Supporting Information for:

Intramolecular NH···Pt Interactions of Platinum(II) Diimine Complexes with Phenyl Ligands

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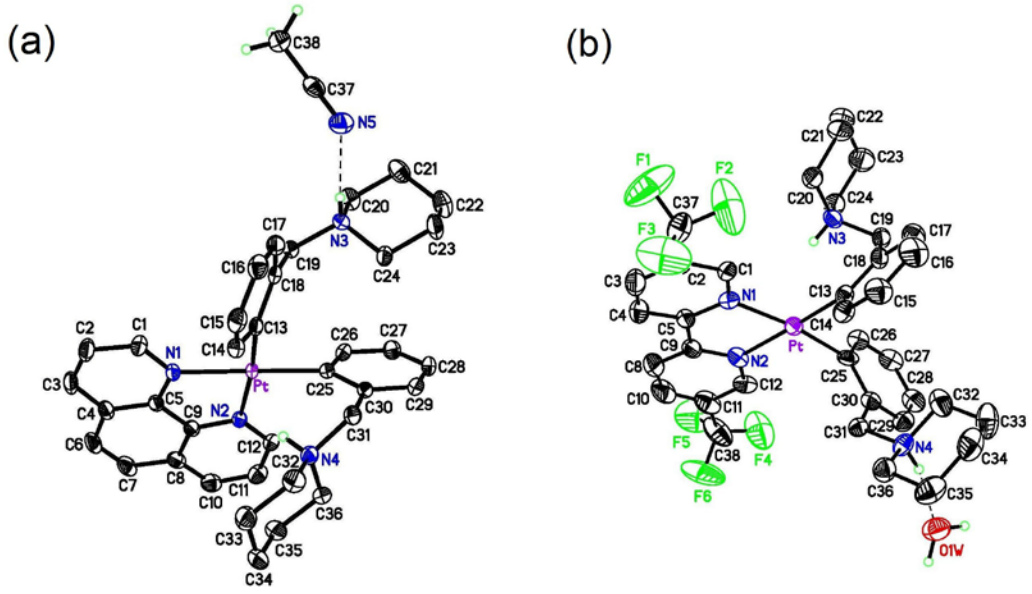

Figure S1. ORTEP diagram of solvated cationic forms of (a) $[Pt(pipNHC)_2(phen)](PF_6)_2.2CH_3CN$ and (b) $[Pt(pipNHC)_2(dtfmbpy)](PF_6)_2.H_2O$ showing N-H···solvent interaction. H-atoms (with the exception of those bonded to N(piperidyl) and solvent) are omitted for clarity

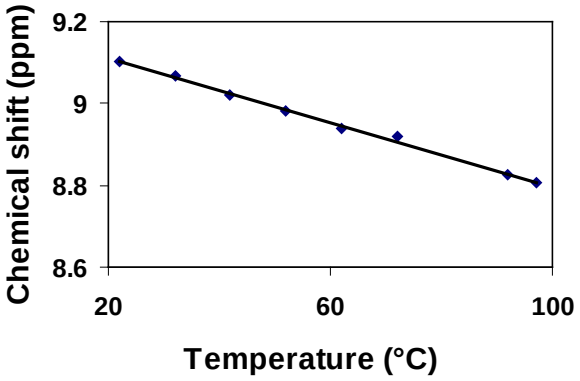

Figure S2. Temperature dependence of the N-H proton chemical shift of $Pt(pipNHC)_2(phen)^{2+}$ in d_7-DMF. Best fit line: $\delta(ppm) = -0.004T(°C) + 9.2$.

