

Supporting Information for:

Platinum(IV)- κ^3 -terpyridine complexes: synthesis with spectroscopic and structural characterization

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General Experimental Procedures. PtCl_2 was prepared using the literature procedure.¹ All other reagents were obtained commercially and were used without further purifications. All reactions were carried out in air under ambient conditions unless otherwise specified. ESI-MS spectra were recorded using an Agilent 1100 LC/MSD spectrometer. UV-Vis data were collected with a Shimadzu UV-3600 spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Varian 300 MHz spectrometer unless otherwise noted. ^{195}Pt NMR spectra were recorded using a Varian 500 MHz NMR. ^1H and ^{13}C chemical shifts were referenced to the residual protio solvent resonance. ^{195}Pt NMR chemical shifts were referenced to an external 0.2 M solution of K_2PtCl_4 in D_2O ($\delta = -1616$ ppm). Elemental microanalyses were performed by Atlantic Microlab, Inc., Norcross, Georgia.

Synthesis of $[\text{Pt}(\text{Bu}_3\text{tpy})\text{Cl}]\text{Cl}\cdot 2\text{CH}_2\text{Cl}_2$, **1:** A portion of $\text{Pt}(\text{COD})\text{Cl}_2$ (286 mg, 0.76 mmol) (COD is 1,5-cyclooctadiene) and Bu_3tpy (317 mg, 0.79 mmol) were stirred in ~40 mL H_2O , ~15 mL MeOH and ~2 mL acetone in air at 80 °C. A yellow solution and undissolved white reactant were evident after 12 hours of stirring. After ~48 hours of stirring the solution was filtered over Celite to remove a minute amount of undissolved starting materials and the methanol and acetone were removed with *in vacuo*. The product was extracted into CH_2Cl_2 to produce a yellow organic layer and a cloudy white aqueous layer. The CH_2Cl_2 was removed *in vacuo* to produce a yellow powder. The powder was washed with diethyl ether for a yield of 93%. Yellow block-shaped crystals were grown in a 78% yield by vapor diffusion of diethyl ether into a solution of **1** in CH_2Cl_2 . UV-vis (CH_3CN) (λ_{max} , nm (ϵ_{M} , $\text{cm}^{-1} \text{M}^{-1}$): 213 (94,500), 256 (66,400), 281 (52,000), 306 (18,200), 315 (24,700), 329 (32,100), 344 (18,200), 373 (6,600). Anal. Calc.: C, 41.59; H, 4.69; N 5.02 %. Found: C, 41.85; H, 4.66; N, 5.25 %. ^1H NMR (δ , ppm, $\{\text{CD}_2\text{Cl}_2\}$) (See Scheme S2 for labeling system): 9.04 (s, 2H, H_4), 8.99 (d, $^4J = 2.17$ Hz, d, $^5J = 0.47$ Hz, 2H, H_3), 8.92 (d, $^3J = 6.06$ Hz, d, $^5J = 0.47$ Hz, 2H, H_1), 7.65 (d, $^3J = 6.06$ Hz, d, $^4J = 2.09$ Hz, 2H, H_2), 1.64 (s, 9H, H_6), 1.51 (s, 18H, H_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , ppm, $\{\text{CD}_2\text{Cl}_2\}$): 168.71 (s, 2C, C(Ar)), 168.15 (s, 2C, C(Ar)), 158.66 (s, 2C, C(Ar)), 154.46 (s, 2C, C(Ar)), 150.93 (s, 2C, C(Ar)), 124.66 (s, 2C, C(Ar)), 124.41 (s, 2C, C(Ar)), 122.81 (s, 2C, C(Ar)), 37.82 (s, 1C, CC_4), 36.61 (s, 2C, CC_4), 30.41 (s, 3C, CH_3), 30.08 (s, 6C, CH_3). ESI-MS (CH_3CN), pos scan, m/z (abundance): 628.05 (1.8), 630.05 (58.4), 631.05 (91.5), 632.10 (100.0), 633.05 (46.5), 634.05 (47.2), 635.10 (12.3), 636.10 (7.3), 637.05 (2.0).

Synthesis of [Pt(^tBu₃tpy)Cl₃][AuCl₂] \cdot 2CH₂Cl₂, **2:** To a solution of **1** (76 mg, 0.1143 mmol) in acetone (~35 mL) was added a solution of KAuCl₄ (43 mg, 0.1143 mmol) in acetone (~5 mL). The reaction flask was covered with foil and allowed to stir for ~14 hours. The precipitate, presumably KCl due to solubility in H₂O, was filtered off over Celite. The acetone was removed *in vacuo* to give a yellow-orange powder. Colorless, plate-shaped crystals and yellow needle-shaped crystals were grown by vapor diffusion of diethyl ether into a solution in CH₂Cl₂. A colorless crystal was mounted for X-ray diffraction and found to have the [Pt(^tBu₃tpy)Cl₃][AuCl₂] \cdot 2CH₂Cl₂ composition. ESI-MS (CH₃CN), pos scan, m/z (abundance): 630.10 (44.3), 631.05 (71.2), 632.10 (74.9), 633.00 (38.2), 634.05 (32.9), 635.05 (8.3), 699.95 (52.5), 700.95 (61.9), 702.00 (100.00), 703.00 (76.3), 704.00 (59.6), 705.00 (21.3), 705.90 (2.7), 706.05 (16.8), 706.95 (10.2), 707.95 (6.2). ESI-MS (CH₃CN), neg scan, m/z (abundance): 266.85 (46.2), 268.75 (26.9), 270.70 (1.2), 336.75 (78.9), 338.75 (100.0), 340.70 (44.7), 342.75 (11.9). ¹⁹⁵Pt NMR (DMF-d₇, 298K): δ Pt(IV) -601 ppm, δ Pt(II) -2737 ppm. Satisfactory elemental analysis for compound **2** was not obtained due to incomplete oxidation.

