SUPPORTING INFORMATION

Competitive Reverse Quartet Mechanisms for Photogenerated Ground State Electron Spin Polarization

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General Experimental. Reagents were used as received and purchased from commercial vendors. Solvents were also purchased from commercial sources and when necessary were purified by passing through activated alumina housed in a custom-built solvent purification system. ^{1}H- and ^{13}C NMR spectra were recorded on a Varian Mercury 400 MHz or a Bruker NEO 400 MHz spectrometer at room temperature. ^{1}H- and ^{13}C chemical shifts are listed in parts per million (ppm) and are referenced to residual protons or carbons of the deuterated solvents, respectively. Infrared spectra were recorded on a Bruker Vertex 80v spectrometer with Bruker Platinum ATR attachment. Elemental analyses were performed by Atlantic Microlabs, Inc. Mass spectra were obtained at Michigan State University Mass Spectrometry and Metabolomics Core facility.

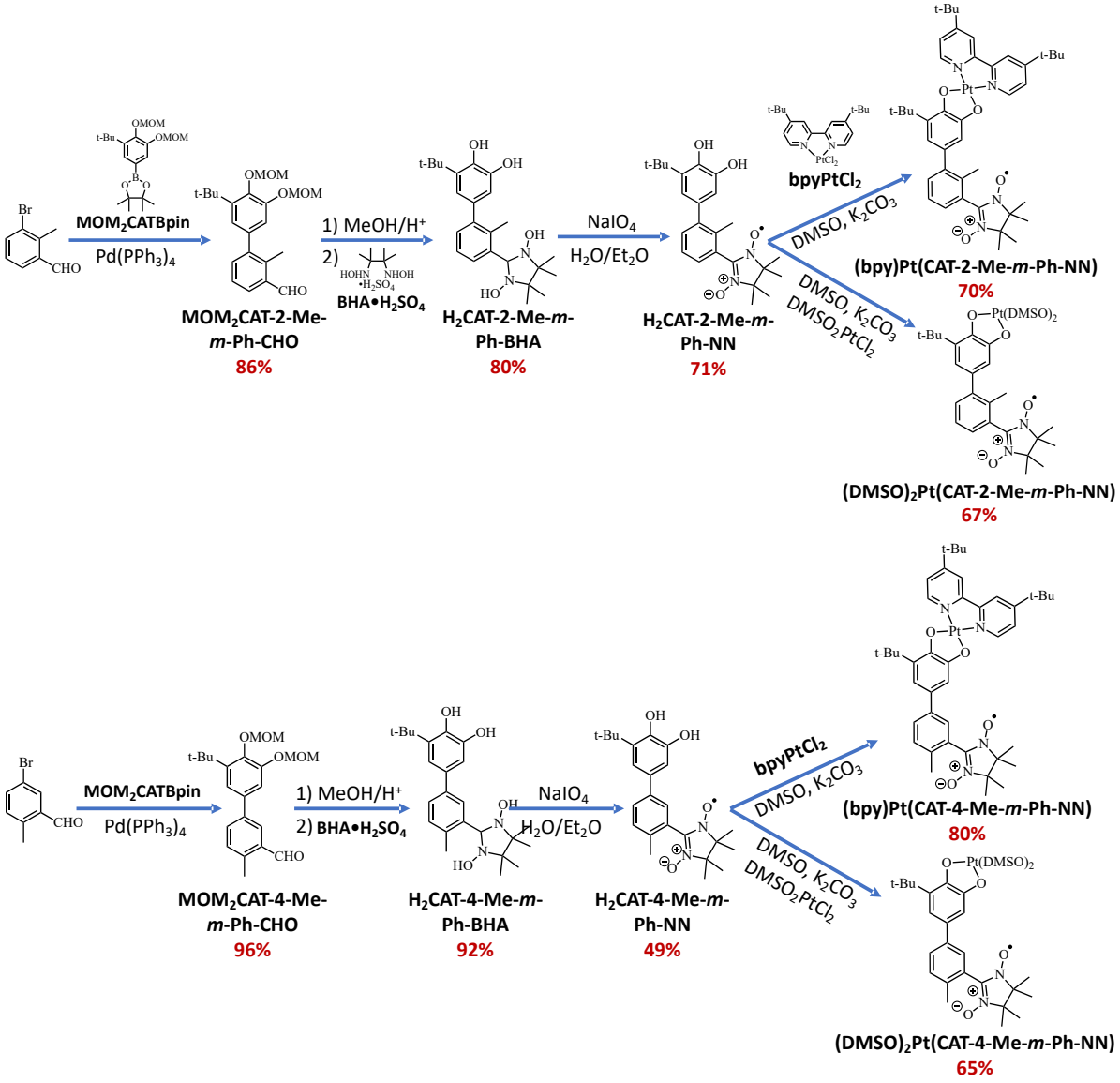
Steady State and Transient EPR Spectroscopies. Samples for steady state and transient EPR measurements were prepared by dissolving solid metal complexes in 2-methyl-THF to a concentration of ~0.5 mM. The samples were placed in 4 mm O.D. quartz EPR tubes and degassed by repeated freeze-pump-thaw cycles. The frozen, degassed samples were then transferred without thawing from liquid nitrogen to the spectrometer cryostat, which was at 20 K. The steady state spectra were collected using field modulation detection with a modulation amplitude of 0.1 mT and a microwave power of 6.3 mW. TREPR time/field dataset were collected with direct detection at the same microwave power as for the steady-state experiments. The samples were irradiated at 532 nm using 10 ns laser flashes from a frequency-doubled Nd:YAG laser with a flash energy of ~4 mJ. Spectra were extracted from the time/field datasets at 0.6 ms after the laser flash. The modified Bruker EPR 200D-SRC X-band spectrometer used for the EPR experiments has been described in detail elsewhere.[1]

