Electronic Supplementary Information

Tuning of Two-Electron Transfer in Terpyridine-based Platinum(II) Pincer Complexes

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Experimental Details

All reagents were purchased from Pressure Chemical, Aldrich or Acros. $Pt(pip_2NCN)Cl$,[1] $Pt(COD)(Ph)Cl$,[2] $Pt(COD)(Mes)Cl$,[3] $[Pt(Ph_2)SEt_2]_2$,[4] pip_2NCNBr (2,6-bis(benzylpiperidine)-bromide),[1] and 4-Bromo-3,5-bis(bromomethyl)anisole[5] were prepared according to published procedures. Acetonitrile and EtOH were distilled from CaH_2 and NaOH/Al(s), respectively, under argon. ^1H NMR spectra were recorded at room temperature using a Bruker AC 400 MHz Spectrometer. Deuterated acetonitrile and chloroform (0.03% tetramethylsilane (TMS) (v/v)) were purchased from Cambridge Isotope Laboratories. UV-visible absorption spectra were recorded using a HP8453 UV-visible spectrometer. Emission spectra were recorded using a SPEX Fluorolog-3 fluorimeter equipped with a double emission monochromator and a single excitation monochromator. Emission spectra were corrected for instrumental response. Mass spectra were recorded using a Micromass Q-TOF-2 hybrid quadrupole time-of-flight mass spectrometer with

electrospray ionization. Elemental analyses were performed by Atlantic Microlabs (Norcross, GA). Cyclic voltammograms were measured using a BAS100B/W Electrochemical Workstation. Scans were collected for 1 or 2 mM samples in acetonitrile solution containing 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$), which was recrystallized from boiling methanol and dried under vacuum prior to use. Voltammograms were recorded using a platinum wire auxiliary electrode, an Ag/AgCl reference electrode (3.0 M NaCl) and a gold working electrode. Between scans, the working electrode was polished with 0.05 μm alumina, rinsed with distilled water and wiped dry. Adsorption causes electrode fouling as indicated by larger ΔE_p values with consecutive cycles. Reported potentials are referenced against Ag/AgCl. Peak currents (i_p) estimated with respect to the extrapolated baseline current as described elsewhere.[1,6] The values of $(E_{pc}+E_{pa})/2$, which is an approximation of the formal potential for a redox couple, are referred to as $E°'$.

The Randles-Ševčik equation (1) relates the current to the square root of the scan rate.

$$i_p = 2.69\text{x}10^5 n^{3/2} A D^{1/2} C v^{1/2} \quad (1)$$

where n=electron stoichiometry, A=electrode surface area, D=diffusion coefficient, and C=concentration. If one relates the change in current (i_p) to the square root of the scan rate ($v^{1/2}$), the slope, as shown in black in the equation above, is given by ($2.69\text{x}10^5 n^{3/2} A D^{1/2}$). We show the result of this experiment in Figure 6. One of the contributing factors to the slope is $n^{3/2}$. We use the first reduction process, which is a Nernstian one-electron process, as an internal standard to eliminate the other factors that contribute to the slope, namely $2.69\text{x}10^5$, A (electrode area), and $D^{1/2}$ (diffusion coefficient). Thus, the ratio of the slopes of the lines shown in Figure 6 will only

give $n^{3/2}$, which relates the electron stoichiometry of the oxidation process to the one electron reduction process. As mentioned in the main text, this ratio should be 2.8 for a two-electron process ($2^{3/2}$). We find 2.4, which gives the number of electron stoichiometry as 1.8 instead of exactly 2. We also note that the oxidation process shows a linear behavior as predicted by the Randles-Ševčik equation.

Synthesis

NO_2-pip$_2$NCNBr. This compound was prepared by a modification of the procedure for the preparation of NO_2-Me_4NCNBr.[7] To 2g (5.7 mmol) of pip$_2$NCNBr was added 5 mL concentrated H_2SO_4 dropwise while stirring at 0 ^{0}C. After subsequent addition of 0.8 mL 16 M HNO_3 while keeping the temperature below 10 ^{0}C, the mixture was left stirring at room temperature for 3 hours. The solution was poured into an ice-water mixture (8 mL water, ~30 g ice), and the pH was brought to 7 by addition of KOH and to 8 by addition of small amounts of K_2CO_3. A white solid (K_2SO_4) was removed by filtration, and the filtrate was extracted with CH_2Cl_2 (4 x 200 mL). The combined extracts were dried over $MgSO_4$ and filtered. The filtrate was reduced to dryness by rotary evaporation and the yellow solid was collected. Yield: 2.1g, 93%. ^{1}H NMR ($CDCl_3$, δ): 1.26 (4H, m, CH_2), 1.62 (8H, m, CH_2), 2.47 (8H, m, CH_2), 3.59 (4H, s, CH_2), 8.27 (2H, s, CH).