Synthesis of [(Pt(^tBu₃tpy)Cl₃)Cl] \cdot 1.5 H₂O, **3:** PhICl₂ (44 mg, 0.159 mmol) was added to a stirring yellow solution of **1** (100 mg, 0.150 mmol) in DMF (~5 mL). The intensity of the yellow color faded immediately as soon as the PhICl₂ was added to the solution of **1**. The solution was allowed to stir for about 17 hours. A 100 mL portion of Et₂O was added to the reaction mixture resulting in the precipitation of a pale yellow solid. The crude product was filtered, washed with Et₂O, and collected in 77% yield. Light yellow block-shaped crystals were grown by vapor diffusion of diethyl ether into a dichloromethane or DMF solution. ¹H NMR (δ , ppm, {CDCl₃}, Varian 500 MHz) (See Scheme S2 for labeling): 9.59 (s, 2H, H₃), 9.45 (s, 2H, H₄), 9.06 (d, ³J = 5.00 Hz, 2H, H₁), 7.83 (d, ³J = 5.00 Hz, 2H, H₂), 1.75 (s, 9H, H₆), 1.62 (s, 18H, H₅). ¹³C{¹H} NMR (δ , ppm, {DMF-d₇}): 172.80 (s, C(Ar)), 170.75 (s, C(Ar)), 157.06 (s, C(Ar)), 151.65 (s, C(Ar)), 150.85 (s, C(Ar)), 127.14 (s, C(Ar)), 128.00 (s, C(Ar)), 128.73 (s, CC₄), 38.49 (s, CC₄), 37.17 (s, CH₃), 30.49 (s, CH₃), 29.87 (s, CH₃). ¹⁹⁵Pt NMR (DMF-d₇, 298K): δ -595 ppm. UV-Vis (CH₂Cl₂) (λ_{\max} , nm (ϵ_M , cm⁻¹ M⁻¹): 336.5 (16,500), 352.5 (16,900). ESI-MS (CH₂Cl₂) pos scan, m/z (abundance): 698.10 (1.2), 700.05 (51.1), 701.10 (66.8), 702.05 (100.0), 703.05 (74.8), 704.10 (81.3), 705.10 (35.8), 706.05 (30.7), 707.10 (9.7), 708.10 (5.8), 709.05 (1.2). The presence of [Pt(^tBu₃tpy)Cl]⁺ in the ESI-MS of **3** is likely due to reduction of [Pt(^tBu₃Cl₃)⁺ under electrospray ionization conditions. Anal. Calcd.: C, 42.36; H, 5.00; N, 5.49; Cl, 18.53 %. Found: C, 42.19; H, 5.03; N, 5.44, Cl 18.29%

Synthesis of [Pt(^tBu₃tpy)Cl][AuCl₂], **4:** To a solution of **1** (120 mg, 0.18 mmol) in acetone (~10 mL) was added a solution lithium acetylacetonate (19 mg, 0.18 mmol) partially dissolved in acetone (~15 mL). To this stirring solution was added drop-wise a solution of KAuCl₄ (68 mg, 0.18 mmol) in acetone (~2 mL) and the resultant solution was allowed to stir for 14 hours. A yellow solution and white precipitate were filtered over Celite. The acetone was removed by vacuum to yield a yellow-orange powder, a portion of which immediately turned to a black and orange inhomogeneous powder. The powder was stirred in ~10 mL dichloromethane to produce a yellow solution over a black precipitate, which was filtered over Celite.

Yellow block-shaped crystals large enough for single crystal X-ray diffraction were grown from layering diethyl ether over a solution of **4** in CH₃CN. Anal. calcd: C, 36.08; H, 3.93; N 4.68 %. Found: C, 36.04; H, 3.93; N, 4.86 %. ¹H NMR (δ, ppm, {CD₂Cl₂}) (See Scheme S2 for labeling): 8.99 (d, ³J = 6.08 Hz, 2H, H₁), 8.23 (s, 2H, H₄), 8.21 (d, ⁴J = 2.22 Hz, 2H, H₃), 7.73 (d, ³J = 6.21 Hz, d, ⁴J = 2.22 Hz, 2H, H₂), 1.62 (s, 9H, H₆), 1.50 (s, 18H, H₅). ¹³C{¹H} NMR (δ, ppm, {CD₂Cl₂}): 168.15 (s, 2C, C(Ar)), 168.02 (s, 2C, C(Ar)), 158.72 (s, 2C, C(Ar)), 151.85 (s, 2C, C(Ar)), 125.95 (s, 2C, C(Ar)), 123.11 (s, 2C, C(Ar)), 121.82 (s, 2C, C(Ar)), 37.88 (s, 1C, CC₄), 36.90 (s, 2C, CC₄), 30.80 (s, 3C, CH₃), 30.54 (s, 6C, CH₃). ESI-MS (CH₃CN), pos scan, m/z (abundance): 630.10 (86.0), 631.05 (99.5), 632.10 (100.0), 633.15 (49.3), 634.05 (46.3), 645.10 (16.5), 636.15 (13.3), 637.10 (7.8). ESI-MS (CH₃CN), neg scan, m/z (abundance): 266.85 (100.0), 268.80 (60.6), 270.85 (10.0).

General Procedure for ¹⁹⁵Pt NMR Analysis: All ¹⁹⁵Pt NMR spectra were obtained at 107.273 MHz on a Varian 500 NMR and reported in ppm relative to the external reference 0.2 M K₂PtCl₄ in D₂O (δ = -1616 ppm). Typical ¹⁹⁵Pt NMR parameters were as follows: pulse width = 8.5 μs (90°), sweep width = 625 kHz, pulse delay = 0.05s, 25K data points, line broadening = 20 Hz.