Because spin polarized transient EPR signals are measured under non-equilibrium conditions of the spin system, microwave saturation does not occur. Instead, in the limit of high microwave power the magnetization precesses about the microwave field in the rotating frame creating so-called Torrey nutations.[2,3] In the high-power limit, the precession frequency is greater than the rate of spin relaxation and the signal decays with T_2. In the limit of low microwave

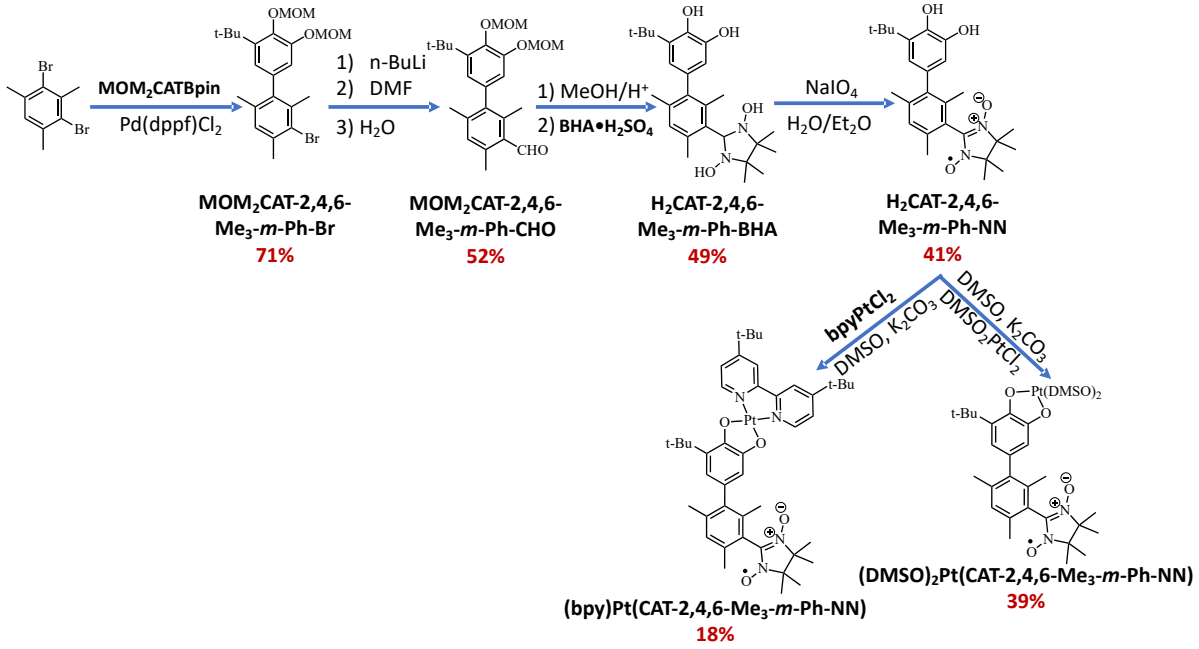
power, the precession frequency is much less than the rate of spin relaxation and the signal decays with T_1. The shape of the TREPR spectrum does not depend on the microwave power. The data presented in the manuscript have been collected at intermediate microwave power and the transients exhibit slow transient nutations with a period of ~6 µs. The spectra have been extracted at 0.6 µs after the laser flash in a 200 ns wide window around the signal maximum. Under these conditions, the spectra are not influenced by the nutation.

The synthesis and characterization of complexes **(bpy)Pt(CAT-*m*-Ph-NN)**,[4] **(bpy)Pt(CAT-6-Me-*m*-Ph-NN)**,[5] **$(DMSO)_2$Pt(CAT-*m*-Ph-NN)**,[4] **$(DMSO)_2$Pt-(CAT-6-Me-*m*-Ph-NN)**,[5] and 2,3-dimethyl-2,3-bis(hydroxyamino)butane (**BHA**),[6] MOM_2CAT-Bpin,[7] (4,4'-di-*tert*-butyl-2,2'-bipyridine)$PtCl_2$[8] (bpy$PtCl_2$), and $(DMSO)_2PtCl_2$[9] have been reported previously. Other reagents and materials are commercially available unless noted otherwise.

Scheme S1. Synthetic Outlines.



Scheme S1, continued.



3'-(*tert*-Butyl)-4',5'-bis(methoxymethoxy)-2-methyl-[1,1'-biphenyl]-3-carbaldehyde (MOM$_2$CAT-2-Me-*m*-Ph-CHO). A solution of 3-bromo-2-methylbenzaldehyde (324 mg, 1.63 mmol), MOM$_2$CatBpin (598 mg, 1.57 mmol), Na_2CO_3 (339 mg, 3.20 mmol), Bu_4NBr (61 mg, 0.19 mmol), and $Pd(PPh_3)_4$ (20 mg, 0.17 mmol) in 4 mL of water and 12 mL of toluene were heated to 85°C under a nitrogen atmosphere for 44h. The reaction was allowed to cool to room temperature, then transferred to a separatory funnel where it was diluted with ca. 20mL of EtOAc and washed with ca. 25 mL of brine. The organic layer was separated, dried with $MgSO_4$, filtered and then concentrated under reduced pressure. The product was purified by silica column chromatography with 15% EtOAc/ hexanes with 1% Et_3N. The product-containing fractions were concentrated to afford the title compound as a colorless oil (504 mg, 86%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 10.37 (s, 3 H), 7.80 (dd, *J* = 1.5, 7.6 Hz, 1 H), 7.49 (dd, *J* = 1.3, 7.6 Hz, 1 H), 7.40 (t, *J* = 7.6 Hz, 1 H), 6.98 (d, *J* = 2.0 Hz, 1 H), 6.93 (d, *J* = 2.0 Hz, 1 H), 5.26 (s, 2 H), 5.19 (s, 2 H), 3.66 (s, 3 H), 3.50 (s, 3 H), 2.56 (s, 3 H), 1.45 (s, 9 H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ = 193.4, 150.4, 145.9, 144.6, 143.7, 138.6, 136.0, 135.8, 135.4, 131.0, 126.3, 122.3, 116.5, 99.7, 96.1, 57.9, 56.7, 35.7, 30.9, 16.7. HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{22}H_{29}O_5$ 373.20095; Found 373.20099.

