchange. ^{1}H NMR of **1d** (500 MHz, $CDCl_3$) δ (ppm): 9.21 (d, *J* = 5.3 Hz, 1H), 8.07 (t, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.67-7.64 (m, 1H), 7.58-7.54 (m, 1H), 7.45 (d, *J* = 7.0 Hz, 2H), 7.32 (t, *J* = 7.0 Hz, 1H), 7.06 (d, *J* = 7.0 Hz, 1H), 6.50 (d, *J* = 9.0 Hz, 1H).

Reaction of L1 with K_2PtCl_4 in Mixed Solvents

AcOH-MeCN (v/v 50:50)

To a dry 25 mL three necked flask were added **L1** (32.0 mg, 0.12 mmol), K_2PtCl_4 (51 mg, 0.12 mmol), glacial acetic acid (4.0 mL), and acetonitrile (4.0 mL). The reaction mixture was stirred at 90 ^oC for 48 hours then cooled to room temperature. Aqueous workup performed by diluting the mixture with dichloromethane and washing with distilled water (3 x 20 mL). The organic phase was dried over $MgSO_4$, filtered, and the solvent removed by rotavapor. The crude product was then examined by NMR and the ratio of **1a** to **1b** was determined to be 100:0.

AcOH-MeCN (v/v 70:30)

The reaction was carried out using the same procedure described above except for the solvents (AcOH-MeCN, v/v 70:30). The crude product was then examined by NMR and the ratio of **1a** to **1b** was determined to be 70:30.

AcOH-MeCN (v/v 80:20)

The reaction was carried out using the same procedure described above except for the solvents (AcOH-MeCN, v/v 80:20). The crude product was then examined by NMR and the ratio of **1a** to **1b** was determined to be 45:55

AcOH-MeCN (v/v 90:10)

The reaction was carried out using the same procedure described above except for the solvents (AcOH-MeCN, v/v 90:10). The crude product was then examined by NMR and the ratio of **1a** to **1b** was determined to be 26:74.

For the time dependent experiments, the reaction was carried out in AcOH-MeCN (v/v 80:20) under reflux condition. The reaction mixture was taken periodically at 10, 20, 40, 80, and 168 h for NMR analysis and the ratio of **1a** to **1b** was determined to be 69:31, 58:42, 25:75, 5:95, and 2:98, respectively.

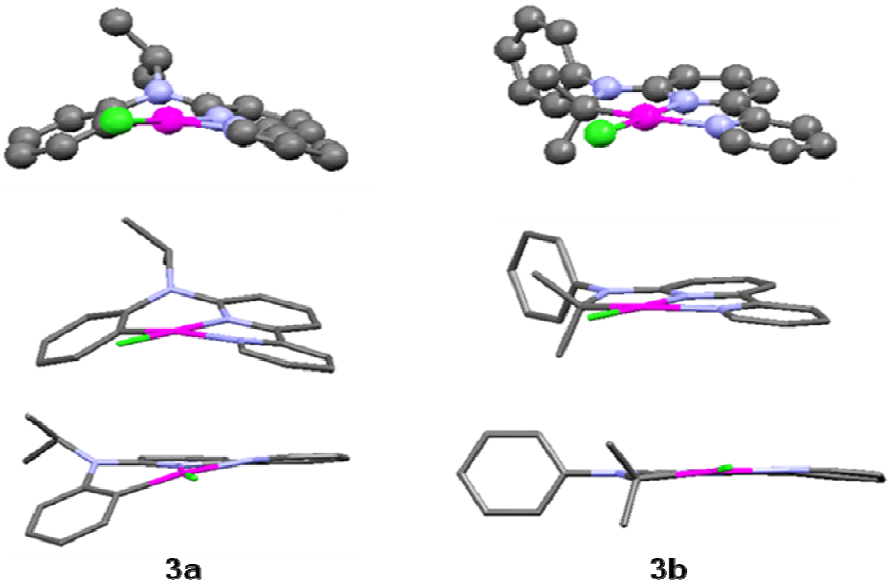


Figure SI-1. Different view of geometries of complexes **3a** and **3b**.