¹⁹⁵Pt NMR Analysis of Compound 2: A sample of [Pt(^tBu₃tpy)Cl]Cl, **1**, (22.7 mg, 0.034 mmol) was dissolved in 370 μL DMF-d₇. Gentle heat was applied with a heat gun to ensure complete dissolution. (39.1 mg, 0.102 mmol) KAuCl₄ was added to the solution of **1** resulting in a fine white precipitate. This mixture was manually swirled for 2 minutes prior to filtering over glass-wool filter-pipet to remove the precipitate. The yellow solution was then transferred to a Young-type NMR tube and immediately subjected to NMR analysis. Over the course of 12 hours, 61 individual runs were conducted at 11-minute intervals (summarized in Figure 2 with final spectrum in Figure S2).

¹⁹⁵Pt NMR Analysis of Compound 3: A sample of [Pt(^tBu₃tpy)Cl]Cl, **1**, (22.8 mg, 0.034 mmol) was dissolved in 370 μL DMF-d₇. Gentle heat was applied with a heat gun to ensure complete dissolution. (10 mg, 0.036 mmol) PhICl₂ was dissolved in the solution of **1** and immediately transferred to a Young-type NMR tube for analysis. Over the course of 12 hours 66 individual runs were conducted at 11-minute intervals (Figure S3).

Electronic Structure Calculations.

DFT calculations used a QS8-2400C computer from Parallel Quantum Solutions (PQS) with the Amsterdam Density Functional Package 2008.01²⁻⁴ on all electron, geometry optimized systems with TZ2P basis sets and the Vosko, Wilk, and Nusair⁵ local density approximation. Calculations were carried out on nine species with symmetry enforced as indicated: [Pt(tpy)Cl]⁺, C_{2v}, [Pt(tpy)Cl₃]⁺, C_{2v}, [Pt(^tBu₃tpy)Cl]⁺, C_s, [Pt(^tBu₃tpy)Cl₃]⁺, C_s, [AuCl₄]⁻, D_{4h}, [AuCl₂]⁻, D_{∞h}, PhICl₂, C_{2v}, PhI, C_{2v}, and Cl₂, D_{∞h}. A comparison of intramolecular distances and angles in transition metal containing species from crystallographic studies (where available) with the computational ones is presented in Table S1.

X-ray Crystallography

A general reference for all crystallographic refinement programs developed by G. Sheldrick is given.⁶

Compound **1** – Crystal data collected on an Bruker Apex II CCD using Mo-K α -radiation (0.71073 Å). Data was corrected for absorption by using numerical faceindexing and structure was solved by direct methods. The Platon program Squeeze used found to account for unrefined electron density of 208 e/unit cell. This was associated with a second molecule of CH₂Cl₂ (that is, 42 e or 168 e/unit cell). This was added into the chemical formula to adjust for density, F000 and molecular weight. An EADP command for N1 and N3 was included within the instruction file to adjust for non-positive definite value of one of the nitrogen atoms.

Compound **2** – Colorless crystal of compound **2** was mounted on a Cryoloop with Paratone-N oil and cooled to 200 K under a stream of nitrogen gas. Data collected on a Bruker APEX II CCD system with Mo-K α -radiation (0.71073 Å) and corrected for absorption by SADABS. Structure solved by direct methods and all non-hydrogen atoms except C16, C17, and C18 were refined as anisotropic by full matrix least squares on F². Carbon atom C16, C17 and C18 were disordered with part occupancies of 60.0 and 40.0 % and were refined as isotropic with DELU and SIMU restraints and fixed bond distances and angles using the restraints of DFIX and DANG. All hydrogen atoms were placed in calculated positions. Apparent disorder of one of the chlorine atoms of a dichloromethane molecule was not treated.

Compound **3** – Two different solvates were prepared and studied.

3-DMF (pictured in Figure S2) - Structure determination used the Bruker SMART X2S benchtop crystallographic system on a colorless crystal with the dimensions of 0.31 mm x 0.28 mm x 0.20 mm mounted on a Mitegen Micromount was automatically centered on a Bruker SMART X2S benchtop crystallographic system. Intensity measurements were performed using a monochromated (Doubly Curved Silicon Crystal) Mo-K α -radiation (0.71073 Å) from a sealed MicroFocus tube. Generator settings were 50 kV, 1 mA. Data collection temperature was -73°C. Data were acquired using three sets of Omega scans at different Phi settings. The frame width was 0.5° with an exposure time of 40.0 s. The detailed data collection strategy was as follows: Detector distance: 40 mm Detector swing angle (fixed 2 Theta): -20°.

Run	Omega (start)	Omega (end)	Phi	Frames
1	-20.0	160.0	0.0	360
2	-20.0	100.0	120.0	240
3	-20.0	40.0	240.0	120

APEX2 software was used for preliminary determination of the unit cell. Determination of integral intensities and unit cell refinement were performed using SAINT. Data were corrected for absorption effects with SADABS using the multiscan technique. XPREP determined the space group to be C 2/c, with $Z = 8$ for the formula unit, $C_{30}H_{42}Cl_4N_4PtO$ (or $C_{27}H_{35}Cl_3N_4Pt, Cl, C_3H_7NO$). The structure was solved with XS and subsequent structure refinements were performed with XL. The final anisotropic full-matrix least-squares refinement on F_o^2 with 372 variables converged at $R_1 = 3.94\%$ for the observed data and $wR_2 = 13.05\%$ for all data. The goodness-of-fit was 1.063. The largest peak on the final difference electron density synthesis was $2.073 e^-/\text{\AA}^3$ and the deepest hole was $-0.734 e^-/\text{\AA}^3$ with an RMS deviation of $0.16 e^-/\text{\AA}^3$. On the basis of the final model, the calculated density is 1.315 g/cm^3 and $F(000) = 3232$. Residual electron density of 2.07 electrons was within 1 angstrom of Pt1 atom. Attempts to fit the second and third residual electron densities of 1.5 and 1.3 electrons as oxygen atoms (associated with water) resulted in very high thermal motion and thus these were not included in the final refinement. Because of the lack of useable electron density, the checkcif indicator of large solvent void could not be addressed. Attempts to model the disorder associated with C atoms C17, C25 were not successful and no attempt was made to model the disorder associated with the solvent.