2-(3'-(*tert*-Butyl)-4',5'-dihydroxy-2-methyl-[1,1'-biphenyl]-3-yl)-4,4,5,5-tetramethylimidazolidine-1,3-diol (H$_2$ CAT-2-Me-*m*-Ph-BHA). MOM$_2$CAT-2-Me-*m*-Ph-CHO (506 mg, 1.36 mmol) was dissolved in 9 mL of MeOH, 2 mL of Et_2O and 1 mL of 12 M HCl was added and the solution was placed under nitrogen and stirred at room temperature for 18 h. After removal of methoxymethyl groups was confirmed by TLC with $FeCl_3$ stain and ^{1}H NMR, the reaction was concentrated to a few milliliters, then diluted with Et_2O, transferred to a separatory funnel and washed twice with ca. 10 mL of brine. The organic layer was separated, dried with

$MgSO_4$, filtered and concentrated to give an off-white solid. To the solid was added **BHA•**H_2SO_4 (503 mg, 2.04 mmol) and K_2CO_3 (188 mg, 1.36 mmol). The contents were purge-pumped three times; backfilling with nitrogen. 5 mL of deoxygenated, anhydrous MeOH was added and the reaction was stirred at room temperature for 2 days. The white precipitate was filtered and air-dried to give the product as a colorless solid (451 mg, 80%). ^{1}H NMR (400 MHz ,DMSO-d_6) δ = 9.42 (s, 1 H), 8.02 (s, 1 H), 7.73 - 7.61 (m, 3 H), 7.16 (t, *J* = 7.6 Hz, 1 H), 7.01 (dd, *J* = 1.3, 7.4 Hz, 1 H), 6.59 (d, *J* = 1.9 Hz, 1 H), 6.50 (d, *J* = 1.9 Hz, 1 H), 4.97 (s, 1 H), 2.27 (s, 3 H), 1.35 (s, 9 H), 1.09 (s, 6 H), 1.08 (s, 6 H). ^{13}C NMR (101 MHz, DMSO-d_6) δ = 144.5, 142.7, 142.2, 139.9, 135.0, 134.8, 131.9, 128.4, 126.6, 124.6, 118.0, 113.9, 85.9, 66.2, 34.3, 29.5, 24.1, 20.2, 17.7. $[M+H]^+$ Calculated for $C_{24}H_{34}N_2O_4$ 415.25913; Found 415.25946.

H_2CAT-2-Me-*m*-Ph-NN. To a suspension of **H_2CAT-2-Me-*m*-Ph-BHA** (100 mg, 0.24 mmol) in 9 mL of Et_2O and 9 mL of H_2O, was added $NaIO_4$ (108 mg, 0.51 mmol) and stirred for 15 minutes. The reaction was transferred to a separatory funnel and the aqueous layer was removed. The organic layer was washed three times with ca. 5 mL of water each time. The organic layer was drained back into the flask where 5 mL of 1 M, pH 7 phosphate buffer solution was added and then with vigorous stirring was added $Na_2S_2O_4$ (71 mg, 0.41 mmol). The solution was stirred for 1 minute, then transferred to a separatory funnel where it was washed three times with ca. 5 mL of brine each time. The organic layer was separated, dried with $MgSO_4$, filtered and concentrated under reduced pressure to afford the title compound as a purple solid (70 mg, 71%). $[M+H]^+$ Calculated for $C_{24}H_{31}N_2O_4$ 412.23566; Found 412.23533.

(Bpy)Pt(CAT-2-Me-*m*-Ph-NN). H_2CAT-2-Me-*m*-Ph-NN (70 mg, 0.17 mmol), bpy$PtCl_2$ (91 mg, 17 mmol) and K_2CO_3 (53 mg, 0.38 mmol) were added to a 15 mL round-bottom flask. The flask was purged-pumped three times; backfilling with nitrogen each time. Then 3 mL of deoxygenated DMSO was added and the reaction was stirred at 30°C for 18 h. The reaction was poured into 100 mL of stirring brine and then the purple precipitate was collected by vacuum filtration through a Büchner funnel. The purple precipitate was collected from the filter paper by redissolving in minimal CH_2Cl_2 (~10 mL), then diluted with ca. 20 mL of Et_2O. The solution was dried with $MgSO_4$, filtered and concentrated under reduced pressure to afford the title compound (104 mg, 70%) as a dark purple solid. Calculated for $C_{42}H_{53}N_4O_4Pt$ 872.37091; Found 872.37269. EPR (X-band: 9.774 GHz): g = 2.0079 a_N =7.49 G.

$(DMSO)_2$Pt(CAT-2-Me-*m*-Ph-NN). H_2CAT-2-Me-*m*-Ph-NN (25 mg, 0.061 mmol), $(DMSO)_2PtCl_2$ (26 mg, 0.062 mmol) and K_2CO_3 (20 mg, 0.14 mmol) were added to a 10 mL round-bottom flask. The flask was purged-pumped three times; backfilling with nitrogen each time. Then 3 mL of deoxygenated DMSO was added and the reaction was stirred at 30°C for 18 h. The reaction was poured into 100 mL of stirring brine and then the purple precipitate was collected by vacuum filtration through a Büchner funnel. The purple precipitate was collected from the filter paper by redissolving in minimal amount ca. 30 mL of Et_2O. The solution was dried with $MgSO_4$, filtered and concentrated under reduced pressure to afford the title compound (31mg, 67%) as a dark purple solid. $[M+H]^+$ Calculated for $C_{28}H_{41}N_2O_6S_2Pt$ 759.2033; Found 759.2054. FT-IR (cm^{-1}): 2955, 2919, 2858, 1558, 1459, 1443, 1418, 1400, 1365, 1327, 1293, 1241, 1141, 1022, 976, 921, 860, 731, 691, 450, 431. EPR (X-band: 9.830 GHz): g = 2.0064 a_N =7.46G.

