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Synthesis and Characterization of Two-Electron Platinum

Reagents

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Abstract

A series of square planar platinum(II) complexes with the *mer*-coordinating tridentate ligand, pip₂NCN⁻ (pip₂NCNH = 1,3-*bis*(piperdylmethyl) benzene) has been synthesized. The lowest emissive excited states of these complexes can be tuned by varying the properties of the monodentate ligand. Colorless halide complexes and the pyridine adduct exhibit weak red emissions originating from a lowest triplet ligand field $({}^{3}LF)$ excited state. In contrast, yellow-green emissions from Pt(pip₂NCN)(4-phenylpyridine)⁺ originate from a lowest ${}^{3}\pi$ - π * state. Similarly, (Pt(pip₂NCN))₂(μ -L)²⁺ dimers exhibit emission from a lowest ${}^{3}LF$ excited state (L=1,2-bis(4-pyridyl)ethane), a lowest ${}^{3}\pi$ - π * excited state (L=*trans*-1,2-bis(4-pyridyl)ethylene or 4,4'-bipyridine) or a lowest triplet metal-to-ligand charge-transfer excited state (L=pyrazine), depending on the bridging ligand.

A series of platinum(II) terpyridyl complexes with aryl ligands has been synthesized. The complexes undergo two one-electron reduction processes near –0.9 and –1.4 V vs. Ag/AgCl. In the cyclic voltammograms of complexes unsubstituted at the 2 and 6 positions of the aryl ligand, the first reduction exhibits larger (>59 mV) differences between the anodic and cathodic peak potentials than observed for complexes with methyl groups at the 2 and 6 positions. The accumulated data are consistent with the formation of dimers that reduce at different potentials than the monomers, causing the first reduction wave to appear broadened. Protection of the axial sites of the metal center appears to interfere with dimerization. 77 K glassy solution emission measurements confirm that steric effects can be utilized to control intermolecular metal…metal and ligand…ligand stacking interactions in solutions of these complexes. The *first* examples of platinum complexes that undergo reversible and cooperative thermal two-electron transfer have been prepared. The tpy ligand of $Pt(tpy)(pip_2NCN)^+$ is tridentate and the pip_2NCN^- ligand is monodentate, bonded through the central aryl group. Cyclic voltammograms of this complex exhibit two reversible one-electron tpy-centered reductions and a nearly reversible two-electron platinum-centered oxidation at ~0.40 V vs. Ag/AgCl. Electrochemical studies of a series of model complexes establish that both potentially tridentate ligands are required for reversible two-electron transfer. A detailed analysis leads to the suggestion that the ligands preorganize around the platinum(II) center, resulting in a 5- or 6-coordinate electrochemically active species.

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List of Abbreviations

[9]aneS ₃	1,4,7-trithiacyclononane
[14]aneS ₄	1,4,7,11-tetrathiacyclotetradecane
2,2'-bpy	2,2'-bipyridine
2-MeTHF	2-methyltetrahydrofuran
3,5-pip ₂ NCNBr	3,5-bis(piperdylmethyl)bromobenzene
А	electrode area
AIBN	2,2'-azobisisobutyronitrile
Ar	aryl
bpa	1,2-bis(4-pyridyl)ethane
bpe	1,2-bis(4-pyridyl)ethylene
bpy	4,4'-bipyridine
BuLi	<i>N</i> -butyllithium
С	concentration
D	diffusion coefficient
COD	1,5-cyclooctadiene
CV	cyclic voltammogram
DMF	dimethylformamide
DMSO	dimethylsulfoxide
dmph	dimethylphenyl
E°'	$(E_{pc}+E_{pa})/2$
en	1,2-ethylenediamine

E _{ox}	oxidation peak potential
E _p	peak potentials
E _{pa}	anodic peak current
E _{pc}	cathodic peak potential
E _{red}	reduction peak potential
ESI	electrospray ionization
Et ₂ O	diethyl ether
EtOH	ethanol
FcH/FcH ⁺	ferrocene/ferrocenium couple
FWHM	full width at half maximum
<i>i</i> _{ox}	oxidation peak current
<i>i</i> p	peak current
i _{pa}	anodic peak current
i _{pc}	cathodic peak current
$i_{ m pc}/i_{ m pa}$	ratio of cathodic peak current/anodic peak current
<i>i</i> _{red}	reduction peak current
LF	ligand field
LMCT	ligand-to-metal charge transfer
m/z	mass/charge
Me	methyl
Me₄NCN ⁻	2,6-bis(dimethylaminomethyl)benzenze
MeOH	methanol
mer	meridional

mes	mesitlyene
MLCT	metal-to-ligand charge transfer
MS	mass spectrometry
Ν	electron stoichiometry
NBS	N-bromosuccinimide
NHE	normal hydrogen electrode
NR	not resolved
Ph	phenyl
phbpyH	6-phenyl-2,2'-bipyridine
phpy	4-phenylpyridine
phtpy	4-phenyl-2,2':6',2"-terpyridine
pipNCBr	2-(piperdylmethyl)bromobenzene
pipNCH	(piperdylmethyl)benzene
pip ₂ NCNBr	2,6-bis(piperdylmethyl)bromobenzene
pip ₂ NCNH	1,3-bis(piperdylmethyl)benzene
ру	pyridine
pydiol	pyridinedimethanol
pyz	pyrazine
Q	charge
Qa	anodic charge
Qc	cathodic charge
SCE	saturated calomel electrode
TBAPF ₆	Tetrabutylammonium hexafluorophosphate

THF	tetrahydrofuran
TMS	tetramethylsilane
tpy	2,2':6',2"-terpyridine
VS.	verses
$\mathbf{W}_{1\!\!/_2}$	peak width at half height
ΔE_p	peak-to-peak separation
ε	molar absorbptivity
Φ	quantum yield
λ	wavelength
λ_{em}	emision wavelength
λ_{ex}	excitation wavelength
λ_{max}	maximum wavelength
τ	lifetime
ν	scan rate

CHAPTER 1:

Introduction: Synthesis and Characterization of Two-Electron Platinum Reagents

Introduction. In 1999, the United States was responsible for approximately 25% of worldwide energy usage and CO_2 emissions,¹ yet accounted for less than 5% of the world's population (Figure 1.1). Only 1% of this energy was derived from sunlight, whereas 85% originated from fossil fuels.² As the rest of the world approaches U.S. levels of per capita energy usage, global consumption and accompanying pollution can be expected to increase dramatically. In fact, the U.S. Department of Energy projects a 60% increase by 2020 in annual global energy consumption and CO_2 emissions from the



Figure 1.1. Graphs depicting A) CO₂ production, B) energy consumption, and C) population of the US and the rest of the world in 1999.

1999 levels.³ Not surprisingly, there is widespread agreement that renewable energy sources, including solar energy, will play a significant role in addressing future global energy needs.⁴⁻⁷ One approach is to develop multielectron photocatalysts for the conversion of light energy to chemical energy. The premise is that an excited molecule is both a better oxidant and reductant than the ground-state molecule. Therefore, light can be used to drive outer-sphere electron-transfer reactions. A critical problem is that most reversible outer-sphere redox-active chromophores undergo one-photon/one-electron chemistry, whereas the most attractive target substrates (*e.g.*, H₂O, CO₂) require multiple redox equivalents for activation. For example, the first step in the four electron oxidation of H₂O to form a hydroxyl radical intermediate is strongly disfavored ($E_{ox} = -2.31 V vs$. NHE), however, the overall potential for oxidation of water to dioxygen is considerably more positive ($E_{ox} = -0.815 V vs$. NHE) pH.7:⁸



In addition, two-electron steps are expected to avoid the formation of damaging radicals that can deactivate catalysts.

The preceding thermodynamic and kinetic considerations provide strong motivation for the design of molecules that will release multiple electrons when excited with light. We have proposed a strategy for designing molecules that will undergo photoinduced outersphere two-electron transfer reactions, and this dissertation describe the first steps toward achieving this goal.