3 – 2 Et₂O (not pictured) - A very pale yellow crystal of compound **3** was mounted on a Cryoloop with Paratone-N oil. Data were collected on a Bruker APEX II CCD systems using Mo-K α -radiation (0.71073 Å) in a nitrogen gas stream at 100(2) K using phi and omega scans. Crystal-to-detector distance was 60 mm and exposure time was 10 seconds per frame using a scan width of 0.5°. Indexing and unit cell refinement indicated a primitive, monoclinic lattice with space group P2(1)/n. Data was corrected for absorption by the program SADABS. Solution by direct methods (SHELXS) and all non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-97). All hydrogen atoms were found from a Fourier difference map and were allowed to refine. Solvent molecules of diethylether were disorder and were treated using a two part model (ratio of 46.5/53.5) and were refined isotropically. EADP restraints were used for carbon atoms C31 C33, C34 C35.

Compound **4** - Yellow crystal of was mounted on a cryoloop with Paratone-N oil and cooled to 100 K in a stream of nitrogen gas. Data collected on a Bruker APEX II CCD system with Mo-K α -radiation (0.71073 Å) and corrected for absorption with SADABS. Structure solved by direct methods and all non-hydrogen atoms refined as anisotropic by full matrix least squares on F^2 . Hydrogen atoms were placed in calculated positions.

Table S1. Comparison of Interatomic Distances and Angles between X-ray Diffraction Data and DFT Calculations

Compound	Interatomic Parameter	X-ray		Ref	DFT
Pt(II)					
[Pt(tpy)Cl] ⁺		average of 6 structures		CSD	[Pt(tpy)Cl] ⁺ , C _{2v}
	Pt-Cl	2.303(4) Å			2.262 Å
	Pt-N	1.93(1)			1.963
		2.02(1), 2.01(2)			2.036 x 2
	Cl-Pt-N	178.4(9)°			180.0°
	N-Pt-N	162.1(8)			161.47
		80.8(7), 81.3(3)			80.73 x 2
[Pt(tpy)Cl ₃] ⁺		unknown			[Pt(tpy)Cl ₃] ⁺ , C _{2v}
	Pt-Cl				2.278 Å
					2.301 x 2
	Pt-N				1.975
					2.033 x 2
	Cl-Pt-N				180.0°
	Cl-Pt-Cl				174.60
					92.70 x 2
	N-Pt-N				162.20
					81.10 x 2
[Pt(^t Bu ₃ tpy)Cl] ⁺		1	4		[Pt(^t Bu ₃ tpy)Cl] ⁺ , C _s
	Pt-Cl	2.3036(6) Å	2.3024(9)	WODQIP'	2.267 Å
	Pt-N	1.922(2)	1.934(3)		1.954
		2.014(2); 2.019(2)	2.016(3); 2.017(3)		2.057 x 2
	Cl-Pt-N	179.40(6)°	179.05(9)		180.0°
	N-Pt-N	161.99(8)	162.01(11)		161.37
		81.12(8); 81.12(8)	80.97(12); 81.09(12)		80.70 x 2

Compound	Interatomic Parameter	X-ray		Ref	DFT
Pt(IV)					
[Pt(^t Bu ₃ tpy)Cl ₃] ⁺		2	3		[Pt(^t Bu ₃ tpy)Cl ₃] ⁺ , C _s
	Pt-Cl	2.314(3) Å	2.3168(16)		2.285 Å
		2.319(3); 2.307(3)	2.2968(18); 2.3108(18)		2.303 x 2
	Pt-N	1.952(9)	1.961(5)		1.978
		2.028(10); 2.027(10)	2.024(5); 2.028(6)		2.048 x 2
	Cl-Pt-N	178.8(3)°	179.28(16)		180.0°
	Cl-Pt-Cl	177.34(11)	178.21(7)		178.86
		90.64(11); 91.57(11)	90.75(7); 90.78(7)		92.37, 88.78
	N-Pt-N	162.3(4)	162.3(2)		161.15
		80.8(4); 81.6(4)	81.4(2); 81.0(2)		80.58 x 2
Au					
[AuCl ₂] ⁻		average of 92 distances		CSD	
	Au-Cl	2.26(3) Å			2.2615 Å
[AuCl ₄] ⁻		average of 608 distances		CSD	
	Au-Cl	2.27(2) Å			2.3134 Å