3'-(*tert*-Butyl)-4',5'-bis(methoxymethoxy)-4-methyl-[1,1'-biphenyl]-3-carbaldehyde (MOM$_2$CAT-4-Me-*m*-Ph-CHO). A solution of 5-bromo-2-methylbenzaldehyde (322 mg, 1.62 mmol), MOM$_2$CatBpin (600 mg, 1.58 mmol), Na_2CO_3 (349 mg, 3.29 mmol), Bu_4NBr (50 mg, 0.16 mmol), and $Pd(PPh_3)_4$ (36 mg, 0.03 mmol) in 4 mL of water and 12 mL of toluene were heated to 85°C under a nitrogen atmosphere for 18h. The reaction was allowed to cool to room temperature, then transferred to a separatory funnel where it was diluted with ca. 20mL of EtOAc and washed with ca. 25 mL of brine. The organic layer was separated, dried with $MgSO_4$, filtered and then concentrated under reduced pressure. The product was purified by silica column chromatography with 10% EtOAc/ hexanes with 1% Et_3N. The product-containing fractions were concentrated to afford the title compound as a colorless oil (567 mg, 96%).^{1}H NMR (400 MHz ,$CDCl_3$) δ = 10.35 (s, 1 H), 7.97 (d, *J* = 2.0 Hz, 1 H), 7.67 (dd, *J* = 2.0, 7.9 Hz, 1 H), 7.32 (d, *J* = 7.9 Hz, 1 H), 7.27 (d, *J* = 2.1 Hz, 1 H), 7.23 (d, *J* = 2.1 Hz, 1 H), 5.26 (s, 2 H), 5.26 (s, 2 H), 3.69 (s, 3 H), 3.55 (s, 3 H), 2.71 (s, 3 H), 1.48 (s, 9 H).^{13}C NMR (101 MHz ,$CDCl_3$) δ = 192.8, 150.5, 145.8, 143.8, 139.5, 139.2, 134.7, 134.3, 132.2, 132.1, 130.3, 119.2, 113.2, 99.1, 95.4, 57.6, 56.4, 35.3, 30.5, 19.2HRMS (ESI) m/z: $[M+Na]^+$ Calculated for $NaC_{22}H_{28}O_5$ 395.18290; Found 395.18291.

2-(3'-(*tert*-Butyl)-4',5'-dihydroxy-4-methyl-[1,1'-biphenyl]-3-yl)-4,4,5,5-tetramethylimidazolidine-1,3-diol (H$_2$CAT-4-Me-*m*-Ph-BHA). MOM$_2$CAT-4-Me-*m*-Ph-CHO (567 mg, 1.52 mmol) was dissolved in 10 mL of MeOH, 1 mL of 12 M HCl was added and the solution was placed under nitrogen and stirred at room temperature for 18 h. After completion was confirmed by TLC with $FeCl_3$ stain and ^{1}H NMR, the reaction was concentrated to a few milliliters, then diluted with Et_2O, transferred to a separatory funnel and washed twice with ca. 10 mL of brine. The organic layer was separated, dried with $MgSO_4$, filtered and concentrated to give an orange solid. To the solid was added **BHA**•H_2SO_4 (563 mg, 2.29 mmol) and K_2CO_3 (212 mg, 1.53 mmol). The contents were purge-pumped three times; backfilling with nitrogen. 5 mL of deoxygenated, anhydrous MeOH was added and the reaction was stirred at room temperature for 2 days. The white precipitate was filtered and air-dried to give the product as a colorless solid (579 mg, 92%). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 9.48 (br. s., 1 H), 8.09 (br. s., 1 H), 7.86 (d, *J* = 2.0 Hz, 1 H), 7.69 (s, 2 H), 7.25 (dd, *J* = 2.0, 7.8 Hz, 1 H), 7.11 (d, *J* = 7.8 Hz, 1 H), 6.93 (d, *J* = 2.0 Hz, 1 H), 6.88 (d, *J* = 2.0 Hz, 1 H), 4.92 (s, 1 H), 2.38 (s, 3 H), 1.36 (s, 9 H), 1.11 (s, 6 H), 1.10 (s, 6 H). ^{13}C NMR (101 MHz, DMSO-d_6) δ = 145.3, 143.4, 139.8, 138.2, 135.7, 135.3, 130.7, 129.8, 126.4, 124.2, 115.2, 110.9, 85.7, 66.2, 34.4, 29.4, 24.1, 18.9, 17.5 HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{24}H_{34}N_2O_4$ 415.25913; Found 415.25940.

H$_2$CAT-4-Me-*m*-Ph-NN. To a suspension of **H$_2$CAT-4-Me-*m*-Ph-BHA** (100 mg, 0.24 mmol) in 9 mL of Et_2O and 9 mL of H_2O, was added $NaIO_4$ (106 mg, 0.50 mmol) and stirred for 15 minutes. The reaction was transferred to a separatory funnel and the aqueous layer was removed. The organic layer was washed three times with ca. 5 mL of water each time. The organic layer was drained back into the flask where 5 mL of 1 M, pH 7 phosphate buffer solution was added and then with vigorous stirring was added $Na_2S_2O_4$ (64 mg, 0.37 mmol). The solution was stirred for 1 minute, then transferred to a separatory funnel where it was washed three times with ca. 5 mL of brine each time. The organic layer was separated, dried with $MgSO_4$, filtered, and concentrated

under reduced pressure to afford the title compound as a purple solid (49 mg, 49%). $[M+H]^+$ Calculated for $C_{24}H_{31}N_2O_4$ 412.23566; Found 412.23545.