Figure 1.2. Minimum energies of the reactants $(D^- + A^+)$, excited donor $(D^{-*} + A^+)$, one-electron intermediate $(D^0 + A^0)$, and two-electron transfer product $(D^+ + A^-)$ expected for a one-photon/two-electron system. Solid arrows show photoexcitation (hv) and forward electron-transfer reactions. Dashed arrows show back electron-transfer reactions

The scheme depicted in Figure 1.2 shows a possible model for photoinduced outer-sphere two-electron transfer. Excitation of a donor molecule (\mathbf{D}^{-}) produces an excited molecule (\mathbf{D}^{*-}) that will transfer one electron to an acceptor (\mathbf{A}^{+}). However in contrast to typical one-photon/one-electron systems, the two-electron transfer product ($\mathbf{D}^{+} + \mathbf{A}^{-}$) is more stable than the one-electron transfer product ($\mathbf{D}^{0} + \mathbf{A}^{0}$), and \mathbf{D}^{0} can transfer a second electron to an acceptor to form a net two-electron product ($\mathbf{D}^{+} + \mathbf{A}^{-}$). This simple model leads to the intriguing prediction that there is a large barrier to the thermal back reaction, $\mathbf{D}^{+} + \mathbf{A}^{-} \rightarrow \mathbf{D}^{-} + \mathbf{A}^{+}$, kinetically stabilizing the two-electron

product. This situation contrasts sharply with traditional outer-sphere one-electron photochemistry, which suffers from energy wasting back electron-transfer reactions. But more importantly, design of such a system would allow for the investigation of the factors governing cooperative two-electron transfer reactions that are critical to chemical catalysis.

From the preceding discussion it is evident that a suitable system for investigation is one that is stable in two oxidation states separated by two charges such that the intermediate state is unstable with respect to the other two states. In order to satisfy this requirement, we have chosen to investigate platinum complexes. These complexes tend to be very efficient at catalyzing organic reactions,^{9,10} and this reactivity can be traced to their tendency to undergo two-electron changes in oxidation state. For example, Pt(II) and Pt(IV) complexes are stable, but monomeric Pt(III) complexes tend to be unstable. The two-electron interconversion between Pt(II) and Pt(IV) typically occurs by inner-sphere mechanisms, namely oxidative addition and reductive elimination reactions, allowing for substrate activation without formation of high-energy, reactive radical intermediates. This behavior suggests that these complexes also could serve as *outer-sphere* cooperative two-electron reagents that are capable of transferring two electrons at the same potential in thermal and photochemical multi-redox catalytic reactions.

A potential drawback to this approach is that the outer-sphere electron-transfer reactions of platinum complexes tend to be slow because of the accompanying large molecular reorganization.¹¹ For example, d⁸ electron Pt(II) complexes favor a four-coordinate square planar geometry, whereas d⁶ electron Pt(IV) complexes favor a six-

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coordinate octahedral geometry. The accompanying ligand association and/or dissociation steps cause these two-electron reactions to be electrochemically irreversible with large overpotentials. This lack of reversibility is a critical problem because it prevents regeneration of the active catalyst and completion of the catalytic cycle. A second concern is the photophysical properties of these complexes. A suitable system must posses a sufficiently long-lived excited state in order to allow for reaction with a substrate. For these reasons, the electrochemical properties and electronic structures of the investigated platinum complexes are a central focus of this dissertation. Chapters 2-6 and 7 describe the synthesis, spectroscopy, and photophysical properties of a series of platinum(II) complexes that are models of two-electron photo-reagents. Chapters 6, 8 and 9 focus on the electrochemical properties of these and related complexes. Chapters 8 and 9 specifically describe the first examples of outer-sphere two-electron platinum reagents.

Electrochemistry of Platinum Complexes. Despite the tendency of platinum complexes to undergo two-electron changes in oxidation state, their electrochemistry is typically irreversible.¹¹ This irreversibility is due to the large molecular reorganization that accompanies two-electron interconversion of square planar Pt(II) and octahedral Pt(IV). However, Hubbard and Anson¹² have shown that the cyclic voltammogram of PtBr₄²⁻ in 1 M NaBr/H₂O exhibits a two-electron platinum oxidation wave at 0.43 V vs SCE. Though the electrochemical oxidation of PtBr₄²⁻ to PtBr₆²⁻ is nearly chemically reversible ($i_{ox}/i_{red}\sim1.25$), the cyclic voltammogram shows a relatively large separation (~130 mV) between the anodic and cathodic peak potentials (ΔE_p), indicating that the redox process is electrochemically irreversible.¹²

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As found for the two-electron oxidation of $PtBr_4^{2-}$, the presence of additional halide ions facilitates two-electron self-exchange between $Pt(en)_2^{2+}$ and $Pt(en)_2Cl_2^{2+}$



Figure 1.3. Proposed intermediate in the self-exchange reaction of $Pt(en)_2^{2+}$ and $Pt(en)_2Cl_2^{2+}$ in the presence of Cl⁻ ions.

(en=1,2-ethylenediamine). In the presence of Cl⁻ ions, this process proceeds by an innersphere pathway that is believed to involve a transition state in which a Cl⁻ from the Pt(IV) complex forms a weak axial interaction with the Pt(II) complex. The other axial site of the Pt(II) complex interacts weakly with a Cl⁻ ion from solution (Figure 1.3). Overall, the reaction can be described as a two-electron transfer from one center to the other mediated by the Cl atom bridge; in that case, a Pt(III) dimer intermediate might be expected. Alternatively, the reaction can be described as a Cl⁺ atom-transfer reaction.¹¹



Figure 1.4. Pt(2,2'-bpy)(mes)₂

If the axial sites of a platinum(II) complex are sterically protected and potential ligands cannot interact with the metal center, then electrochemically reversible oneelectron oxidation is possible. For example, the mesityl groups of Pt(2,2'bipyridine)(mes)₂ (Figure 1.4) effectively block the axial sites of the platinum center, and Kaim and coworkers¹³⁻¹⁶ have observed an electrochemically reversible one-electron platinum-centered oxidation at 0.45 V vs FcH/FcH⁺ (Δ E=60 mV). The methyl groups presumably prevent ligands from binding at the axial sites and stabilizing Pt(IV). In fact a second irreversible platinum-centered oxidation is observed at more positive potentials.¹³⁻¹⁶ In a related study, Usón *et al.*¹⁷⁻¹⁹ synthesized Pt(C₆Cl₅)₄²⁻ (Figure 1.5). This complex undergoes electrochemically reversible (Δ E_p=60 mV) one-electron platinum-centered oxidation at 0.51 V vs SCE.¹⁷ The Pt(III) adduct is both air and moisture stable in solution and the solid state. X-ray crystal structures were obtained for both the Pt(II) and Pt(III) complexes, and both anions showed virtually identical square planar geometries.¹⁸



Figure 1.5. $Pt(C_6Cl_5)_4^{2-}$

The Pt(III) complex was oxidized to Pt(IV) under very oxidizing conditions (e.g., $Cl_2/AlCl_3$), resulting in an effectively six-coordinate octahedral Pt(IV) product, $Pt(C_6Cl_5)_4$.¹⁹ X-ray crystallography revealed a very distorted structure in which the platinum interacts with the *ortho*-Cl atoms of two $C_6Cl_5^-$ groups, resulting in long Pt-Cl distances of ~2.6 Å.¹⁹ The chloro groups are relatively poor ligands, and this presumably accounts for the relative stabilities of the Pt(III) and Pt(IV) oxidation states.

On the other hand, Endicott *et. al.*²⁰ observed a two-electron platinum-centered oxidation of $Pt([14]aneS_4)^{2+}$ (Figure 1.6) in a 0.1 M LiCl solution (80% CH₃CN/20% H₂O). At 0.1 V/s this electrochemically irreversible oxidation process occurs at 0.8 V vs Ag/AgCl, with a peak-to-peak (ΔE_p) separation of 127 mV.²⁰ Evidently the presence of halide ions facilitates the conversion of 4-coordinate Pt(II) to 6-coordinate Pt(IV) by allowing formation of a 5-coordinate Pt(II) adduct prior to electron transfer. The resulting redox unstable Pt(III) complex rapidly transfers a second electron to the electrode or to another Pt(III) center in a disproportionation reaction.



Figure 1.6. Two-electron oxidation of $Pt([14]aneS_4)^{2+}$ to $Pt([14]aneS_4)Cl_2^{2+}$.