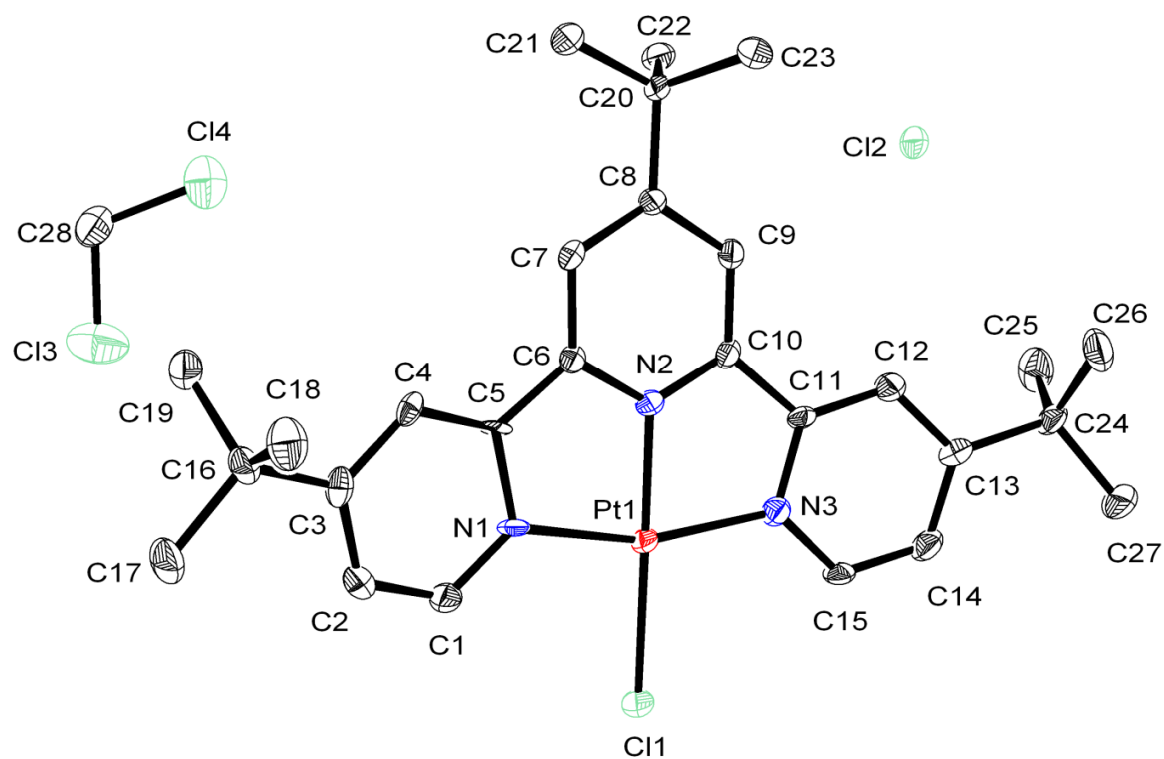


Figure S1. ORTEP of 1, with thermal ellipsoids drawn at the 50% probability level. The hydrogen atoms have been removed for clarity.

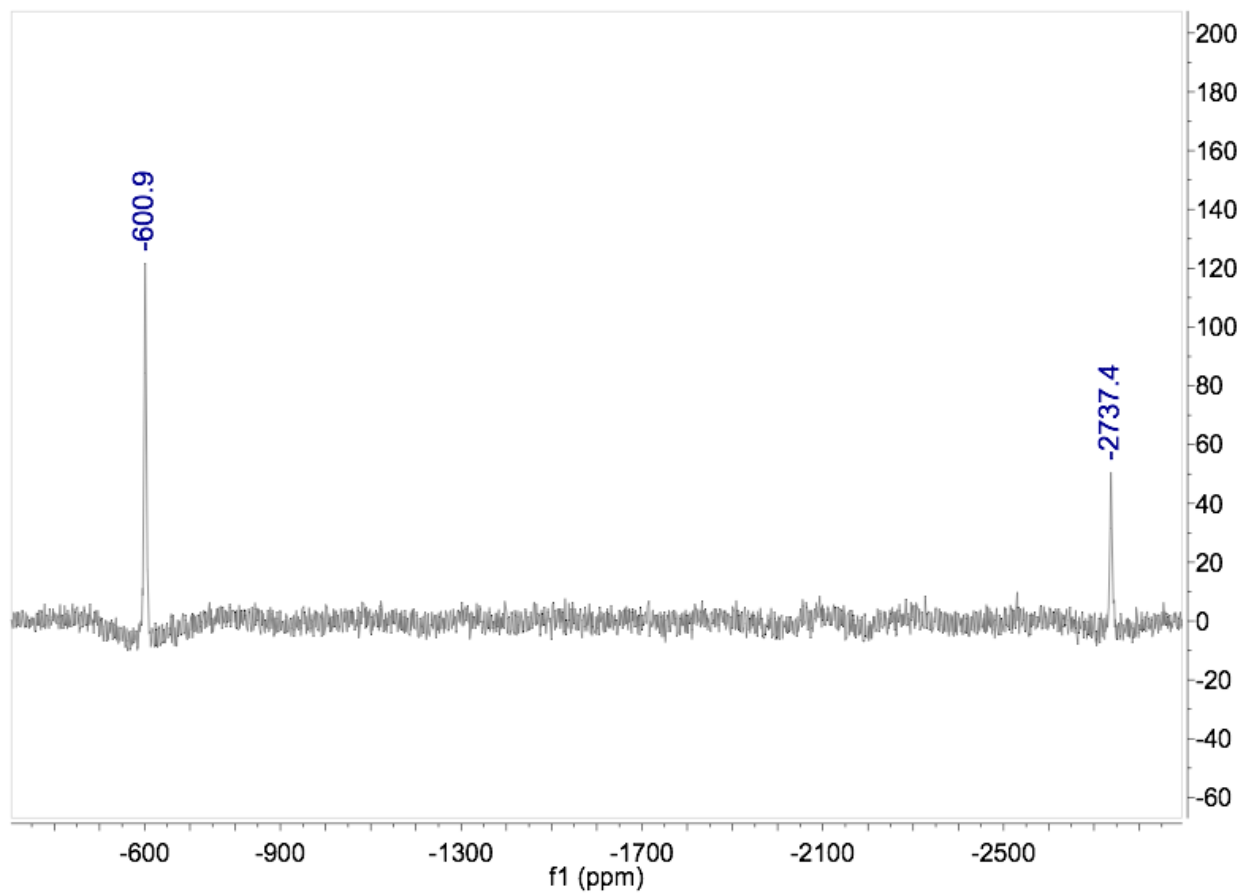


Figure S2. ^{195}Pt NMR of 1 with 1.1 equivalents of KAuCl_4 after 17 hours.