(Bpy)Pt(CAT-4-Me-*m*-Ph-NN). H_2CAT-4-Me-*m*-Ph-NN (49 mg, 0.12 mmol), $BpyPtCl_2$ (64 mg, 12 mmol) and K_2CO_3 (38 mg, 0.27 mmol) were added to a 10 mL round-bottom flask. The flask was purged-pumped three times; backfilling with nitrogen each time. Then 3 mL of deoxygenated DMSO was added and the reaction was stirred at 30°C for 18 h. The reaction was poured into 100 mL of stirring brine and then the purple precipitate was collected by vacuum filtration through a Büchner funnel. The purple precipitate was collected from the filter paper by redissolving in minimal CH_2Cl_2 (~10 mL), then diluted with ca. 20 mL of Et_2O. The solution was dried with $MgSO_4$, filtered, and concentrated under reduced pressure to afford the title compound (83 mg, 80%) as a dark purple solid. $[M]^+$ Calculated for $C_{42}H_{53}N_4O_4Pt$ 872.37091; Found 872.37263. λ_{max} (CH_2Cl_2) = 574 nm (ε_{max} = 5123 M^{-1} cm^{-1}). FT-IR (cm^{-1}): 2955, 2922, 2858, 1616, 1554, 1461, 1420, 1401, 1362, 1329, 1291, 1243, 1166, 1136, 1025, 978, 850, 808, 756, 673, 635, 598, 560, 538, 458, 421. EPR (X-band: 9.776 GHz): g = 2.0081 a_N =7.44 G.

$(DMSO)_2$PtCAT-4-Me-*m*-Ph-NN. H_2CAT-4-Me-*m*-Ph-NN (25 mg, 0.061 mmol), $(DMSO)_2PtCl_2$ (26 mg, 0.062 mmol) and K_2CO_3 (18 mg, 0.13 mmol) were added to a 10 mL round-bottom flask. The flask was purged-pumped three times; backfilling with nitrogen each time. Then 3 mL of deoxygenated DMSO was added and the reaction was stirred at 30°C for 18 h. The reaction was poured into 100 mL of stirring brine and then the purple precipitate was collected by vacuum filtration through a Büchner funnel. The purple precipitate was collected from the filter paper by redissolving in minimal amount ca. 30 mL of Et_2O. The solution was dried with $MgSO_4$, filtered and concentrated under reduced pressure to afford the title compound (30mg, 65%) as a dark purple solid. $[M+H]^+$ Calculated for $C_{28}H_{41}N_2O_6S_2Pt$ 759.2033; Found 759.2047. EPR (X-band: 9.830 GHz): g = 2.0068 a_N =7.21G.

3-Bromo-3'-(*tert*-butyl)-4',5'-bis(methoxymethoxy)-2,4,6-trimethyl-1,1'-biphenyl (MOM_2CAT-2,4,6-Me_3-*m*-Ph-Br). 2,4-dibromomesitylene (626 mg, 2.25 mmol), MOM_2CatBpin (285 mg, 0.749 mmol), $Pd(dppf)Cl_2$ (6 mg, 0.008 mmol), Na_2CO_3 (176 mg, 1.66 mmol), and Bu_4NBr (24 mg, 0.074 mmol) were added to a 25 mL round bottom flask, purge-pumped three times, and back-filled with nitrogen. 12 mL of deoxygenated toluene and 4 mL of deoxygenated H_2O were added, and the contents were heated to 65 °C for 21h. The reaction was cooled to room temperature, transferred to a separatory funnel, diluted with ca. 10 mL of EtOAc, and washed with ca. 20 mL of brine. The organic layer was separated, dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The product was purified by silica column chromatography with 10% EtOAc/hexanes with 1% Et_3N (R_f=0.53). The product-containing fractions were concentrated to afford 239 mg (71%) of the title compound as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.01 (s, 1 H), 6.77 (d, *J* = 1.9 Hz, 1 H), 6.72 (d, *J* = 1.9 Hz, 1 H), 5.27 (s, 2 H), 5.15 (s, 2 H), 3.69 (s, 3 H), 3.50 (s, 3 H), 2.43 (s, 3 H), 2.17 (s, 3 H), 1.97 (s, 3 H), 1.42 (s, 9 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 150.0, 144.6, 143.4, 140.9, 136.7, 136.1, 135.8, 134.9, 129.3, 125.3, 121.4, 115.6, 99.0, 95.5, 57.4, 56.2, 35.2, 30.6, 23.9, 22.0, 20.6. $[M+Na]^+$ Calculated for $C_{23}H_{31}BrO_4Na$ 475.1286; Found 475.1284.