MeO-pip$_2$NCNBr. This compound was prepared by a modification of the procedure for the preparation of MeO-Me_4NCNBr.[8] To a 10 mL benzene solution of piperidine (1.03 mL, 1.05 mol) at 0 ^{0}C was added dropwise 15 mL of a benzene solution of 4-bromo-3, 5-bis(bromomethyl)anisole (0.78 g, 2.1 mmol). After stirring overnight, the mixture was filtered. The resulting pale yellow filtrate was rotary evaporated to give a yellow oil. The product was

used without further purification. ^{1}H NMR ($CDCl_3$, δ): 1.47 (4H, m, CH_2), 1.63 (8H, m, CH_2), 2.48 (8H, m, CH_2), 3.55 (4H, s, CH_2), 3.82 (3H, s, CH_3), 7.05 (2H, s, CH).

Pt(NO_2-pip$_2$NCN)Br. This compound was prepared by a modification of the procedure for the preparation of Pt(NO_2-Me_4NCN)Br.[7] To a 20 mL suspension of $[Pt(Ph_2)SEt_2]_2$ (0.15g, 0.17 mmol) in benzene at room temperature under argon was added 15 mL of a benzene solution of NO_2-pip$_2$NCNBr (0.132 g, 0.34 mmol) dropwise. The solution was refluxed for 3h. After the yellow solution cooled to room temperature, it was reduced to dryness by rotary evaporation. The remaining yellow solid was washed with ether and collected over a frit. No impurities were detectable in the ^{1}H NMR spectrum, and the material was used without further purification. Yield: 0.155 g, 78%. ^{1}H NMR ($CDCl_3$,δ): 1.48 (8H, m, CH_2), 1.62 (4H, m, CH_2), 1.82 (8H, m, CH_2), 3.27 (4H, m, CH_2), 4.13 (4H, m, CH_2), 4.33 (4H, s with Pt satellites, J_{Pt-H} = 26 Hz, CH_2), 7.76 (2H, s, CH).

Pt(MeO-pip$_2$NCN)Br. This compound was prepared by a modification of the procedure for the preparation of Pt(MeO-Me_4NCN)Cl.[9] To a 20 mL THF solution of MeO-pip$_2$NCNBr (0.29 g, 0.74 mmol) at -78 ^{o}C under argon was added ^{n}BuLi (0.93 mL, 1.6 M in hexane), causing the color of the solution to change from yellow to purple. After allowing the solution to warm to room temperature, $Pt(SEt_2)_2Cl_2$ (0.33g, 0.74 mmol) in 15 mL THF was added to the flask. The mixture was stirred at room temperature for 12 hours. The orange-yellow solution was rotary evaporated to dryness. The solid was sonicated in hexanes and collected by vacuum filtration. The light orange product was used without further purification. Yield: 0.30 g, 70%. ^{1}H NMR ($CDCl_3$,δ): 1.47-1.75 (12H, m, CH_2), 3.27 (4H, m, CH_2), 3.76 (3H, s, CH_3), 4.08 (4H, m, CH_2), 4.25 (4H, s with Pt satellites, CH_2), 6.47 (2H, s, CH).

[Pt(^{t}Bu$_3$tpy)(mes)](BF$_4$). This compound was prepared by a modification of the procedure for the preparation of [Pt(tpy)(mes)]BF$_4$.[10] To a 25 mL acetone solution of Pt(COD)(Mes)Cl (0.100 g, 0.218 mmol) in the dark was added AgBF$_4$ (0.043 g, 0.22 mmol). After stirring for 30 min, the mixture was filtered through Celite. The filtrate was stirred with ^{t}Bu$_3$tpy (0.218 mmol, 0.090 mg) for 4 hours before removal of the solvent by rotary evaporation. The residue was dissolved in a minimum amount of dichloromethane. Addition of hexanes afforded a bright yellow solid. Yield: 0.158 g, 90%. Anal. Calcd. for [$C_{36}H_{46}N_3Pt$](BF$_4$).0.5H_2O: C, 53.27; H, 5.84; N, 5.18. Found: C, 53.20; H, 5.89; N, 5.27. MS(ESI): *m/z* = 715.334 (Pt(^{t}Bu$_3$tpy)(mes))$^+$. ^{1}H NMR ($CDCl_3$, δ): 1.41 (18H, s, CH_3), 1.61 (9H, s, CH_3), 2.33 (3H, s, CH_3), 2.48 (6H, s, CH_3), 6.84 (2H, s, CH), 7.39 (2H, d, CH), 8.04 (2H, d with Pt satellites, J_{Pt-H} =55 Hz, CH); 8.37 (2H, s, CH); 8.46 (2H, s, CH).