The preceding systems suggest that platinum (II) complexes with pendant donor

groups that both block the axial sites and are capable of binding to the metal center should undergo reversible and cooperative two-electron oxidation to Pt(IV). However, complexes investigated by Schröder and Grant,²¹⁻²³ such as Pt([9]aneS₃)₂²⁺ (Figure 1.7), undergo sequential one-electron chemistry. For example the cyclic voltammogram of Pt([9]aneS₃)₂²⁺ exhibits a one-electron wave at 0.46 V vs FcH/FcH⁺ (ΔE_p =145 mV) corresponding to generation of a Pt(III) species.²¹ The X-ray crystal structure of Pt([9]aneS₃)₂²⁺ shows that two S atoms from each ligand are bonded to the metal center in a square planar arrangement with long interactions between the Pt and remaining two S



Figure 1.7. $Pt([9]aneS_3)_2^{2+}$

atoms (3.233 Å).²² In analogy to the $Pt(C_6Cl_5)_4^{2-}$ system, it is possible that the soft S atoms are poor ligands for stabilizing a hard Pt(IV) center, accounting for the Pt(III)/Pt(IV) couple being shifted to much higher potentials than the Pt(II)/Pt(III) couple. Thus, these observations have suggested to us that it is important to consider the hard/soft properties of the pendant donor groups that are capable of binding to the metal center. In a related study, Sargeson and co-workers²⁴ have stabilized a Pt(IV) center using the hard nitrogen-donor groups of a sepulchrate ligand (Figure 1.8). Though it seems conceivable that this ligand could stabilize Pt(II), Pt(III) and Pt(IV), the platinum(IV) complex undergoes two sequential and irreversible one-electron reductions in acetone. The irreversibility apparently results from ligand decomposition.²⁴



Figure 1.8. Pt(1,3,6,8,10,13,16,19-Octaazabicycloo[6.6.6]icosane)⁴⁺: a platinum(IV) sepulchrate complex.

Strategy. The preceding discussion leads us to the conclusion that electronic and steric properties, as well as conformational flexibility, influence the relative stabilities of Pt(II), Pt(III) and Pt(IV) oxidation states and the kinetics of their interconversion. Because reorganization energies for two-electron processes are expected to be large, the ligands bonded to the metal center must be sufficiently flexible in order to accommodate both the octahedral coordination geometry of the d⁶ Pt(IV) configuration as well as the square planar geometry of the d⁸ Pt(II) configuration. Our approach is to bind two *mer*-coordinating potentially tridentate ligands around a platinum center (Figure 1.9). These

ligands are capable of stabilizing both the square planar geometry of d⁸ Pt(II) complexes and the octahedral geometry of d⁶ Pt(IV) complexes. In the octahedral Pt(IV) complexes, both ligands are tridentate occupying all six binding sites around the metal center. In the square planar Pt(II) case, one ligand will remain tridentate, while the other coordinates in a monodentate fashion through the central binding site. Thus, these systems are engineered to eliminate complications that arise due to ligand association and dissociation and can interconvert by simply transferring two electrons. By varying the properties of the ligands we can optimize the properties of these complexes and fully probe the factors governing cooperative outersphere two-electron transfer reactions.



Figure 1.9. Schematic representation of a reversible two-electron platinum reagent.

In order to overcome problems associated with previously investigated systems, we have focused our efforts on the following *mer*-coordinating potentially tridentate ligands: pip₂NCN⁻, tpy, phtpy, and phbpy (Figure 1.10). The first ligand in this series, pip₂NCN⁻, can act as the pivot ligand, interconverting between monodentate and tridentate coordination geometries (Figure 1.9). Moreover, van Koten and coworkers²⁵⁻³² have previously shown that this type of ligand is capable of stabilizing both Pt(II) and Pt(IV) oxidation states. The remaining three ligands are known to bind to Pt(II) to produce luminescent complexes.³³⁻³⁸ Thus these ligands are expected to impart desirable photophysical properties to our two-electron reagents. Chapters 2-7 of this dissertation describe the development of platinum chemistry with these ligands, emphasizing the novel pip₂NCN⁻ ligand. Chapters 8 and 9 describe the first examples of platinum complexes that undergo reversible outer-sphere two-electron transfer.





Chapter 2 describes a series of square planar Pt(II) complexes with the *mer*coordinating tridentate ligand, pip₂NCN⁻ (pip₂NCNH = 1,3-*bis*(piperdylmethyl)benzene). The X-ray crystal structures of pip₂NCNBr, $Pt(pip_2NCN)Cl$ and $[Pt(pip_2NCN)(CH_3N=C(CH_3)_2)][CF_3SO_3]$ are reported. The colorless metal complexes exhibit weak red-orange to red emissions originating from a lowest spin-forbidden ligand field excited state.

Chapter 3 describes how the energies of the lowest excited states of Pt(pip₂NCN)(pyridyl)⁺ complexes can be tuned by varying the properties of the pyridyl

ligand. The X-ray crystal structures of salts of Pt(pip₂NCN)(pyridine)⁺, Pt(pip₂NCN)(4phenylpyridine)⁺, Pt(pip₂NCN)(pyridine-2,6-dimethanol)⁺, and [(Pt(pip₂NCN))₂(μ -4,4'bipyridine)]²⁺ are reported. Red emission from Pt(pip₂NCN)(pyridine)⁺ in rigid media originates from a lowest triplet ligand field excited state, whereas yellow-green emissions from Pt(pip₂NCN)(4-phenylpyridine)⁺ and [(Pt(pip₂NCN))₂(μ -bipyridine)]²⁺ originate from a lowest pyridyl ligand-centered triplet π - π * state. These data indicate that substitution of the pyridyl ligand results in a dramatic change in the orbital character of the emissive state.

Chapter 4 describes the synthesis and characterization of a series of $(Pt(pip_2NCN))_2(\mu-L)^{2+}$ dimers bridged by a series of nitrogen-donor ligands (L=pyrazine (pyz), *trans*-1,2-bis(4-pyridyl)ethylene (bpe), 1,2-bis(4-pyridyl)ethane (bpa), or 4,4'-bipyridine (bpy)). The X-ray crystal structures of salts of $(Pt(pip_2NCN))_2(\mu-pyz)^{2+}$ and $(Pt(pip_2NCN))_2(\mu-bpe)^{2+}$ are reported. The bpa dimer exhibits a broad, low energy emission from a lowest ³LF excited state. The bpe and bpy dimers exhibit structured emission from a lowest ³ π - π * excited state, and the pyz dimer exhibits intense emission tentatively assigned to a lowest triplet metal-to-ligand charge transfer excited state.

Chapter 5 describes the synthesis of a series of platinum(II)-terpyridyl complexes with aryl ligands (phenyl (Ph), dimethylphenyl (dmph), and mesityl(mes)). The X-ray crystal structures of salts of Pt(phtpy)(Ph)⁺, Pt(tpy)(3,5-dmph)⁺, Pt(tpy)(mes)⁺ and Pt(phtpy)(mes)⁺ are reported. The electrochemical properties of these complexes are described in Chapter 6. A series of cyclic and differential pulse voltammograms were recorded at room temperature, 0° and -40°C, and the complexes were found to undergo two one-electron reductions. In all cases the second reduction process is

electrochemically reversible. However, the first reduction only appears as an electrochemically reversible wave for complexes with an axially protected metal center (*e.g.*, Pt(tpy)(mes)⁺). The accumulated data are consistent with stacking of the planar complexes to form dimers that reduce at different potentials than the monomers and cause the first reduction process to appear irreversible. Protection of the axial sites of the metal center appears to interfere with dimerization. The spectroscopic and photophysical properties of this series of complexes are described in Chapter 7. Emission measurements confirm that steric effects can be utilized to control intermolecular metal…metal and ligand…ligand stacking interactions in 77 K frozen solutions of these complexes.

Chapter 8 describes the synthesis and characterization of first examples of platinum complexes that undergo reversible and cooperative thermal two-electron transfer, [Pt(tpy)(pip₂NCN)](BF₄) and [Pt(phtpy)(pip₂NCN)](BF₄). The cyclic voltammograms of these complexes in acetonitrile solution (0.1 M TBAPF₆, 0.25 V/s) each exhibit two reversible one-electron reduction processes and a nearly reversible twoelectron oxidation process at ~0.40 V vs Ag/AgCl.

Chapter 9 discusses the mechanism of the reversible two-electron oxidation process observed for [Pt(tpy)(pip₂NCN)](BF₄). A series of model complexes are reported, and electrochemical studies establish that both potentially tridentate ligands are required for reversible two-electron oxidation (Figure 1.9). A detailed analysis leads to the suggestion that the ligands are preorganized around the platinum(II) center to give a 5- or 6-coordinate electrochemically active species.