3'-(*tert*-Butyl)-4',5'-bis(methoxymethoxy)-2,4,6-trimethyl-[1,1'-biphenyl]-3-carb-aldehyde (MOM$_2$CAT-2,4,6-Me$_3$-*m*-Ph-CHO). MOM$_2$CAT-2,4,6-Me$_3$-*m*-Ph-Br (239 mg, 0.529 mmol) was added to an oven-dried 50 mL flask, purge-pumped three times, and back-filled with nitrogen. Then 20 mL of freshly distilled THF was added and the solution was cooled to -78 °C. *t*-BuLi in pentane (0.75 mL, 1.6M, 1.20 mmol) was added dropwise and the reaction stirred for 30 min at -78 °C. The reaction was placed win a 3:2 ethylene glycol: ethanol dry ice bath, warmed to -40 °C, and stirred for 1 h. The reaction was cooled to -78 °C, and DMF (0.12 mL, 1.6 mmol) was added dropwise. The reaction was stirred for 1 h at -78 °C, then warmed to room temperature, and 1 mL of water was added. The mixture was stirred overnight for 16h, then transferred to a separatory funnel, diluted with EtOAc, and washed with brine. The organic layer was separated, dried with $MgSO_4$, filtered, and concentrated. The product was purified by silica column chromatography with 10% EtOAc/ hexanes with 1% Et_3N (R_f=0.32). The product-containing fractions were concentrated to afford 110 mg (52%) of the title compound as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.62 (s, 1 H), 7.01 (s, 1 H), 6.79 (d, *J* = 1.8 Hz, 1 H), 6.72 (d, *J* = 1.8 Hz, 1 H), 5.28 (s, 2 H), 5.16 (s, 2 H), 3.69 (s, 3 H), 3.50 (s, 3 H), 2.60 (s, 3 H), 2.31 (s, 3 H), 2.05 (s, 3 H), 1.43 (s, 9 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 193.8, 150.1, 144.7, 143.5, 142.1, 141.4, 139.5, 139.1, 134.7, 130.9, 130.8, 121.4, 115.6, 99.0, 95.5, 57.5, 56.2, 35.2, 30.6, 21.5, 20.5, 17.3. $[M^+H]^+$ Calculated for $C_{24}H_{34}O_5$ 401.23225; Found 401.23258.

2-(3'-(*tert*-Butyl)-4',5'-dihydroxy-2,4,6-trimethyl-[1,1'-biphenyl]-3-yl)-4,4,5,5-tetramethylimidazolidine-1,3-diol (H$_2$CAT-2,4,6-Me$_3$-*m*-Ph-BHA). MOM$_2$CAT-2,4,6-Me$_3$-*m*-Ph-CHO (110 mg, 0.274 mmol) was dissolved in 10 mL of MeOH, 1 mL of 12 M HCl was added and the solution was placed under nitrogen and stirred at room temperature for 18 h. After completion was confirmed by TLC with $FeCl_3$ stain and ^{1}H NMR, the reaction was concentrated to a few milliliters, then diluted with Et_2O, transferred to a separatory funnel and washed twice with ca. 10 mL of brine. The organic layer was separated, dried with $MgSO_4$, filtered and concentrated to give a pale colorless solid. To the solid was added **BHA**•H_2SO_4 (94.6 mg, 0.384 mmol) and K_2CO_3 (35.4 mg, 0.256 mmol). The contents were purge-pumped three times; backfilling with nitrogen. Deoxygenated, anhydrous MeOH (5 mL) was added and the reaction was stirred at room temperature for 2 days. The precipitate was filtered and air-dried to give the product as a pale-yellow solid (ca. 60 mg, 49%). Due to the instability of this molecule it was used directly in the next step without further purification.

H$_2$CAT-2,4,6-Me$_3$-*m*-Ph-NN. To a suspension of **H$_2$CAT-2,4,6-Me$_3$-*m*-Ph-BHA** (60 mg, 0.135 mmol) in 6 mL of Et_2O and 6 mL of H_2O, was added $NaIO_4$ (58 mg, 0.271 mmol) and stirred for 15 minutes. The reaction was transferred to a separatory funnel and the aqueous layer was removed. The organic layer was washed three times with ca. 5 mL of water each time. The organic layer was drained back into the flask where 5 mL of 1 M, pH 7 phosphate buffer solution was added and then with vigorous stirring was added $Na_2S_2O_4$ (36 mg, 0.205 mmol). The solution was stirred for 10 minutes, then transferred to a separatory funnel where it was washed three times with ca. 5 mL of brine each time. The organic layer was separated, dried with $MgSO_4$, filtered, and concentrated under reduced pressure to afford the title compound as a purple solid (25 mg, 41%). $[M+H]^+$ Calculated for $C_{26}H_{34}N_2O_4$ 438.2519; Found 438.2531. EPR (X-band: 9.776 GHz): g = 2.0083 a_N =6.85 G.

(Bpy)Pt(CAT-2,4,6-Me$_3$-*m*-Ph-NN). H$_2$CAT-2,4,6-Me$_3$-*m*-Ph-NN (75 mg, 0.12 mmol), BpyPtCl$_2$ (92 mg, 12 mmol) and K_2CO_3 (52 mg, 0.27 mmol) were added to a 10 mL round-bottom flask. The flask was purged-pumped three times; backfilling with nitrogen each time. Then 3 mL of deoxygenated DMSO was added and the reaction was stirred at 25°C for 18 h. The reaction was poured into 100 mL of stirring brine and then the purple precipitate was collected by vacuum filtration through a Büchner funnel. The purple precipitate was collected from the filter paper by redissolving in minimal CH_2Cl_2 (~10 mL), then diluted with ca. 20 mL of Et_2O. The solution was dried with $MgSO_4$, filtered and concentrated under reduced pressure to afford the title compound (28mg, 18%) as a dark purple solid. $[M+H]^+$ Calculated for $C_{44}H_{58}N_4O_4Pt$ 901.4109; Found 901.4117. FT-IR (cm^{-1}): 2955, 2916, 2850, 1555, 1422, 1405, 1386, 1355, 1326, 1291, 1240, 1215, 1069, 1019, 976, 916, 858, 810, 796, 758, 735, 691, 671, 641, 605, 576, 540, 455, 431. EPR (X-band: 9.884 GHz): g = 2.0080 a_N =7.51 G.