[Pt(^{t}Bu$_3$tpy)(ph)](BF$_4$). This product was isolated as a bright green-yellow solid by following the procedure for [Pt(^{t}Bu$_3$tpy)(mes)]BF$_4$ and substituting Pt(COD)(Ph)Cl (0.100 g, 0.241 mmol) for Pt(COD)(mes)Cl. Yield: 0.118 g, 65%. Anal. Calcd. for [$C_{33}H_{40}N_3Pt$](BF$_4$).3/4 CH_2Cl_2: C, 49.18; H, 5.07; N, 5.10. Found: C, 49.11; H, 5.11; N, 5.22. MS(ESI): *m/z* = 673.287 (Pt(^{t}Bu$_3$tpy)(ph))$^+$. ^{1}H NMR ($CDCl_3$, δ): 1.47 (18H, s, CH_3), 1.60 (9H, s, CH_3), 7.14 (1H, t, CH), 7.25 (2H, t, CH), 7.46 (2H, d, CH), 7.51 (2H, d with Pt satellites, J_{Pt-H} =35 Hz, CH), 8.31 (2H, d with Pt satellites, J_{Pt-H} =55 Hz, CH), 8.37 (2H, s, CH), 8.46 (2H, s, CH).

[Pt(pip$_2$NCN)(^{t}Bu$_3$tpy)](BF$_4$). A mixture of Pt(pip$_2$NCN)Cl (0.100 g, 0.2 mmol) and AgBF$_4$ (0.079 g, 0.2 mmol) in 35 mL of acetone was allowed to stir for 45 minutes in the dark at room temperature. The resulting precipitate was removed by vacuum filtration through Celite. After addition of ^{t}Bu$_3$tpy (0.080 g, 0.20 mmol), the filtrate was allowed to stir for 18 hours, and the solvent was removed by rotary-evaporation. The yellow solid was dissolved in dichloromethane,

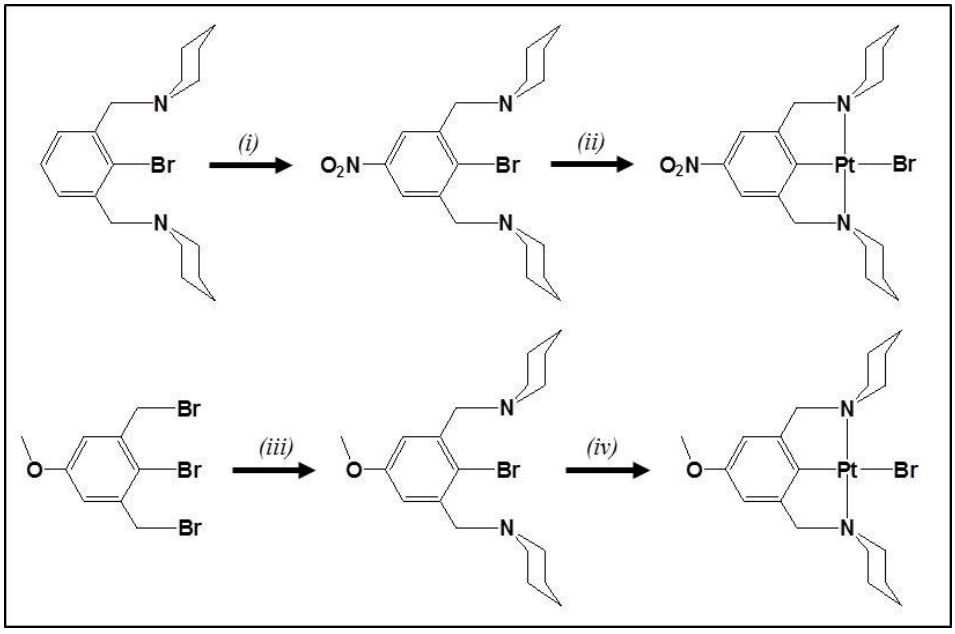
and hexanes were added to induce precipitation. The product was washed with hexanes and dried under vacuum. Yield 0.15 g, 78%. Anal. Calcd. for $[C_{45}H_{62}N_5Pt](BF_4).1/2CH_2Cl_2$: C, 54.76; H, 6.32; N, 7.02. Found: C, 54.58; H, 6.41; N, 6.82. MS(ESI): *m/z* = 955.476 ((Pt(pip_2NCNH)(^{t}Bu$_3$tpy).BF_4)$^+$), *m/z* =867.485 (Pt(pip_2NCN)(^{t}Bu$_3$tpy)$^+$). ^{1}H NMR ($CDCl_3$, δ): 1.13 (8H, m, CH_2), 1.21 (4H, m, CH_2), 1.46 (18H, s, CH_3), 1.63 (9H, s, CH_3), 2.30 (8H, m, CH_2), 3.71 (4H, s, CH_2), 7.15 (3H, m, CH), 7.31 (2H, d, CH), 7.97 (2H, d with Pt satellites, J_{Pt-H} = 42 Hz, CH), 8.32 (2H, s, CH), 8.45 (2H, s, CH). ^{1}H NMR (CD_3CN, δ): 1.03 (8H, m, CH_2), 1.16 (4H, m, CH_2), 1.40 (18H, s, CH_3), 1.57 (9H, s, CH_3), 2.28 (8H, m, CH_2), 3.68 (4H, s, CH_2), 7.10 (3H, m, CH), 7.49 (2H, d, CH), 7.93 (2H, d with Pt satellites, J_{Pt-H} = 42 Hz, CH), 8.29 (2H, s, CH), 8.40 (2H, s, CH).