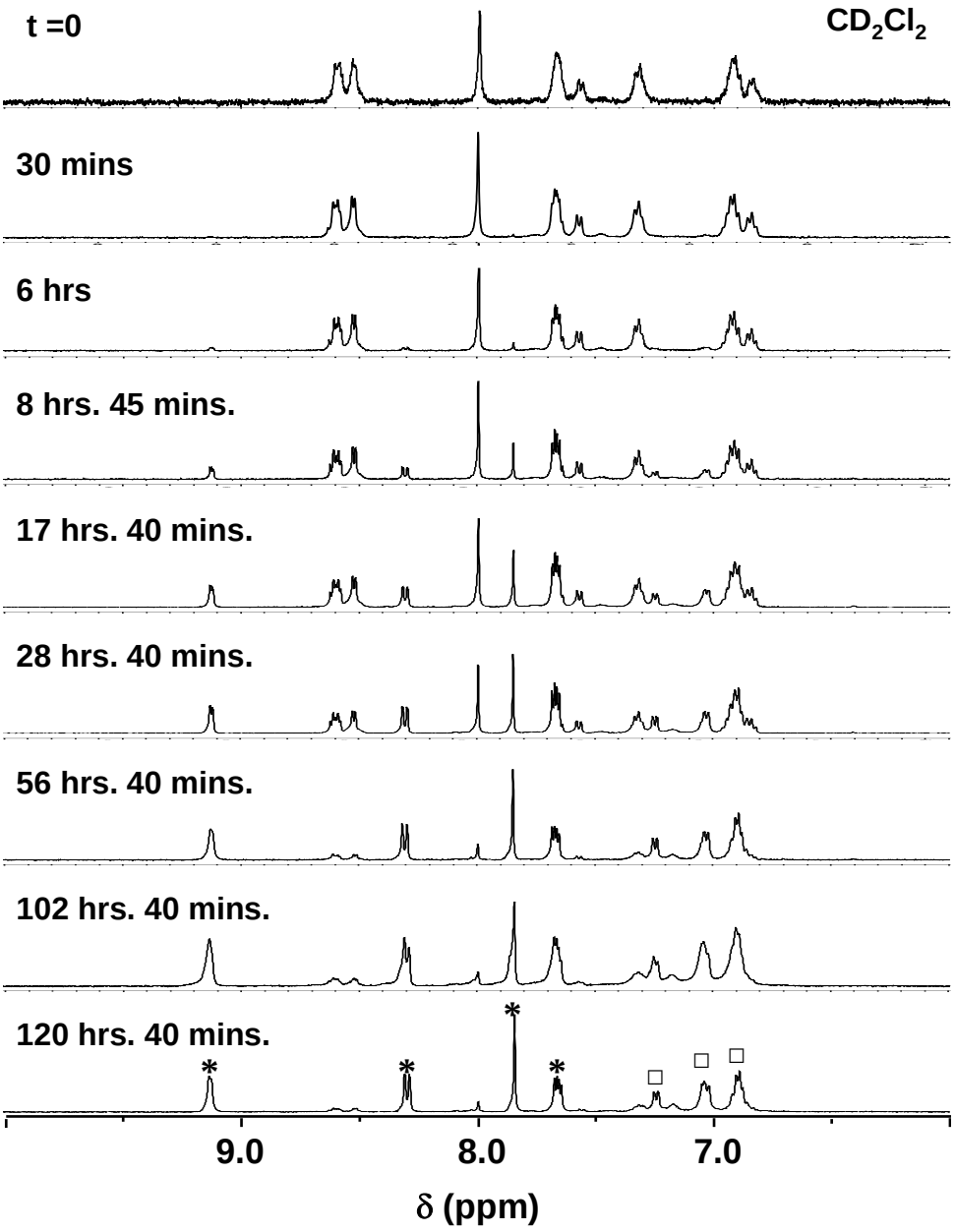

Figure S3. ^{1}H NMR spectra of the aromatic region of a solution of $Pt(pipNHC)_2(phen)^{2+}$ in CD_2Cl_2 after addition of two equivalents of TBAOH. The time at which two equivalents of base were added is designated as t=0; the first spectrum was recorded immediately following addition of base. The asterisk and the square markers in the last spectrum represent resonances consistent with protons of free phenanthroline and aromatic protons of *cis*-$Pt(pipNC)_2$, respectively.