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CHAPTER 2:

Synthesis, Structures and Emissive Properties of Platinum(II) Complexes with a Cyclometallating Aryldiamine Ligand.[†]

Introduction

There is growing interest in the spectroscopy and photochemistry of square planar platinum(II) complexes with *mer*-coordinating tridentate ligands.²⁻⁴ In these systems, the fourth coordination site on the metal center is available for substrate binding. In addition, the tendency of platinum complexes to undergo two-electron processes suggests the intriguing possibility of single-photon, multielectron photocatalysis. Thus far, researchers have focused primarily on platinum(II) terpyridyl systems, such as Pt(tpy)L⁺ (tpy = 2,2':6',2"-terpyridine; L= Cl, Me, Ph).^{3,4} In rigid media, these compounds often exhibit long-lived emission originating from metal-to-ligand charge transfer (MLCT) or terpyridyl ligand-localized π - π * excited states. Currently we are examining the spectroscopy of related platinum(II) complexes with the goal of learning to tune their electronic structures and control



[†] Most of the contents of Chapter 2 have appeared in a manuscript in *Inorganic Chemistry*.¹

their photochemical properties. The present investigation was inspired by the studies of van Koten and coworkers⁵⁻⁹ which detail the rich thermal chemistry of complexes with cyclometallating aryldiamine ligands, such as the 2,6bis(dimethylaminomethyl)phenyl anion (Me₄NCN⁻).

In this chapter, we report the synthesis and characterization of a new series of Pt(II) complexes based on the pip_2NCN^- ligand¹⁰ with the general formula Pt(pip_2NCN)L. The influence of the monodentate (L = imine, Cl⁻, Br⁻, I⁻) and tridentate (pip_2NCN^-) ligands on the electronic structures of these complexes is discussed.

Experimental

K₂PtCl₄ was obtained from Pressure Chemical Company (Pittsburg, PA). 2,2'-azobisisobutyronitrile (AIBN), 2-bromo-*m*-xylene, 1,5-cyclooctadiene, and methyl sulfide were obtained from Aldrich Chemical Company (Milwaukee, WI). All other reagents were obtained from Acros (Pittsburg, PA). Tetrahydrofuran (THF) was distilled from Na(s)/benzophenone, and ethanol was distilled from zinc metal/potassium hydroxide. All other chemicals were used as received. Syntheses involving amines were carried out under an argon atmosphere using standard Schlenk techniques. Argon was pre-dried using activated sieves and trace oxygen was removed with activated R3-11 catalyst from Schweizerhall (New Jersey). Chromatography was carried out using a Biotage flash40i system with pre-packed silica cartridges.

¹H NMR spectra were recorded at room temperature using a Bruker AC 250 MHz instrument. Deuterated solvents, CDCl₃ (0.03 % tetramethylsilane (TMS)

(v/v)), were purchased from Cambridge Isotope Laboratories (Andover, MA). Proton resonances were assigned with the aid of decoupling experiments. Cyclic voltammetery was carried out using a standard three-electrode cell and a CV50w potentiostat from Bioanalytical Systems (West Lafayette, IN). Scans were collected in methylene chloride solution containing 0.1 M TBAPF₆. All scans were recorded using a platinum wire auxiliary electrode, a Ag/AgCl (3.0 M NaCl), reference electrode and a 0.79 mm² gold working electrode. Between scans, the working electrode was polished with 0.05 μ m alumina, rinsed with distilled water and wiped dry using a Kimwipe. Reported potentials are referenced against Ag/AgCl. Peak currents (*i*_p) were estimated with respect to the extrapolated baseline current as described elsewhere.¹¹ Under these conditions, the ferrocene/ferrocenium (FcH/FcH⁺) couple occurs at 0.45 V.

UV-visible absorption spectra were recorded using a single-beam Cary-14 spectrophotometer equipped with computer control by OLIS. Emission spectra were recorded with a SPEX Fluorolog-3 fluorimeter equipped with a double emission monochromator (305, 320 and 385 nm cut-off filters) and a single excitation monochromator. 77 K glassy solutions were prepared by inserting a quartz EPR tube containing a 3:1 EtOH:MeOH solution of the complex into a quartz-tipped finger dewar. Emission spectra were corrected for instrumental response. Emission samples for lifetime measurements at 77 K were excited using the third harmonic (355 nm) of a Continuum Surelite Nd:YAG with 4-6 ns pulse widths. Emission transients were detected using a modified PMT connected to a Tektronix TDS580D oscilloscope and modeled using in-house software on a Microsoft Excel platform.

Under these conditions, the emission decay of $[Ru(bpy)_3]Cl_2$ in a 4:1 EtOH:MeOH 77 K glassy solution was single exponential corresponding to a 5.1 µs lifetime, as expected.¹²

PtCl₂(SMe₂)₂: The complex was prepared according to the procedure of Asselt and coworkers.¹³ The isolated product was a mixture of *cis* and *trans* isomers. A sample of K₂PtCl₄ (5.0 g, 12.05 mmol) was dissolved in 100 ml of distilled H₂O. The solution was bubbled degassed with argon for ten minutes, and SMe₂ (2.75 ml, 12.05 mmol) was added to the red solution. The solution was stirred at 80 °C for 45 minutes. The yellow suspension was cooled to room temperature, and extracted with CH₂Cl₂ (3 x 75 ml). The combined CH₂Cl₂ layers (bottom) were dried over anhydrous magnesium sulfate, filtered, and rotary-evaporated to dryness. The yellow solid was collected. Yield: 4.5 g, 96%. ¹H NMR (CDCl₃, δ): 1.46 (2.39-2.68, two singlets with ¹⁹⁵Pt satellites).

Pt(COD)Cl₂. The complex was prepared according to the procedure of McDermott and coworkers.¹⁴ A sample of K₂PtCl₄ (20.0 g, 0.048 mol) was dissolved in 320 ml of distilled H₂O. The red solution was bubbled degassed with argon for ten minutes, and glacial acetic acid (480 ml) and COD (20 ml, 0.176 mmol) were added to the solution. The solution was stirred at 80°C for 1.5 hrs. The volume was reduced to ~100 ml by rotoary-evaporation, and a yellow solid was collected by vacuum filtration. The yellow impurities were removed by washing the solid with 200 ml of H₂O, EtOH and Et₂O. The white crystalline solid was dried under vacuum. Yield: 17.3 g, 96%. ¹H NMR (CDCl₃, δ): 2.16-2.38 (4H, m, CH₂), 2.69-2.74 (4H, m, CH₂), 5.62 (4H, s (with Pt satellites, J_{H-Pt} = 67 Hz), CH).

Pt(COD)I₂. The complex was prepared according to the procedure of Clark and coworkers.¹⁵ A sample of Pt(COD)Cl₂ (0.876 g, 2.29 mmol) was dissolved in 100 ml acetone, and a large excess NaI was added to the solution. The color of the mixture immediately turned yellow. After stirring for 1 hour, the solvent was removed by rotary-evaporation. The solid was treated with CH₂Cl₂ (3 x 50 ml) and water (100 ml). The organic layers (bottom) were collected, dried over anhydrous MgSO₄, filtered, and roto-evaporated to dryness to give a yellow solid. Yield 1.275 g, 97.8%. ¹H NMR ((CD₃)₂SO, δ): 1.83-2.34 (8H, m, CH₂), 5.68 (4H, s (with Pt satellites, J_{H-Pt} = 67 Hz), CH).