[Pt(pip_2NCNH_2)(^{t}Bu$_3$tpy)](PF_6)$_3$. 0.100 g (0.105 mmol) of [Pt(pip_2NCN)(^{t}Bu$_3$tpy)]BF_4 was dissolved in ~5 mL acetone, and HNO_3 (1 M) was added dropwise until the red solution turned bright yellow. Water (20 mL) was added and the volume was reduced to ~20 mL by rotary evaporation. The mixture was filtered and 3 mL of concentrated aqueous NH_4PF_6 was added to precipitate the product. The yellow solid was collected by vacuum filtration, washed with ether and dried under vacuum. Yield 0.123 g, 90%. The product was recrystallized by diffusing diethyl ether into an acetone solution of the complex. Anal. Calcd. for $[C_{45}H_{64}N_5Pt](PF_6)$: C, 41.42; H, 4.94; N, 5.37. Found: C, 41.15; H, 5.04; N, 5.33. MS(ESI): *m/z* = 434.235 (Pt(pipNCNH_2)(^{t}Bu$_3$tpy)$^{3+}$), *m/z* =1159.400 ((Pt(pip_2NCNH_2)(^{t}Bu$_3$tpy).2PF_6)$^+$). ^{1}H NMR (CD_3CN, δ): 1.20-170 (12H, m, CH_2), 1.46 (18H, s, CH_3), 1.63 (9H, s, CH_3), 2.83 (4H, m, CH_2), 3.33 (4H, m, CH_2), 4.68 (4H, d, CH_2), 7.07 (2H, broad, NH), 7.53 (3H, m, CH), 7.66 (2H, d, CH), 7.83 (2H, d with Pt satellites, J_{Pt-H} = not resolved, CH), 8.40 (2H, s, CH), 8.49 (2H, s, CH).

[Pt(pip$_2$NCN)(toltpy)](BF$_4$). This product was isolated as a red solid by following the procedure for [Pt(pip$_2$NCN)(^{t}Bu$_3$tpy)]BF$_4$ and substituting toltpy (0.065 g, 0.20 mmol) for ^{t}Bu$_3$tpy. Yield: 0.12 g, 68%. Anal. Calcd. for [$C_{40}H_{44}N_5Pt$](BF$_4$).3/4 CH_2Cl_2: C, 52.05; H, 4.88; N, 7.45. Found: C, 52.20; H, 4.84; N, 7.26. MS(ESI): *m/z* = 877.339 ((Pt(pip$_2$NCNH)(toltpy).BF$_4$)$^+$, *m/z* =789.3 (Pt(pip$_2$NCN)(toltpy)$^+$). ^{1}H NMR ($CDCl_3$, δ): 1.15-1.26(12H, m, CH_2), 2.18 (3H, s, CH_3), 2.32 (8H, m, CH_2), 3.76 (4H, s, CH_2), 7.17-7.26 (5H, m, CH), 7.42 (2H, t, CH), 7.90(2H, d, CH) , 8.14 (2H, d with Pt satellites, J_{Pt-H} = not resolved, CH), 8.33 (2H, t, CH), 8.53 (2H, s, CH), 8.63 (2H, d, CH).

[Pt(NO$_2$-pip$_2$NCN)(tpy)](BF$_4$). This product was isolated as an orange solid by following the procedure for [Pt(pip$_2$NCN)(^{t}Bu$_3$tpy)]BF$_4$ and substituting Pt(NO$_2$pip$_2$NCN)Br for Pt(pip$_2$NCN)Br (0.075 g, 0.13 mmol) and tpy (0.03 g, 0.13 mmol) for ^{t}Bu$_3$tpy. Yield: 0.09 g, 86%. *Anal*. *Calc.* for [$C_{33}H_{33}N_6O_2Pt$](BF$_4$)1.5 CH_2Cl_2: C, 44.70; H, 4.35; N, 9.07. Found: C, 44.52; H, 4.40; N, 9.06. MS(ESI): *m/z* = 832.281 ((Pt(NO$_2$- pip$_2$NCNH)(tpy).BF$_4$)$^+$), *m/z* =744.267 (Pt(NO$_2$-pip$_2$NCN)(tpy)$^+$). ^{1}H NMR ($CDCl_3$,δ): 1.10 (8H, m, CH_2), 1.23 (4H, m, CH_2), 2.32 (8H, m, CH_2), 3.75 (4H, s, CH_2), 7.45 (2H, t, CH), 7.96 (2H, d with Pt satellites, J_{Pt-H} =not resolved, CH), 8.02 (2H, s, CH), 8.31 (2H, t, CH), 8.52 (2H, d, CH), 8.64 (3H, m, CH).