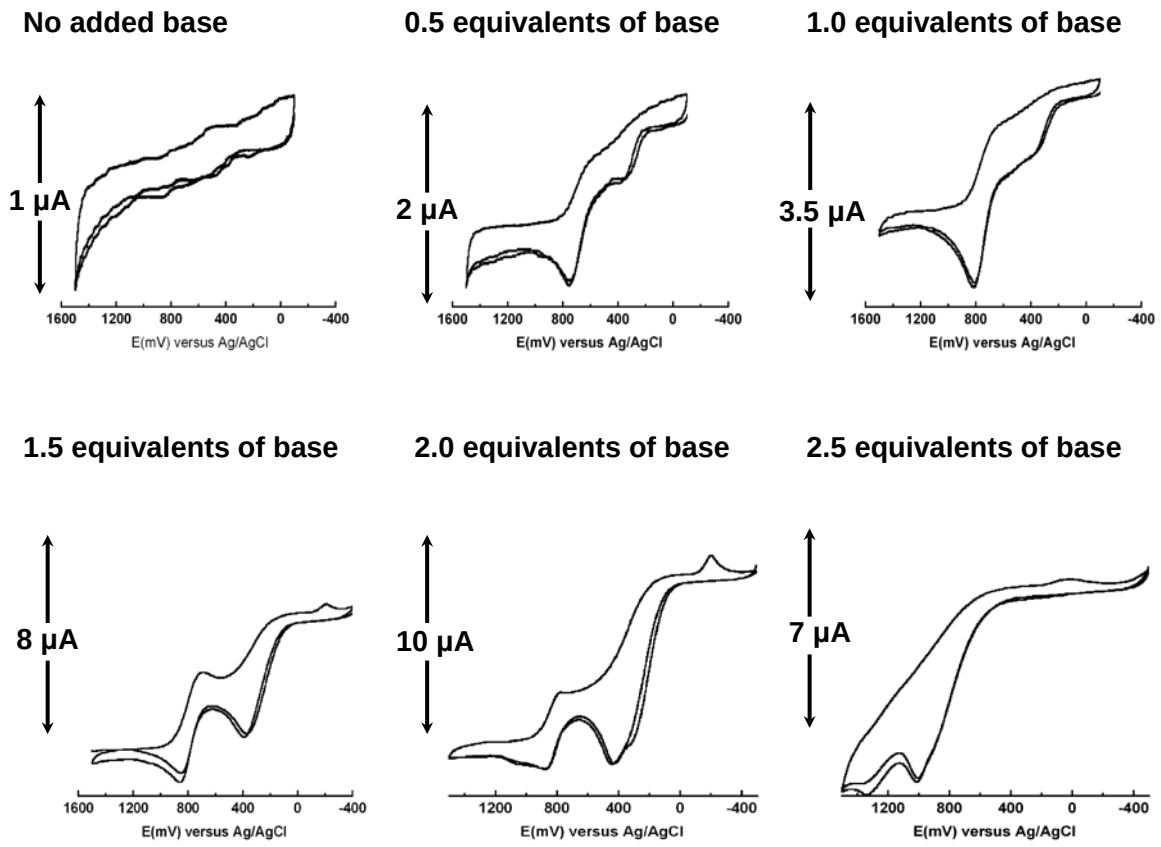

Figure S4. Cyclic voltammograms of 1.0 mM $[Pt(pipNHC)_2(phen)](PF_6)_2$ (0.1 M $TBAPF_6/CH_2Cl_2$) on addition of base (TBAOH) at a sweep rate of 0.025V/s (Au working electrode).