2,6-(CH₂Br)₂C₆H₃Br. The synthesis of this compound was originally reported by Kiyooka and coworkers.¹⁶ **Caution: The reaction produces a strong lachrymator, to which some people are highly allergic**. The *m*-bromoxylene (25 g, 0.135 mol) was dissolved in CCl₄ (250 ml). *N*-bromosuccinimide (NBS, 60 g, 0.338 mol) and azobisisobutyronitrile (AIBN, ~25 mg) were added, and the mixture was allowed to reflux for 72 hours. Additional aliquots of AIBN (~25 mg) were added to the reaction mixture at 24 hours intervals. The mixture was allowed to cool to room temperature and filtered. The solvent was removed by rotary-evaporation to give a red-orange oil. After dissolution in 200 ml of CH₂Cl₂, 50 ml of hexanes were added and the solution was cooled to -25° C to induce precipitation. The off-white crystals were collected by vacuum filtration. Repeating the CH2Cl2/hexanes steps, over a period of several days, resulted in multiple crops of the product being collected. ¹H NMR (CDCl₃, δ): 4.62 (4H, s, benzylic CH₂), 7.27 (1H, t, CH), and 7.39 (2H, d, CH).

pip₂NCNBr (1). The synthesis of this compound was originally reported by Schimmelpfennig and coworkers.¹⁰ A mixture of bis(bromomethyl)bromobenzene (10 g, 29 mmol) and piperdine (29 mL, 293 mmol) in 300 mL of benzene was refluxed for 48 hours. The white solid [C₃H₁₀NH₂]Br was removed by filtration and discarded. The solvent was removed by rotary-evaporation, leaving an orange oil. The oil was dissolved in CH₂Cl₂ and layered with hexanes. The volume was reduced by rotary-evaporation until solid began to form, and the flask was cooled to -25° C to induce crystallization. The resulting off-white crystals were collected, washed with hexanes and dried in vacuo. Multiple crops were collected, and crystallization sometimes took several weeks. Yield 5.4 g, 53%. Anal. Calcd. for C₁₈H₂₇N₂Br: C, 61.57; H, 7.75; N, 7.98. Found: C, 61.36; H, 7.66; N, 8.00. ¹H NMR (CDCl₃, *δ*): 1.46 (4H, d, CH₂), 1.58-1.64 (8H, m, CH₂), 2.47 (8H, d, CH₂), 3.57 (4H, s, benzylic CH₂), 7.24 (2H, d, CH), and 7.39 (1H, t, CH). UV-vis: (MeOH) λ_{max}, nm (ε,cm⁻¹M⁻¹): 265 (<330), 285 (<40).

pip₂**NCNH.** All glassware and compounds were rigorously dried prior to use because this reaction was found to be extremely sensitive to moisture. Under an Ar(g) atmosphere, 0.184 mL (0.29 mmol) of *N*-butyllithium solution (1.6 M in hexanes) was added to a stirred solution of **1** (0.10 g, 3.1 mmol) in 20 mL of THF at -70° C. The solution was stirred for 30 minutes, and then warmed to room temperature. Methanol (10 ml) was added to quench the reaction, and the solution was rotary-evaporated to dryness. The solid was treated with CH_2Cl_2 (3 x 10 ml) and water (20 ml). The organic layers (bottom) were collected and dried over anhydrous MgSO₄, filtered and rotary-evaporated to dryness. ¹H NMR (CDCl₃, δ): 1.4-1.45

(4H, m, CH₂), 1.52-1.62 (8H, m, CH₂), 2.37 (8H, m, CH₂), 3.46 (4H, s, benzylic CH₂), 7.17-7.26 (4H, m, CH).

Pt(pip₂NCN)Cl (2). All glassware and compounds were rigorously dried prior to use because this reaction was found to be extremely sensitive to moisture. Under an Ar(g) atmosphere, 1.92 mL (3.1 mmol) of N-butyllithium solution (1.6 M in hexanes) was added to a stirred solution of 1 (1.08 g, 3.1 mmol) in 50 mL of THF at -70° C. The solution of lithiated ligand was cannula transferred to a mixture of PtCl₂(SMe₂)₂ (1.0 g, 2.6 mmol) in 50 mL THF. After 18 hours, excess NaCl (> 10 equivalents) was added and the dark brown mixture was stirred for an additional 2 hours. The solvent was removed by rotary-evaporation leaving a dark brown solid. The solid was washed with water, and the dark brown impure product was extracted with CH_2Cl_2 (3 x 50 mL). Purification by flash chromatography (silica, CH_2Cl_2) afforded the product as a white solid. Yield 0.55 g, 43 %. Anal. Calcd. for C₁₈H₂₇N₂ClPt: C, 43.08; H, 5.42; N, 5.58. Found: C, 42.98; H, 5.44; N, 5.43. ¹H NMR (CDCl₃, *d*): 1.43 (4H, m, CH₂), 1.54-1.79 (8H, m, CH₂), 3.25 (4H, m, CH₂), 3.95 (4H, m, CH₂), 4.25 (4H, s with Pt satellites, J_{H-Pt} =47 Hz, benzylic CH₂), 6.80 (2H, d, CH), and 6.98 (1H, t, CH). In chapter 3 we report a higher yielding procedure for preparing this product.

[Pt(pip₂NCN)(H₂O)](CF₃SO₃). A mixture of silver triflate (0.0514 g, 0.199 mmol) and **2** (0.100 g, 0.199 mmol) in 15 mL of acetone was stirred for 20 minutes at room temperature. The resulting AgCl precipitate was removed by filtration through celite. The solution was rotary-evaporated to dryness and washed with ether. ¹H NMR (CD₃CN, δ): 1.4-1.85 (12H, m, CH₂), 3.14-3.37 (4H, m, CH₂), 3.39-3.48 (4H,

m, CH₂), 4.35 (4H, s with Pt satellites, $J_{\text{H-Pt}}$ =51 Hz, benzylic CH₂), 6.83 (2H, d, CH), and 7.01 (1H, t, CH).

Pt(pip₂NCN)Br (3). The metathesis was accomplished by stirring 0.200 mg (0.399 mmol) of **2** in 25 mL of acetone with excess KBr for 1 hour. After removal of the solvent, the white solid was washed with H₂O, hexanes and ether. Anal. Calcd. for C₁₈H₂₇N₂BrPt: C, 39.56; H, 4.98; N, 5.13. Found: C, 39.33; H, 4.86; N, 5.14. ¹H NMR (CDCl₃, δ): 1.38 (4H, m, CH₂), 1.59-1.79 (8H, m, CH₂), 3.26 (4H, dd, CH₂), 4.06 (4H, dd, CH₂), 4.25 (4H, s with Pt satellites, *J*_{H-Pt}=47 Hz, benzylic CH₂), 6.80 (2H, d, CH), and 6.99 (1H, t, CH).

Pt(pip₂NCN)I (4). Method A. The metathesis was accomplished by stirring 0.100 g (0.200 mmol) of 2 in 25 mL acetone with excess NaI(aq) for 3 hours. After removal of solvent, the residue was treated with CH_2Cl_2 (50 mL) and water (50 mL). The organic layer was dried over MgSO₄ and evaporated to dryness to give a very pale yellow solid. Yield 0.104 g, 92 %.

Method B. All glassware and reagents were rigorously dried prior to use because this reaction was found to be extremely sensitive to moisture. Under an Ar(g) atmosphere, 674 μ l (0.90 mmol) of *N*-butyllithium solution (1.6 M in hexane) was added to a stirred solution of **1** (0.38 g, 0.90 mmol) in 25 mL of THF at -70° C. The solution of lithiated ligand was cannula transferred to a mixture of Pt(COD)I₂ (0.50 g, 0.90 mmol) in 50 mL THF at -70° C. The solvent was removed by rotaryevaporation leaving a dark yellow residue. After dissolving the residue in CH₂Cl₂, hexanes were added, and the mixture was filtered. The yellow filtrate was evaporated to dryness, and hexanes were added to the yellow powder. The mixture was filtered

and the solid washed with hexanes until the product was nearly colorless. Yield 0.30 g, 56 %. Anal. Calcd. for $C_{18}H_{27}N_2IPt$: C, 36.43; H, 4.59; N, 4.72. Found: C, 36.49; H, 4.70; N, 4.57. ¹H NMR (CDCl₃, δ): 1.32 (4H, m, CH₂), 1.46-1.85 (8H, m, CH₂), 3.25 (4H, m, CH₂), 4.25 (8H, m, aliphatic CH₂, benzylic CH₂), 6.81 (2H, d, CH), and 7.02 (1H, t, CH).