[Pt(MeO-pip$_2$NCN)(tpy)]OTf. To a 15 mL 9:1 acetone-water solution of Pt(MeO-pip$_2$NCN)Br (0.05 g, 0.052 mmol) was added AgOTf (0.013 g, 0.052 mmol), and the mixture was stirred for 30 minutes in the dark. After filtering through Celite, tpy (0.02 mg, 0.085 mmol) was added to the filtrate, and the solution was stirred for 4 hours. The red solution was reduced to dryness by rotary evaporation. The residue was dissolved in dichloromethane, and hexanes were added. The orange-red solid was collected by vacuum filtration and dried. Yield: 0.03 g, 40%. MS(ESI): *m/z* = 879.25 ((Pt(MeO-pip$_2$NCNH)(tpy).OTf)$^+$), *m/z* =729.24 (Pt(MeO-pip$_2$NCN)(tpy)$^+$). ^{1}H NMR ($CDCl_3$,δ): 1.16-1.23 (12H, m, CH_2), 2.36 (8H, m, CH_2), 3.75 (4H, s, CH_2), 3.89 (3H, s, CH_3), 6.92 (2H, s, CH), 7.44 (2H, t, CH), 8.16 (2H, d with Pt satellites, J_{Pt-H} = not resolved, CH), 8.28 (2H, t, CH), 8.55 (2H, m, CH), 8.66 (3H, m, CH).



Scheme S1. Synthesis of Z-pip$_2$NCNBr (Z=NO_2, MeO) ligand precursors and the Pt(Z-pip$_2$NCN)Br complexes. (i) H_2SO_4 / HNO_3, KOH / K_2O_3 (ii) $[Pt(Ph_2)SEt_2]_2$, benzene (iii) piperidine, benzene, 0 ^{o}C (iv) $Pt(SEt_2)_2Cl_2$, nBuLi, THF, -78^{o}C.

Data Summary of ^{1}H NMR Spectroscopy

The ^{1}H NMR spectra of the pincer ligands, their platinum halide complexes and each the terpyridyl complexes (except [Pt(pip$_2$NCNH$_2$)(^{t}Bu$_3$tpy)](PF$_6$)$_3$) were recorded in CDCl$_3$ (Figures S1-S3). For reasons of solubility, the ^{1}H NMR spectrum of [Pt(pip$_2$NCNH$_2$)(^{t}Bu$_3$tpy)](PF$_6$)$_3$ was recorded in CD$_3$CN (Figure S3). Drawings showing the proton labeling schemes (A-L) are included with each spectrum. Resonances were assigned by comparison with those of related complexes, analysis of splitting patterns, COSY spectroscopy in the case of Pt(NO$_2$-pip$_2$NCN)(tpy)$^{+}$ and the presence of ^{195}Pt satellites associated with resonances C and G.

For the Z-pip$_2$NCNBr ligand precursors and the Pt(Z-pip$_2$NCN)Br complexes, the ^{1}H NMR spectra exhibit patterns consistent with effective C_{2v} symmetry and are qualitatively similar to those of pip$_2$NCNBr, pip$_2$NNN and their palladium(II)/platinum(II) analogs (Figure S1 and S2).[1, 11-13]