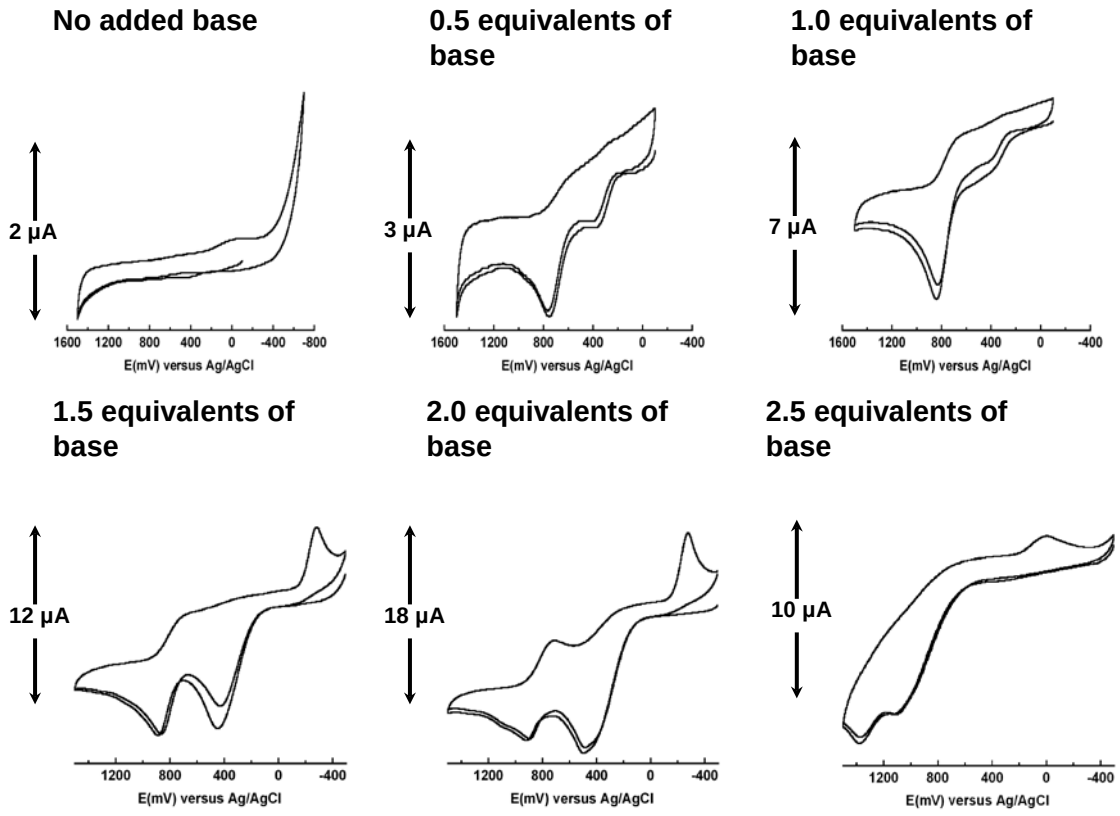

Figure S5. Cyclic voltammograms of 1.0 mM $[Pt(pipNHC)_2(phen)](PF_6)_2$ (0.1 M $TBAPF_6/CH_2Cl_2$) on addition of base (TBAOH) at a sweep rate of 0.750 V/s (Au working electrode).

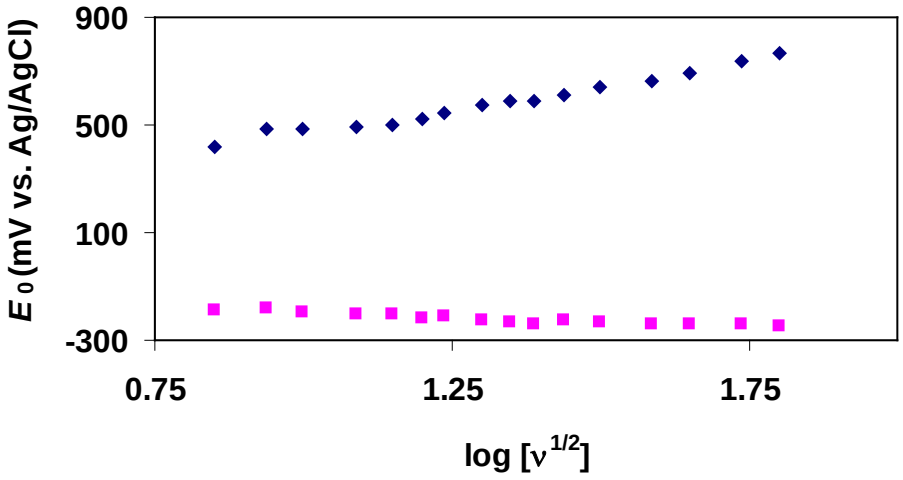

Figure S6. Peak potentials for the anodic redox process near 0.5 V (♦, E_{pa}) and the cathodic process near -0.2 V vs. Ag/AgCl (■, E_{pc}) as a function of the square root of the sweep rate (ν) for $Pt(pipNC)_2(phen)$ in 0.1 M $TBAPF_6/CH_2Cl_2$ (Au working electrode).