[Pt(pip₂NCN)(CH₃N=C(CH₃)₂)](CF₃SO₃) (5). A mixture of silver triflate (0.0514 g, 0.199 mmol) and 2 (0.100 g, 0.199 mmol) in 15 mL of acetone was stirred for 20 minutes at room temperature. The resulting AgCl precipitate was removed by filtration through celite. After addition of excess methylamine (approx. 0.3 mL of 40% aqueous solution), the filtrate was stirred for one hour. The solvent was removed, and the off-white solid was dissolved in CH₂Cl₂ and filtered. The filtrate was rotary-evaporated to dryness and product was collected. Yield 0.106 g, 79 %. Anal. Calcd. for [C₂₂H₃₆N₃Pt](CF₃SO₃) • H₂O: C, 39.20; H, 5.44; N, 5.96. Found: C, 39.24; H, 5.16; N, 6.10. ¹H NMR (CDCl₃, δ): 1.44-1.79 (10H, m, CH₂), 2.33 (3H, s, CH₃), 2.85 (3H, s, CH₃), 3.10-3.34 (8H, m, CH₂), 3.64 (3H, s, CH₃), 4.35 (4H, s with Pt satellites, *J*_{H-Pt}=55 Hz, benzylic CH₂), 6.89 (2H, d, CH), and 7.03 (1H, t, CH).

X-ray Crystallography: Colorless plates of pip₂NCNBr were obtained by slow evaporation of a CH₂Cl₂/hexanes solution. Colorless plates of Pt(pip₂NCN)Cl were similarly obtained. Diffraction data for crystals of pip₂NCNBr (1) and Pt(pip₂NCN)Cl (2) were collected at room temperature using a Siemens P3/PC diffractometer (Mo K α radiation and graphite monochromater, $\lambda = 0.71073$ Å).

	$C_{18}H_{27}BrN_2(1)$	C ₁₈ H ₂₇ ClN ₂ Pt (2)	$[C_{22}H_{36}N_3Pt)](CF_3SO_3)$ (5)
fw, g/mol	351.33	501.96	686.70
Space group	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$
<i>a</i> , Å	10.081(1)	9.897(2)	10.709(2)
b, Å	10.153(2)	10.191(2)	11.2321(10)
<i>c</i> , Å	10.390(1)	19.174(4)	12.447(2)
lpha, °	66.05(1)	75.09(3)	110.509(8)
<i>β</i> , °	79.07(1)	76.14(3)	112.417(10)
γ, °	64.51(1)	71.00(3)	91.066(9)
V, Å ³	877.1(2)	1741.2(6)	1276.1(3)
Ζ	2	4	2
<i>T</i> , K	295(2)	298(2)	150(2)
Reflns collected	4227	8506	13454
Ind reflns	3998	8039	6136
R _{int}	0.0179	0.0168	0.0244
GOF on F^2	1.054	1.061	1.099
$R_1/wR_2 \left[I \ge 2\sigma(I)\right]^a$	0.0400/0.0797	0.0275/0.0566	0.0314/0.0723
R_1/wR_2 (all data) ^a	0.0792/0.0935	0.0451/0.0630	0.0387/0.0761

Table 2.1. Crystallographic Data for Compounds 1, 2 and 5.

^a $R_1 \Sigma || F_o |$ - $|F_c || \Sigma |F_o |$, $wR_2 = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2]^{\frac{1}{2}}$.

Intensities were corrected for Lorentz, polarization and absorption effects (empirical ψ -scans). A decay correction was applied to the data based on three standard reflections monitored every 300 reflections. Colorless irregular chunks of [Pt(pip_2NCN)(CH_3N=C(CH_3)_2)](CF_3SO_3) (5) were grown by slow evaporation of a CH_2Cl_2 solution. Diffraction data were collected at 150 K using a Siemens SMART 1K CCD diffractometer (Mo K α radiation and graphite monochromater, $\lambda = 0.71073$ Å). Data frames were processed using the Siemens SAINT program.¹⁷ Intensities

were corrected for Lorentz, polarization and decay effects. Absorption and beam corrections based on the multi-scan technique were applied using SADABS.¹⁸ The structures were solved using SHELXTL v5.03¹⁹ and refined by full-matrix least squares on F^2 . For all compounds non-hydrogen atoms were located directly by successive Fourier calculations and refined anisotropically. Ligand H atoms were either found directly or calculated based on geometric criteria and allowed to ride on their respective atoms. The isotropic displacement parameters for the H atoms were defined as a times U_{eq} of the adjacent atom where a = 1.5 for -CH₃ and 1.2 for all others. In the case of 5, the imine moiety is disordered over two conformations. The refined occupancies of N3 and C19 in the major conformer are 67 and 64 %, respectively. One of the piperidyl rings in complex 5 also is disordered as indicated by the enlarged anisotropic displacement parameters, however a chemically reasonable disorder model was not obtained. The final difference Fourier map showed highest residual electron density peaks within 1 Å of the Pt atom, or near the disordered piperidyl ring. Crystallographic data are summarized in Table 2.1.

Results and Discussion

Synthesis. The synthesis of 2,6-(CH₂Br)₂C₆H₃Br was originally reported by Kiyooka and coworkers.¹⁶ Caution: The reaction produces a strong lachrymator, to which some people are highly allergic. This reaction was followed by GCMS, and the reaction was stopped when the product $(2,6-(CH_2Br)_2C_6H_3; m/z = 343 \text{ g})$ was the major product. Impurities observed for this reaction were never collected, but included $((CH_2Br)(CH_3)C_6H_3Br; m/z = 263)$ where bromination of only one CH₃ group occurred, and a species with a m/z = 422 consistent with an extra Br atom.

Procedures for synthesizing the pip₂NCNBr ligand precursor and the complexes were adapted from those developed by van Koten and co-workers²⁰ for related compounds. A solution of 2,6-(CH₂Br)₂C₆H₃ was refluxed with excess piperdine, to give the product and the bromide salt of protonated piperdine, which is only slightly soluble in CH₂Cl₂. After dissolving the crude product in CH₂Cl₂, the majority of the piperidyl salt was removed by vacuum filtration, and the product was precipitated by adding hexanes and cooling to -25° C. However due to the slight solubility of the piperidyl salt, the first crop usually contained some [C₅H₁₀NH]Br. Subsequent crops yielded off-white crystals of the product. Various platinum starting materials were prepared according to literature procedure,¹³⁻¹⁵ resulting in microcrystalline products in high yields (>95%)

The synthesis of complexes **2**, **3**, **4**, and **5** is shown in Scheme 2.1. The colorless complexes were characterized by ¹H NMR spectroscopy and elemental analysis. Reaction of the ligand precursor (**1**) with *N*-butyllithium and the appropriate platinum starting material ($PtCl_2(SMe_2)_2$ or $Pt(COD)I_2$) afforded complexes **2** and **4**. These reactions are extremely moisture sensitive and care must be taken to exclude water. A major side product is the protonated ligand, pip₂NCNH.

Substitution of the chloride in complex 2 with other ligands (bromide, iodide or imine) is straightforward. The bromide (3) and iodide (4) complexes were prepared in nearly quantitative yields by the metathesis reaction of 2 with the appropriate sodium halide in acetone. It is worth noting that we were unable to synthesize 2 by metathesis of 4 using excess NaCl in acetone. A second strategy for



(*i*) THF, BuLi, -70° C; Pt(SMe₂)₂Cl₂, 20° C; (*ii*) THF, BuLi, -70° C; Pt(COD)I₂, 20° C; (*iii*) excess NaBr, acetone, 20° C; (*iv*) AgCF₃SO₃, acetone; NH₂CH₃(aq), 20° C.

Scheme 2.1: Synthesis of 2-5.

replacing the chloride ligand in **2** is to react a solution of the complex with a silver salt (*e.g.*, AgCF₃SO₃). After removal of the silver chloride by filtration, the appropriate ligand is added to the filtrate.²¹ When acetone was used as the solvent and methylamine was added to the filtrate, the N-bound Schiff-base adduct, **5**, was isolated in high yield. Kozelka and Bois²² have previously suggested that a platinum(II) center can activate a coordinated acetone ligand toward condensation with primary amines, and a similar reaction is believed to occur during formation of

5. While platinum complexes with aryl-substituted imines are well known,²³ to our knowledge, this is the first example of a platinum complex with a *N*-isopropylidenemethylamine ligand. Complex **5** is an off-white solid, which slowly turns dark brown/black over a period of several weeks.

Crystal Structures. The structures of compounds **1**, **2** and **5** were confirmed by single-crystal X-ray diffraction. ORTEP diagrams are shown in Figures 2.1, 2.2 and 2.3, and relevant data are summarized in Tables 2.1 and 2.2. Complex **2** crystallizes with two unique molecules, **A** and **B**, in the asymmetric unit cell. In the structure of **5**, N3 and C19 of the *N*- isopropylidenemethylamine ligand are disordered and refined to give an approximately 65% population for the major conformer.