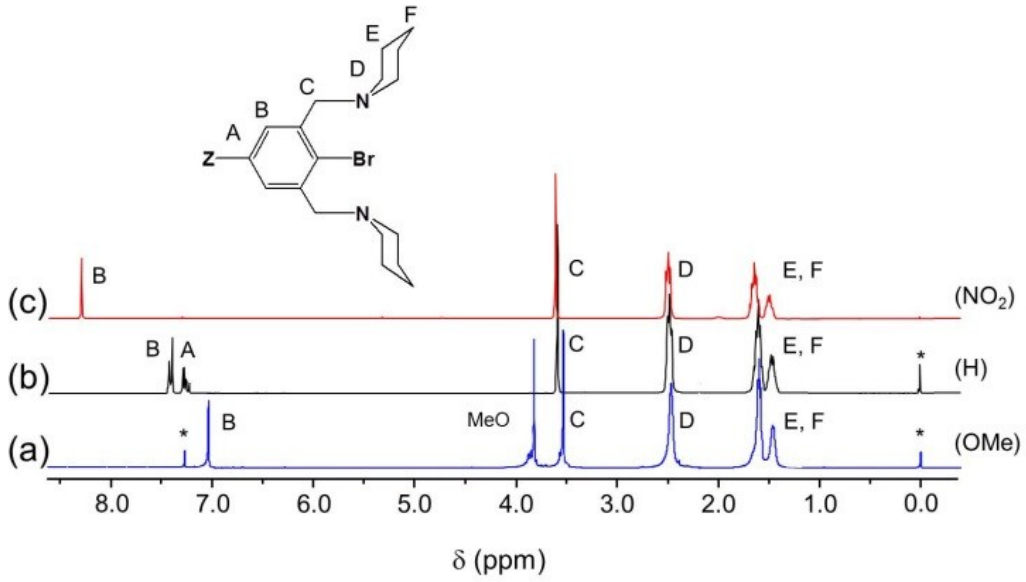


Figure S1. ^{1}H NMR spectra of Z-pip$_2$NCNBr ligand precursors in $CDCl_3$. (a) MeO-pip$_2$NCNBr, (b) pip$_2$NCNBr, (c) NO_2-pip$_2$NCNBr. The asterisks * denote TMS (0.0 ppm) and $CHCl_3$ (7.26 ppm).

As expected, for the Z-pip$_2$NCNBr (Z=NO_2, H, MeO) series, the meta phenyl proton resonances shift upfield with increasing electron donation by the para-substituent. The resonances for the Pt(Z-pip$_2$NCN)Br (Z=NO_2, 7.76; Z=H, 6.80; Z=MeO, 6.47 ppm) analogs follow a similar trend, albeit each is shifted upfield by 0.5-0.6 ppm from those of the ligand precursors (Figure S2). Comparable chemical shifts are observed for platinum halide complexes with the Z-Me$_4$NCN- ligand (Z=NO_2, 7.74 ppm; Z=MeO, 6.45 ppm).[8, 14]

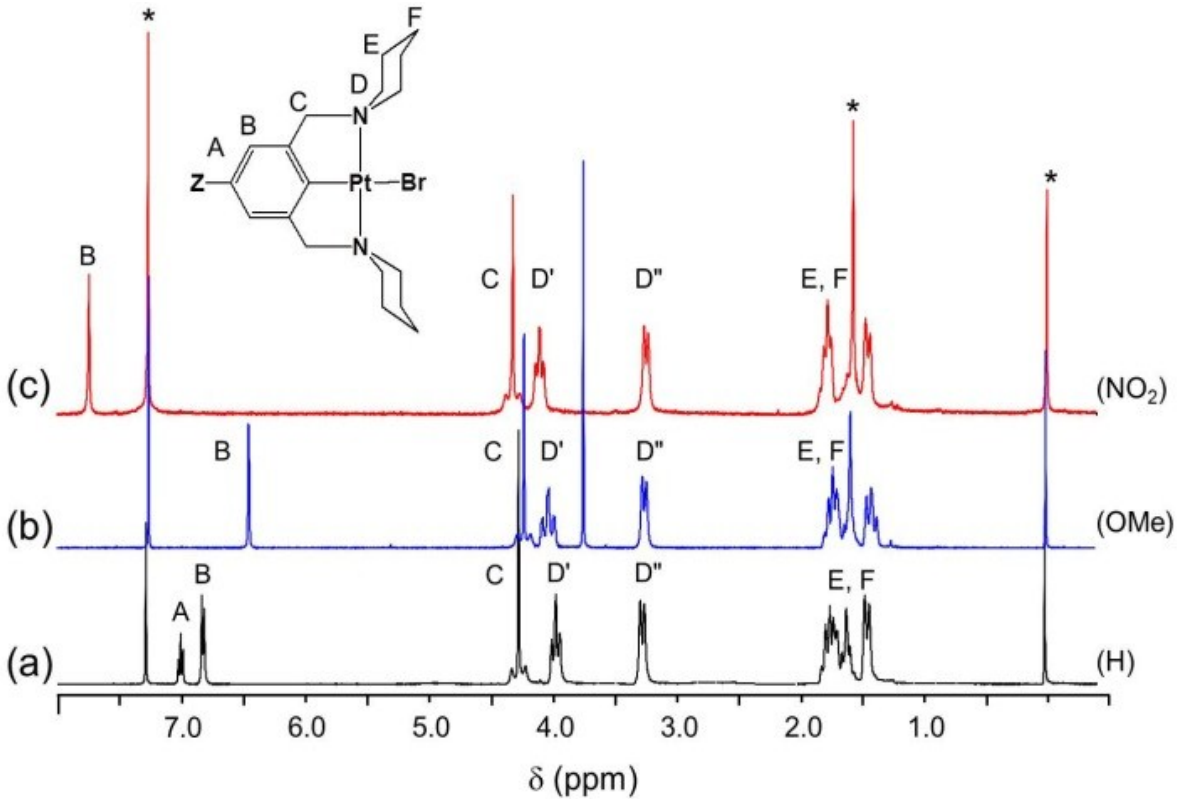


Figure S2. ^{1}H NMR spectra of Pt(Z-pip$_2$NCN)Br complexes in $CDCl_3$ (a) Pt(pip$_2$NCN)Br, (b) Pt(MeO-pip$_2$NCN)Br, (c) Pt(NO_2-pip$_2$NCN)Br. The asterisks * denote $CHCl_3$ (7.26 ppm), water (1.55 ppm) and TMS (0.0 ppm).