(DMSO)$_2$PtCAT-2,4,6-Me$_3$-*m*-Ph-NN. H$_2$CAT-2,4,6-Me$_3$-*m*-Ph-NN (20 mg, 0.04 mmol), $(DMSO)_2PtCl_2$ (19.2 mg, 0.04 mmol) and K_2CO_3 (13.8 mg, 0.10 mmol) were added to a 10 mL round-bottom flask. The flask was purged-pumped three times; backfilling with nitrogen each time. Then 3 mL of deoxygenated DMSO was added and the reaction was stirred at 30°C for 18 h, then transferred to a separating funnel, diluted with methylene chloride, and washed with water followed by brine. The organic layer was separated, dried over $MgSO_4$, filtered, and concentrated. The product was purified by silica-gel column chromatography with 60% EtOAc/ hexanes (R_f=0.25). The product-containing fractions were concentrated to afford 14 mg (39%) of the title compound as a pink solid. HRMS (ESI) m/z: $[M]^+$ Calculated for $C_{30}H_{45}N_2O_6PtS_2$ 788.2367; Found 788.2400. EPR (X-band: 9.884 GHz): g = 2.0078 a_N =7.51 G.

Figure S1 illustrates relevant frontier π-MOs, configurations, and states. Note that the electronic transitions for the NN radical shown in ***Figure 3B*** involve mixed configurations.[4, 10] Such configurational mixing is common for alternant π-systems such as that of NN.[11]

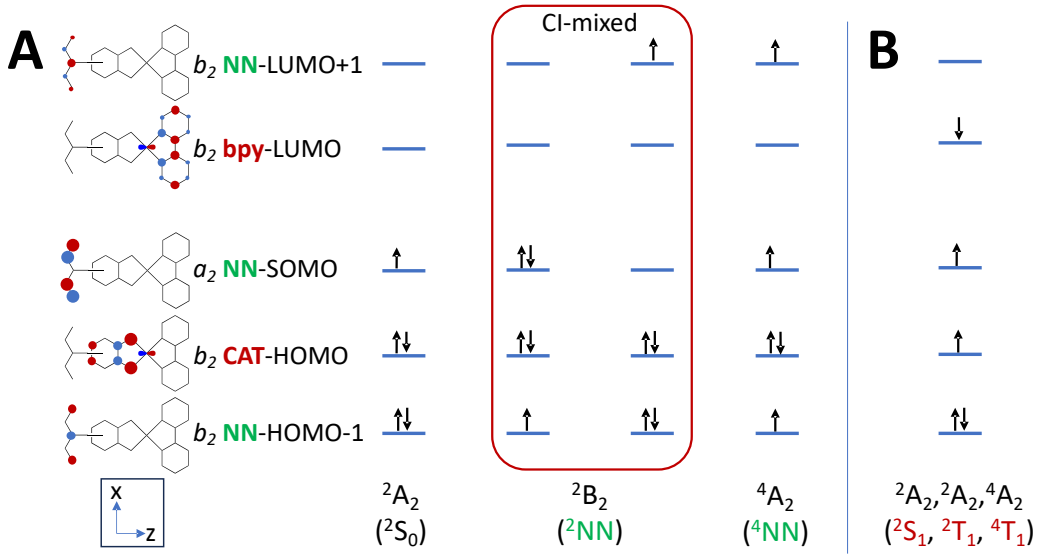


Figure S1. Frontier MOs, configurations, and NN/LL'CT-derived MO and state symmetries using idealized C_{2v} symmetry. **A:** Cartoons of π-frontier MOs consistent with previously published TDDFT calculations, as well as ground- and NN-based excited configurations. Mixing of excited $^2B_2$ NN-based configurations pushes low-energy ^{2}NN component close to that of ^{4}NN (see ***Figure 2A***). This 2B2/2NN state is manifest in the optical transitions shown in ***Figure 4B***. **B:** configuration and states arising from one-electron promotion from CAT HOMO to bpy LUMO (LL'CT excited states).

The $(DMSO)_2Pt$(CAT-Bridge-NN) complexes exhibit nearly identical cw-EPR spectra to the (bpy)Pt(CAT-B-NN) complexes (***Figure S2A***, ***C***), but show no TREPR signal upon irradiation at 532 nm as shown in ***Figure S2B***, ***D***. Thus, photons absorbed by the NN radical do not result in spin polarization.