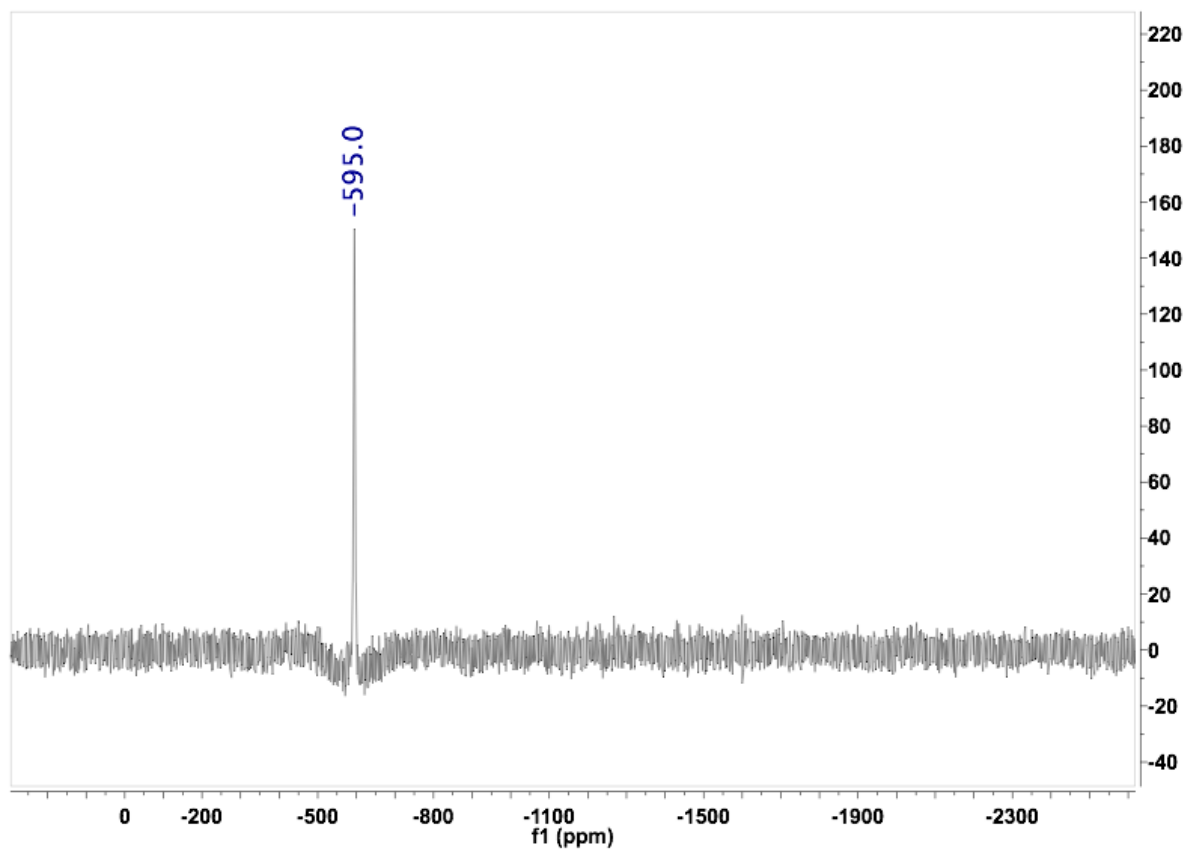


Figure S3. ^{195}Pt NMR of **1** with 1.1 equivalents of PhICl_2

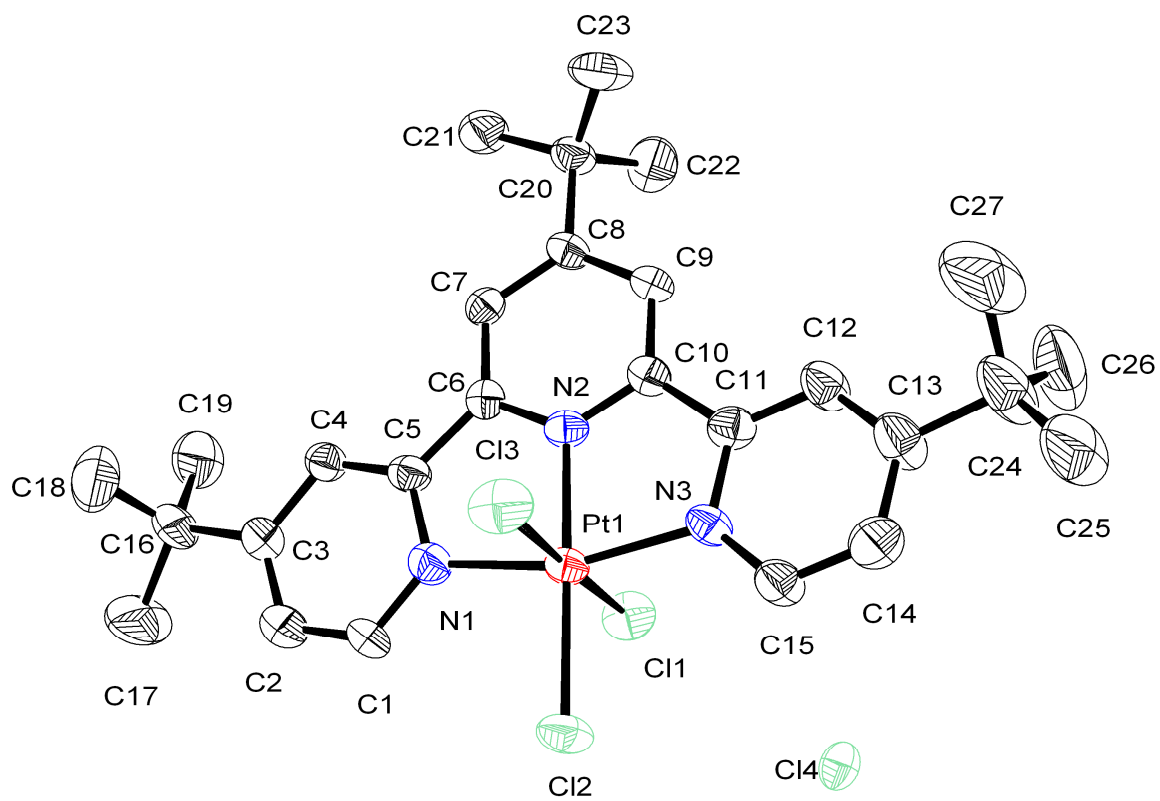


Figure S4. ORTEP of **3**, with thermal ellipsoids drawn at the 50% probability level. One equivalent of DMF solvent is present in the asymmetric unit. Solvent molecule and the hydrogen atoms have been omitted for clarity.