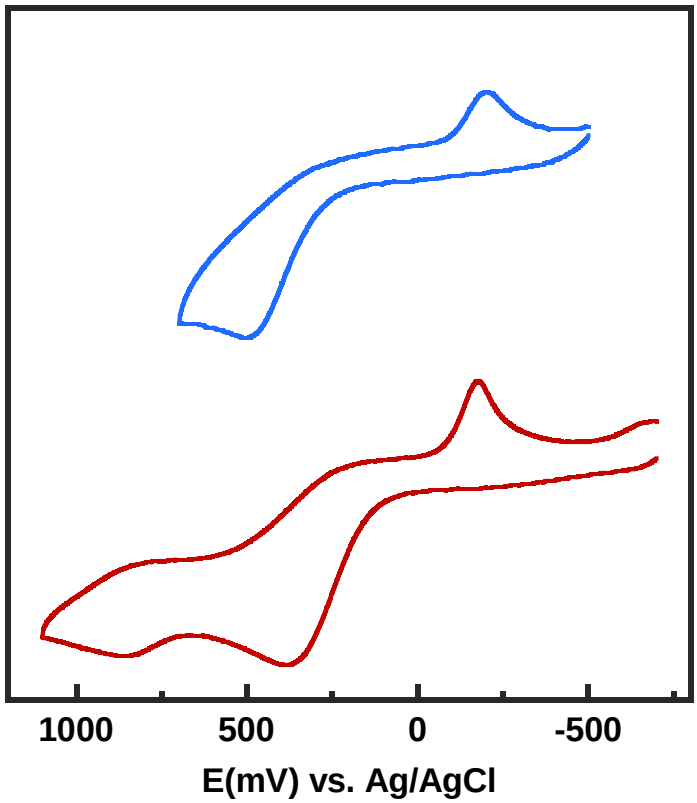

Figure S7. Cyclic voltammograms of directly synthesized $Pt(pipNC)_2(phen)$ (*c.f.*, deprotonation of $Pt(pipNHC)_2(phen)^{2+}$) in 0.1 M $TBAPF_6$/MeCN (——) and 0.1 M $TBAPF_6/CH_2Cl_2$ (——) at a sweep rate of 0.750 V/s (Au working electrode).

Table S1. UV-Visible Absorption Spectroscopy Data.

Compound	**Solvent**	**Wavelength (nm) (ε, 10^4 x M^{-1} cm^{-1})**
$Pt(pipNHC)_2(phen)^{2+}$	CH_3CN	275 (2.75), 320sh (0.32), 347 (0.34), 364 (0.35)
$Pt(pipNC)_2(phen)$	CH_3CN	268 (2.59), 357sh (0.33), 375sh (0.30), 441 (0.26)
$Pt(pipNHC)_2(phen)^{2+}$	DMSO	271 (2.55), 350sh (0.29), 400 (0.19)
$Pt(pipNC)_2(phen)$	DMSO	271 (2.54), 300sh (0.93), 355sh (0.30), 441 (0.19)
$Pt(pipNHC)_2(phen)^{2+}$	Acetone	347sh (0.25), 364 (0.25)
$Pt(pipNC)_2(phen)$	Acetone	363 (0.24), 378sh (0.23), 449 (0.16)
$Pt(pipNHC)_2(phen)^{2+}$	MeOH	273 (1.82), 315sh (0.36), 349sh (0.23), 366 (0.23)
$Pt(pipNC)_2(phen)$	MeOH	269 (1.82), 365 (0.19), 439 (0.11)
$Pt(pipNHC)_2(phen)^{2+}$	$CHCl_3$	277 (2.22), 346sh (0.23), 363 (0.20)
$Pt(pipNC)_2(phen)$	$CHCl_3$	271 (2.26), 295sh (1.08), 353 (0.24), 369sh (0.20), 426 (0.17)
$Pt(pipNHC)_2(phen)^{2+}$	CH_2Cl_2	277 (2.92), 325 (0.48), 348 (0.36), 365 (0.38)
$Pt(pipNC)_2(phen)$	CH_2Cl_2	271 (2.98), 295sh (1.41), 353 (0.35), 421 (0.27)
$Pt(pipNHC)_2(bpy)^{2+}$	DMSO	322 (0.24), 353 (0.083), 392 (0.065)
$Pt(pipNC)_2(bpy)$	DMSO	355sh (0.080), 374sh (0.064), 437 (0.055)
$Pt(pipNHC)_2(dtfmbpy)^{2+}$	DMSO	278 (0.52), 323sh (0.14), 375sh (0.032), 436 (0.026)
$Pt(pipNC)_2(dtfmbpy)$	DMSO	360sh (0.10), 480sh (0.027)