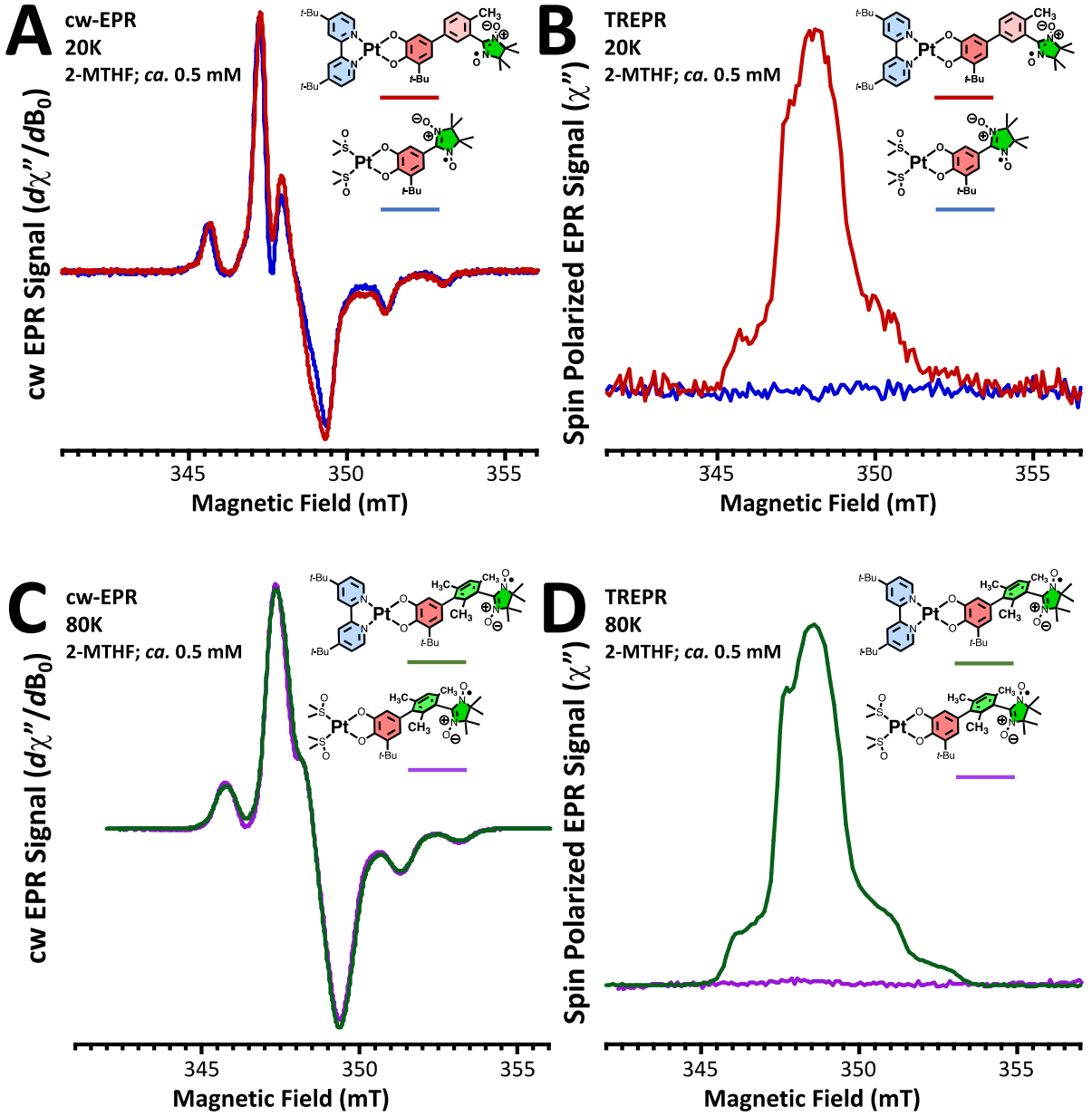


Figure S2. cw- (**A**, **C**) and TREPR spectra (**B**, **D**) of (bpy)Pt(CAT-B-NN) (— and —), and $(DMSO)_2Pt$(CAT-B-NN) complexes (— and —) lacking the diimine required for the LL'CT chromophore. Spectra **A** and **B** were collected at 20 K, while spectra **C** and **D** were collected at 80 K as described in the text/SI. Note lack of TREPR signals upon irradiation of the NN radical (**B** and **D**), irrespective of the bridge fragment or temperature.

Figure S3 shows EPR spectra of ***m*-Ph** in a glassy solvent (**A**), and in a poor solvent (DMSO, **B**, lower) the latter resulting in the formation of aggregates with broadened EPR signals. Thus,

the well-resolved spectra in the manuscript suggest the lack of aggregation. In both solvents, the complexes are stable to extended photolysis.

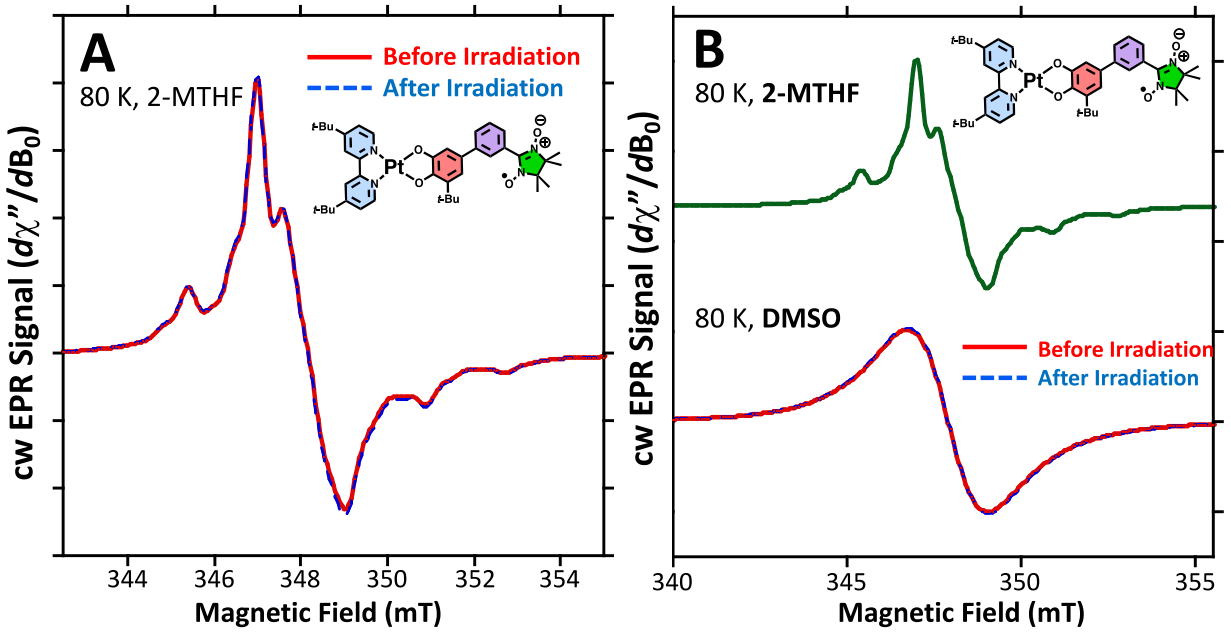


Figure S3. **A:** cw-EPR spectrum of ***m*-Ph** in 2-MTHF (0.5 mM) at 80K illustrating resolved *g*- and N-hyperfine anisotropy. Spectra recorded before and after 532 nm irradiation are identical consistent with photostability under experimental conditions. **B:** cw-EPR spectrum of **m-Ph** in 2-MTHF (top; 0.5 mM) and DMSO (bottom; 0.5 mM) both at 80K illustrating resolved *g*- and N-hyperfine anisotropy in 2-MTHF and a broadened, featureless spectrum in DMSO consistent with aggregation (*e.g.*, exchange narrowing).

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