Figure 2.1. ORTEP diagrams of pip₂NCNBr with 50% probability ellipsoids. H-atoms omitted for clarity.



Figure 2.2. ORTEP diagrams of Pt(pip₂NCN)Cl with 50% probability ellipsoids. H-atoms omitted for clarity.



Figure 2.3. ORTEP diagrams of Pt(pip₂NCN)(CH₃N=C(CH₃)₂)⁺ with 50% probability ellipsoids. Anion and H-atoms omitted for clarity. N3 and C19 of the *N*-isopropylidenemethylamine ligand are disordered and refined to give an approximately 65% population for the major conformer.

In the crystal structure of the ligand precursor **1**, the piperidyl rings adopt a chair conformation and are rotated away from the bulky Br substituent on the aromatic ring (Figure 2.1). In the structures of complexes **2** (Figure 2.2) and **5** (Figure 2.3), each piperidyl ring remains in a chair conformation, however, the N atoms are bonded to the metal center, effectively making the Pt atom an equatorial substituent on each piperidyl ring. Thus, the piperidyl rings are splayed away from the monodentate ligand (Cl⁻ or *N*-isopropylidenemethylamine) and do not appear to interfere with its binding to Pt. Despite the presence of the bulky piperidyl rings, the approximately square planar coordination geometries of the resulting complexes are very similar to those of related complexes with NCN⁻ ligand systems.^{7,24-30}

The Pt-C distances for **2** (1.910(4), 1.899(5) Å) are slightly shorter than for **5** (1.919(5) Å) as expected from the relative *trans* influence of Cl⁻ and imine. These relatively short Pt-C distances are typical of complexes with the related Me₄NCN⁻ tridentate ligand: [Pt(Me₄NCN)(H₂O)](CF₃SO₃) (1.903(2) Å),³⁰ Pt(Me₄NCN)Br (1.90(1) Å),²⁵ and Pt(Me₄NCN)I (1.933(6) Å).²⁴ The Pt-Cl distances of 2.432(1) and 2.420(2) Å for **2** fall within the 2.43 to 2.41 Å range observed for related chloride substituted complexes.²⁷⁻²⁹ Similarly, the Pt-N(piperidyl) distances for **2** (2.115(4), 2.099(3), 2.101(4), and 2.094(3) Å) and **5** (2.108(3) and 2.104(3) Å) are as expected for complexes with this type of chelating ligand.^{24-27,29} For both complexes, the N(piperidyl)-Pt-N(piperidyl) angles (**2**, 164.29(13), 164.75(14); **5**, 163.21(14)°) substantially deviate from ideal *trans*-coordination. The deviation of this bond angle from 180° in related complexes has been attributed to the geometric preferences of the two five-membered chelate rings.^{29,30} For both **2** and **5**, these five-membered

Pt(pip ₂ NCN)Cl (2)	$[C_{22}H_{36}N_3Pt)][CF_3SO_3]$ (5)
1.910(4), 1.899(5)	1.919(5)
2.115(4), 2.099(3)	2.108(3)
2.101(4), 2.094(3)	2.104(3)
2.432(1), 2.420(2)	2.191(9), 2.150(14)
1.523(5), 1.511(6)	1.526(5)
1.523(5), 1.528(5)	1.509(6)
1.512(6), 1.505(6)	1.506(6)
1.484(6), 1.512(6)	1.527(8)
82.3(2), 82.5(2)	82.0 (2)
82.0(2), 82.4(2)	81.4 (2)
177.50(13), 178.76(14)	175.4(5), 164.5(10)
164.29(13), 164.75(14)	163.21(14)
108.1(3), 107.1(2)	107.5(2)
106.5(3), 107.5(2)	105.7(3)
109.4(4), 110.4(4)	109.2(3)
110.2(4), 110.4(3)	108.6(4)
99.13(10), 96.53(10),	98.3(2), 98.6(3)
97.82(11), 97.36(11)	98.4(2), 96.8(3)
	Pt(pip ₂ NCN)Cl (2) 1.910(4), 1.899(5) 2.115(4), 2.099(3) 2.101(4), 2.094(3) 2.432(1), 2.420(2) 1.523(5), 1.511(6) 1.523(5), 1.528(5) 1.512(6), 1.505(6) 1.484(6), 1.512(6) 82.3(2), 82.5(2) 82.0(2), 82.4(2) 177.50(13), 178.76(14) 164.29(13), 164.75(14) 108.1(3), 107.1(2) 106.5(3), 107.5(2) 109.4(4), 110.4(4) 110.2(4), 110.4(3) 99.13(10), 96.53(10), 97.82(11), 97.36(11)

Table 2.2. Selected distances (Å) and angles (°) for compounds 2 and 5.

^a L = Cl for **2**; L = N(3) and N(3') (disordered imine) for **5**.

rings are slightly puckered, resulting in displacement of the benzylic carbons above and below (**2A**: C7/C13 = 0.49/0.58 Å; **2B**: C7/C13 = 0.53/0.52 Å; **5**, C7 = 0.54, C13 = 0.73 Å) the platinum coordination plane (defined by the four atoms directly bonded to Pt). To accommodate this puckering, the planar phenyl ring is rotated slightly about the Pt-C bond, forming dihedral angles of approximately 10° (**2**, 10.3, 9.2; **5**, 11.4° for major; 16.2° for minor conformer) with the Pt coordination plane. These twist angles are somewhat smaller than the 12.3° to 13.7° angles observed for structures of other platinum complexes with related NCN⁻ ligands,^{7,25-32} except Pt(Me₄NCN)I which exhibits a dihedral angle of 9.5°.²⁴

In crystals of **5**, the planar imine ligand lies nearly perpendicular to the platinum coordination plane, forming a 87.5(2)° dihedral angle (89.3° for minor conformer). This orientation is consistent with steric as well as electronic considerations since the Pt-imine π -interactions do not directly compete with the Pt-phenyl π -interactions (*vide infra*). Nevertheless, there is no direct evidence of strong metal-imine π -bonding, as the N3-C19 bond length of 1.27(2) Å (N3'-C19', 1.26(4) Å) is similar to that observed in structures of related iminium ions, [H(CH₃)N=C(CH₃)₂](BPh₄) (1.261(7) Å), [(CH₃)₂N=C(CH₃)₂](BPh₄) (1.291(8) Å),³³ and [(CH₃)₂N=C(CH₃)₂](ClO₄) (1.30(2) Å).³⁴ The Pt-N(imine) distance for **5** (major, 2.191(9) Å; minor conformer, 2.150(14) Å) is comparable to that observed for [Pt(Me₄NCN)(Hdptf)](CF₃SO₃) (2.16(1) Å) with an imine ligand (Hdptf = *N*,*N'*-di-*p*-tolylformamidine), though somewhat longer than observed for the deprotonated complex, Pt(Me₄NCN)(dptf) (2.132(6) Å).²⁶ The corresponding C1(phenyl)-Pt-N3(imine) bond angle (175.4(5)°) of the major conformer is nearly linear, though the

angle of the minor conformer refines to give a somewhat smaller value (C1-Pt-N3', $164.5(10)^{\circ}$).

¹**H NMR spectroscopy.** A general labeling scheme for non-equivalent protons (A – 1) is shown in Scheme 2.1 and Figure 2.6 for complex **5**. The ¹H NMR spectra of Pt(pip₂NCN)(H₂O)⁺ (Figure 2.4), **2-4** (Figure 2.5), and **5** (Figure 2.6) exhibit a characteristic doublet and triplet between 6.8 and 7.1 ppm due to the protons on the phenyl ring (A, B). The resonances near 4.3 ppm arising from the benzylic protons (C) exhibit distinct Pt satellites with *J*_{Pt-H} values of 50 Hz for Pt(pip₂NCN)(H₂O)⁺, 47 Hz for the chloride and bromide derivatives and 55 Hz for the imine complex; the coupling for the iodo complex was not resolved because of coincidental overlap of piperidyl aliphatic proton resonances. These coupling constants are characteristic of values observed for related platinum(II) complexes.^{5,25-27,29,31,35} Two distinct resonances between 2.9 and 4.1 ppm are attributable to the diastereotopic protons (D' and D") of the α-carbons of the piperidyl rings (Figure 2.4). Similarly, the remaining aliphatic protons (E, F) are diastereotopic, accounting for the complexity of the splitting patterns further upfield.