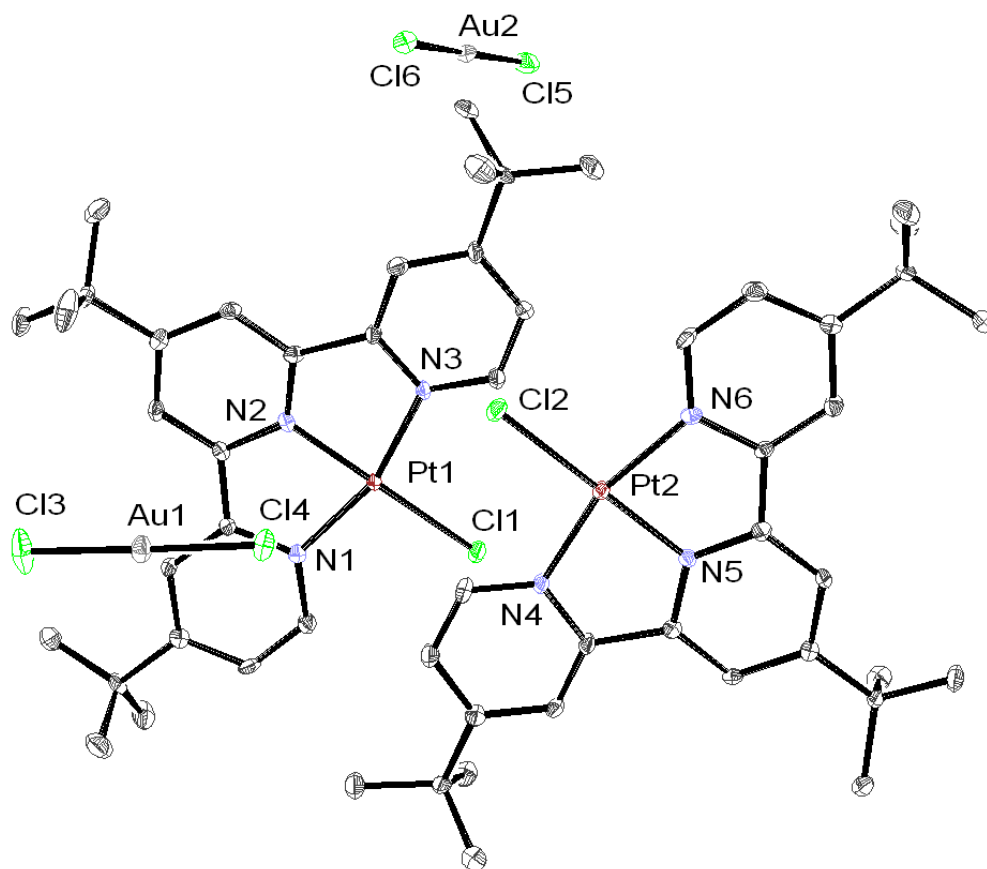
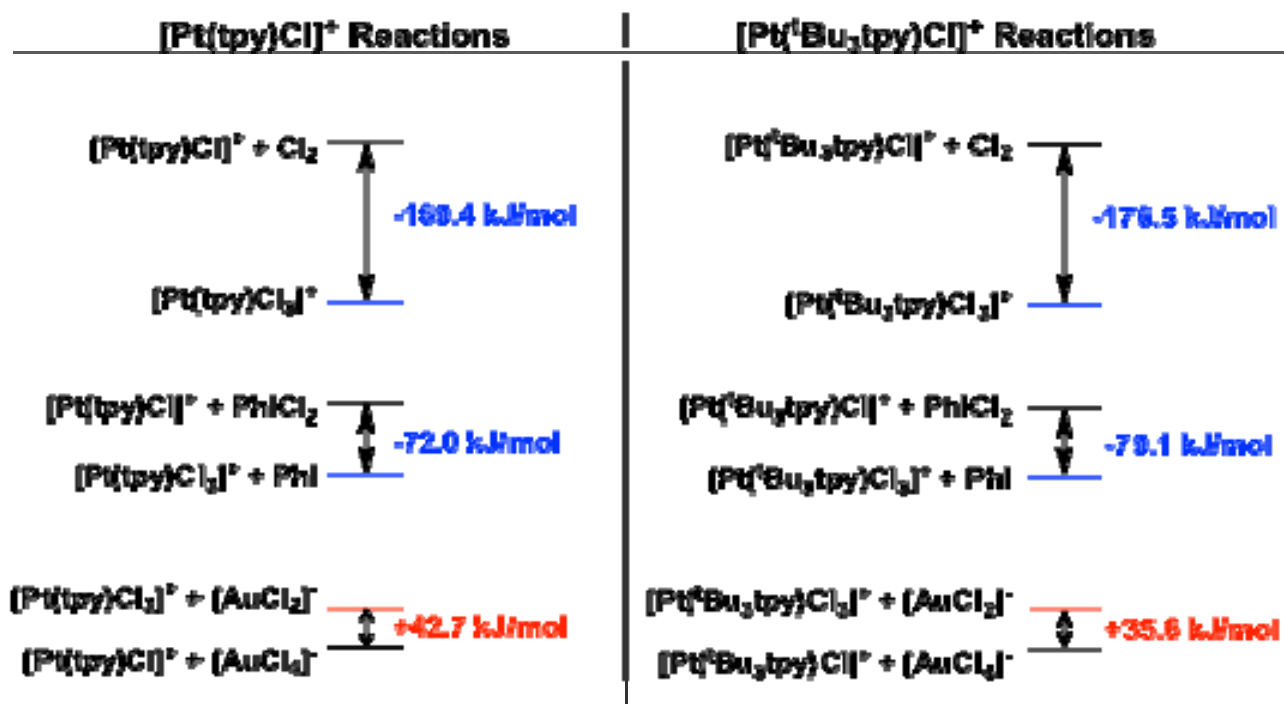
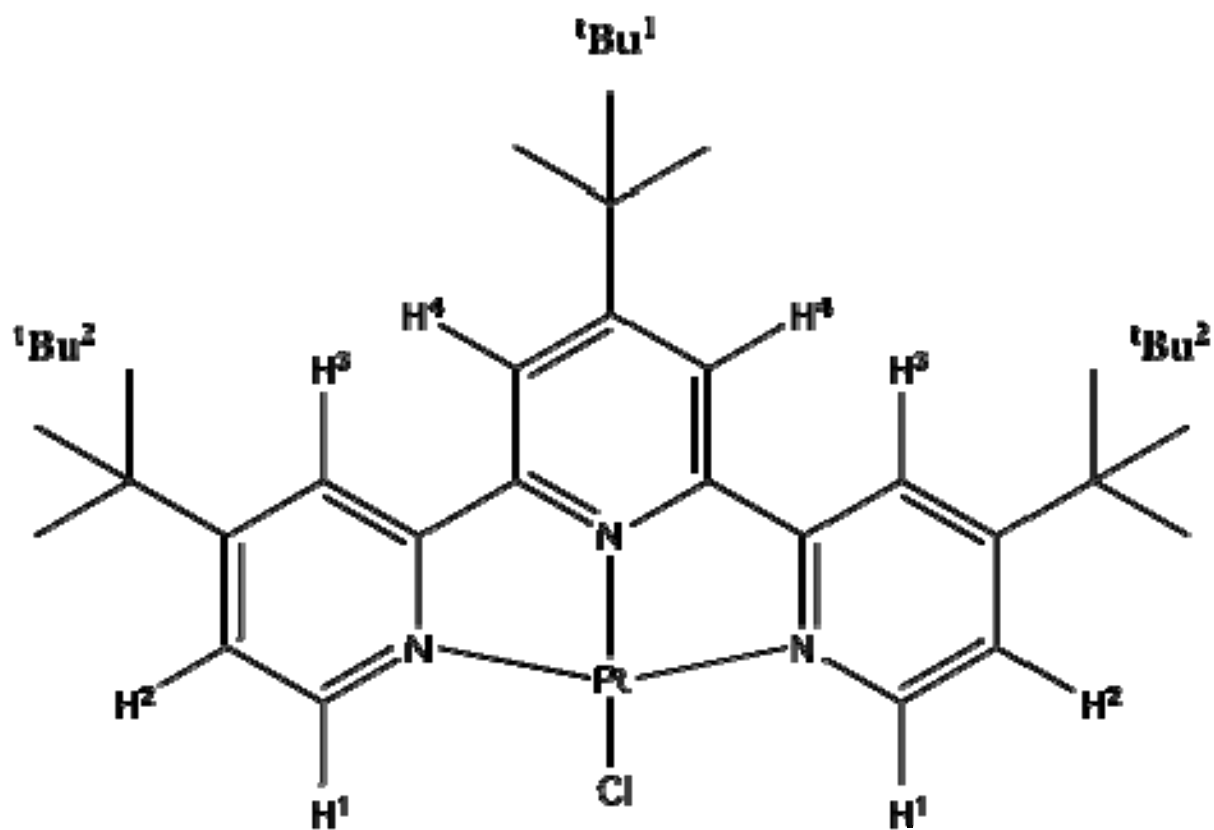


Figure S5. ORTEP of **4**, with thermal ellipsoids drawn at the 50% probability level. Two equivalents of the salt are present in the asymmetric unit with no solvent, as shown. Hydrogen atoms are omitted for clarity.



Scheme S1. DFT calculations for the oxidation reactions of compound 1 compared to [Pt(tpy)Cl]⁺ with Cl₂, PhCl₂, and [AuCl₄]⁻



Scheme S2. ${}^1\text{H}$ NMR Labeling scheme

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