Coordination to the metal causes the methoxy methyl proton resonance to shift upfield by 0.06 ppm, whereas the benzylic (C) and α-piperidyl resonances (D) of each complex are shifted downfield by ~0.7 ppm and ~0.8-1.7 ppm, respectively. These shifts suggest that upon coordination, the electron density decreases near the amine coordination site. The para-phenyl substituent has little influence on the benzylic proton resonances (C) near 4.3 ppm for the ligand precursors (±0.01 ppm) and 3.55 ppm for the platinum complexes (±0.08 ppm). For the complexes, the benzylic resonances appear with distinct Pt satellites (J_{Pt-H}: Z=NO_2, 45; Z=H, 47; Z=MeO, 43 Hz), confirming coordination of the piperidyl groups. Unlike the ligand precursors, the α-piperidyl protons are diastereotopic, giving rise to two resonances (D' and D''). As expected for strong coupling between the axial α- and β-protons,[15] the axial proton resonance (D') has the appearance of a triplet, whereas the equatorial proton resonance (D'') has the appearance of a doublet. Interestingly, the MeO and NO_2 substituents do not shift the D'' resonance, but cause D' to shift downfield by 0.02 ppm and 0.08 ppm, respectively. As in the case of the ligands, the chemical shifts (1.4-1.8 ppm) of the β- and γ- piperidyl proton resonances (E and F) are relatively insensitive the para-substituent.

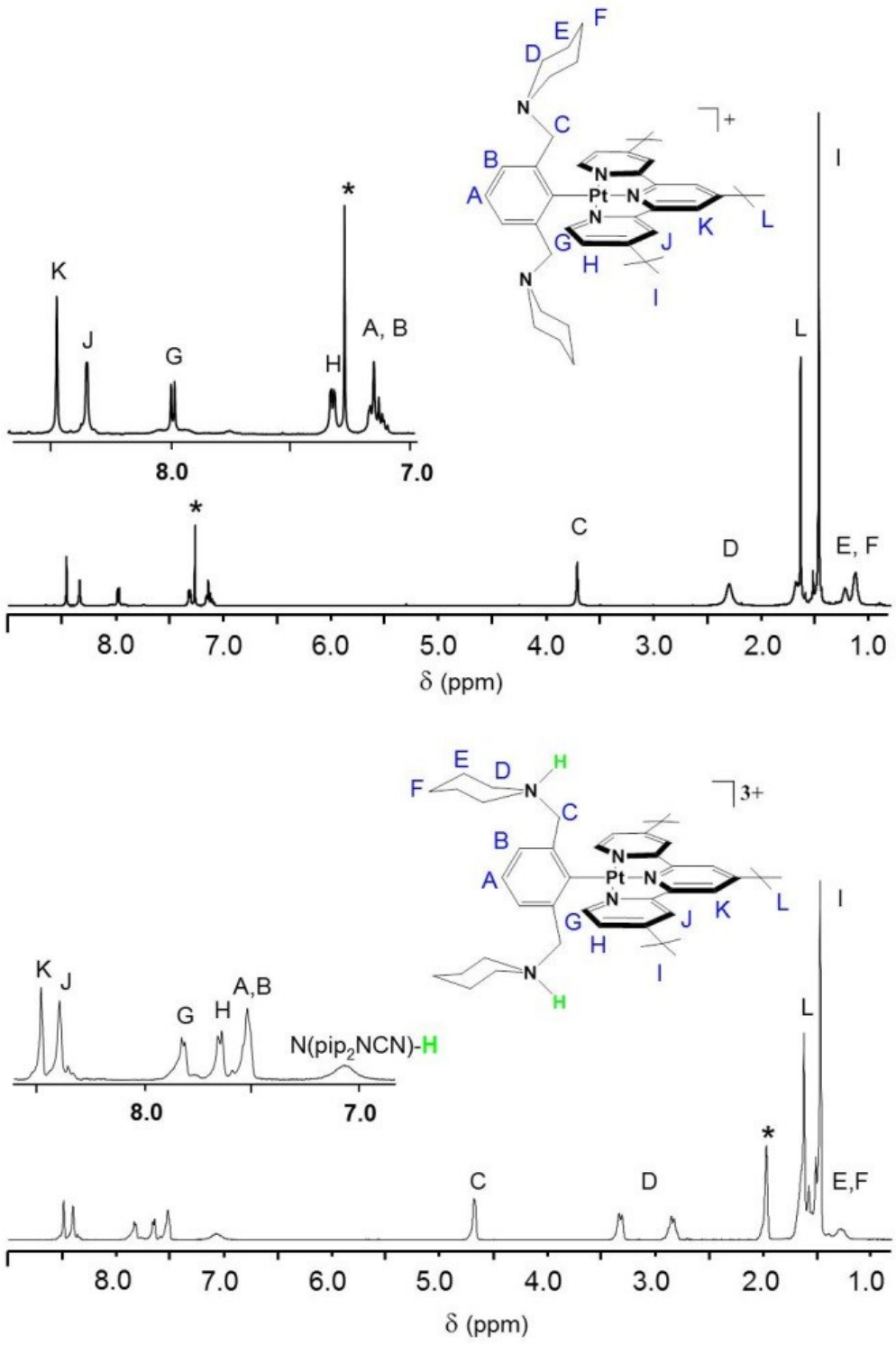


Figure S3. ^{1}H NMR spectra of $[Pt(pip_2NCN)(^{t}Bu_3tpy)](BF_4)$ in $CDCl_3$ (top) and $[Pt(pip_2NCNH_2)(tBu_3tpy)](PF6)_3$ in CD_3CN (bottom). The asterisks * denote $CHCl_3$ (7.26 ppm) and CH_3CN (1.97 ppm).

As in the case of the deprotonated complex, the phenyl proton resonances of $Pt(pip_2NCNH_2)(^tBu_3tpy)^{3+}$ overlap and appear as a multiplet at 7.53 ppm (Figure S3). The 0.43 ppm downfield shift from the corresponding resonances for $[Pt(pip_2NCN)(^tBu_3tpy)]^+$ (7.10 ppm) reflects the electron-withdrawing of the piperidinium groups. The resonance for the pip_2NCN^- benzylic protons (C) appears as a doublet (4.1 Hz) without ^{195}Pt satellites. The α-piperidyl protons (D) are diastereotopic (2.83, 3.33 ppm) and appear as multiplets shifted ~0.4 ppm upfield from those of $Pt(pip_2NCN)Br$. Resonances arising from protons E and F overlap with the *t*-butyl resonances further upfield. Interestingly, all terpyridine resonances except G are shifted *downfield* by 0.1-0.2 ppm from the corresponding resonances of $[Pt(pip_2NCN)(^tBu_3tpy)]^+$. The *t*-butyl resonances, I and L, appear as singlets upfield (1.63, 1.46 ppm, respectively). For reasons that are not fully understood, the resonances for $Pt(pip_2NCNH_2)(^tBu_3tpy)^{3+}$ in the spectrum in Figure S3 are significantly broader than those in previously reported spectra of $Pt(pip_2NCNH_2)(tpy)^{3+}$ and $Pt(pip_2NCNH_2)(phtpy)^{3+}$.[16]

Data Summary of Electronic Spectroscopy

Table S1 UV-visible absorption data for $[Pt(Ph)(^tBu_3tpy)]^+$ and $Pt(Z\text{-}pip_2NCN)(R\text{-}tpy)]^+$ complexes in dichloromethane and $Pt(pip_2NCNH_2)(^tBu_3tpy)]^{3+}$ in acetonitrile.

Compound	Absorption Bands λ_{max}, nm (ε, $cm^{-1}M^{-1}$)
$[Pt(Ph)(^tBu_3tpy)]^+$	251(29600), 274(32700), 285(27500), 307(13000), 321(16600), 342(8900), 360 (2400), 392(2500), 425(2900), 471sh(600)
$[Pt(pip_2NCN)(^tBu_3tpy)]^+$	261(45800), 273(45900), 283(44000), 319(22800), 365(4200), 390(3200), 420(2700), 458 (1800), 490(800), 535(300)
$[Pt(NO_2\text{-}pip_2NCN)(tpy)]^+$	244(29600), 274(27300), 315(20800), 339 (18200), 361(9700), 393(3700), 431 (1500), 481(400), 528(300)
$[Pt(pip_2NCN)(toltpy)]^+$	241(29800), 260(32500, 270(35000), 285(34800), 317(20700), 339(15400), 362(7000), 401(3200), 426(2500), 458(1100), 500(550), 562(280)
$[Pt(pip_2NCNH_2)(^tBu_3tpy)]^{3+}$	218(64800), 252(41300), 271(38600), 283(33700), 311(19200), 329(17100), 346 (8700), 362(2700), 382(2900), 403(1500)

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