The ¹H NMR spectrum of **5** is shown in Figure 2.6. A series of 2D NMR experiments was undertaken to assign the ¹H NMR spectrum of complex **5** (Figures 2.7 and 2.8). Resonances for the eight protons labeled D' and D" occur between 3.10-3.34 ppm. The 2D COSY (Figure 2.7) spectrum indicates that these protons are coupled to each other and to protons E. These experiments also revealed weak coupling between three apparent singlets at 2.33, 2.85 and 3.64 ppm, assigned to methyl protons G, H and I, respectively. Resonance I exhibits strongest coupling to



Figure 2.4. ¹H NMR spectrum of [Pt(pip₂NCN)(H₂O)](CF₃SO₃) in CD₃CN showing ¹H NMR labeling scheme and diastereotopic piperidyl protons.



Figure 2.5. ¹H NMR spectra of A) 2, B) 3 and C) 4 in CDCl₃.



Figure 2.6. ¹H NMR spectrum of 5 showing ¹H NMR labeling scheme.



Figure 2.7. 2D COSY NMR spectrum of 5 in CDCl₃.


Figure 2.8. 2D NOESY NMR spectrum of 5 in CDCl₃.



Figure 2.9. Cyclic Voltammograms of **2-4** in CH₂Cl₂/0.1 M TBAPF₆ at 250 mV/s vs. Ag/AgCl

Compound	Absorption λ_{max} , nm (ϵ , cm ⁻¹ M ⁻¹)	Emission	
		λ_{max} , nm	FWHM, ^a cm ⁻¹
imine (5)	258 (11000), 273sh (7,600), 290sh (3350)	640	4000
Cl ⁻ (2)	264 (9800), 275 (9050), 295sh (3500)	705	3700
Br ⁻ (3)	266 (8500), 276 (8150), 298sh (2800)	718	3600
I ⁻ (4)	272sh (8700), 283 (9300), 380sh (220)	765	~3700

Table 2.3. UV-visible absorption (MeOH) and 77 K emission (3:1 EtOH:MeOH)spectroscopic data for 2-5.

^a FWHM full width at half maximum of emission intensity.

G and slightly weaker coupling to H. G and H are very weakly coupled. The ¹H NMR spectrum of *N*-isopropylidenemethylamine also shows three resonances (CDCl₃: CMe₂, 1.80, 1.98; NMe, 3.06 ppm) with weak coupling between the C-methyl and N-methyl protons ($J_{trans}=1.3$ Hz; $J_{cis}=0.7$ Hz), and exceedingly weak fourbond coupling between the C-methyl protons (< 0.4 Hz).³⁶ Therefore, the COSY spectrum indicates that resonance G arises from the N-methyl protons, as expected from chemical shift considerations. To confirm this notion we recorded a NOESY spectrum (Figure 2.8) showing that G and H are coupled strongly, as are H and I. G and I are only weakly coupled. Taken together, these data are consistent with methyl groups G and I in a *trans*-configuration as shown in Scheme 2.1 and Figure 2.6.

Electronic Structures. To investigate their electronic structures, cyclic voltammograms of **2-4** (Figure 2.9) were recorded in methylene chloride solution (0.1 M TBAPF₆). Compound **2-4** exhibit irreversible oxidations near 1.15, 1.05, and 0.90 V vs. Ag/AgCl, respectively, similar to that observed for Pt(Me₄NCN)Cl (0.76 V vs.

FcH/FcH⁺, THF, 0.1 M TBAPF₆).³⁷ This behavior is characteristic of metal-centered oxidation of platinum(II) complexes, resulting in large structural reorganization.³⁸ Similar irreversible waves have been reported for related complexes with NCN⁻ pincer ligands.³⁷ At present, no definitive mechanistic information is available for these systems, and a two-electron ECE mechanism is at least as likely as any other. Nevertheless, the electrochemical behavior of these compounds is markedly different than that observed for nearly reversible cooperative two-electron reagents, such as $Pt(2,2':6',2''-terpyridine)(pip_2NCN)^+$ discussed in Chapter 8.³⁹

UV-visible absorption and 77 K emission data for complexes 2-5 are summarized in Table 2.3 and Figure 2.10. The compounds dissolve to give colorless solutions that absorb strongly in the UV region. Between 260 and 285 nm, each compound exhibits two intense absorption features $(7,000-11,000 \text{ cm}^{-1}\text{M}^{-1})$. The relatively large separation between these bands 1300-2100 cm⁻¹ is consistent with two distinct spinallowed charge-transfer transitions. The ligand precursor 1 (ε <350 cm⁻¹M⁻¹) and *N*isopropylidenemethylamine ($\varepsilon < 100 \text{ cm}^{-1}\text{M}^{-1}$)^{40,41} only absorb weakly at these wavelengths, indicating the involvement of the Pt center in the electronic transitions. Both MLCT and ligand-to-metal charge-transfer (LMCT) transitions can occur in this region, 42,43 whereas d \rightarrow p transitions in platinum(II) complexes typically occur at shorter wavelengths.⁴²⁻⁴⁶ Similar intense charge-transfer bands (260-305 nm) also are found in the absorption spectrum of the closely related complex, cis-Pt(2-Me₂NCH₂C₆H₄)₂.^{47,48} van Koten and coworkers⁴⁷ have noted that those bands are strongly shifted to shorter wavelengths in the spectrum of the palladium(II) analogue, confirming significant MLCT character of the observed transitions.⁴⁸ For complexes



Figure 2.10. (a) Room-temperature UV-visible absorption spectra in methanol solution for compounds 2 (- - -), 3 (.. - -), 4 (-----), and 5 (.....).

2-5, the two bands shift to lower energy along the series 5 > 2 > 3 > 4, as expected for predominantly Pt \rightarrow phenyl(pip₂NCN) charge-transfer transitions, in which the excited states are stabilized by increasing electron density on the metal



center. Not surprisingly, the red shift (~1000 cm⁻¹) for the monohalide series (Cl⁻ (2), Br⁻ (3), I⁻ (4)) is somewhat less than that observed for MLCT transitions in the spectra of the dihalide complexes, such as Pt(2,2'-bpy)X₂ (~1500 cm⁻¹, bpy=2,2'bipyridine)⁴⁹ and *trans*-Pt(PPh₃)₂X₂ (~3000 cm⁻¹).⁴³

In the absorption spectra of **5**, **2** and **3**, a weak shoulder (~3000 M⁻¹cm⁻¹) appears near 300 nm in the low-energy tail of the charge-transfer bands. The band shifts to lower energy along the series 5 > 2 > 3 and may correspond to the triplet component of a spin-allowed MLCT transition; the apparent singlet-triplet splitting (2000-3000 cm⁻¹) is similar to that observed for MLCT states of Pt(II) diimine complexes (2000-5000 cm⁻¹).^{50,51} At longer (~1000 cm⁻¹) for the monohalide series (Cl⁻ (**2**), Br⁻ (**3**), I⁻ (**4**)) is somewhat less than that observed for MLCT transitions in the spectra of the dihalide complexes, such as Pt(2,2'-bpy)X₂ (~1500 cm⁻¹, bpy=2,2'bipyridine)⁴⁹ and *trans*-Pt(PPh₃)₂X₂ (~3000 cm⁻¹).⁴³

In the absorption spectra of 5, 2 and 3, a weak shoulder ($\sim 3000 \text{ M}^{-1} \text{ cm}^{-1}$) appears near 300 nm in the low-energy tail of the charge-transfer bands. The band shifts to lower energy along the series 5 > 2 > 3 and may correspond to the triplet component of a spin-allowed MLCT transition; the apparent singlet-triplet splitting (2000-3000 cm⁻¹) is similar to that observed for MLCT states of Pt(II) diimine complexes (2000-5000 cm⁻¹).^{50,51} At longer wavelengths, the complexes exhibit long tailing absorption profiles, attributable to ligand field transitions. In this region, a weak shoulder occurs near 380 nm (220 M⁻¹cm⁻¹) in the spectrum of the iodide complex. As expected from relative ligand field strengths, Pt(Me₄NCN)Br exhibits a similar broad band at slightly shorter wavelength (CHCl₃: 365 nm, ~280 M⁻¹cm⁻¹).⁴⁷ While none of these complexes are luminescent in fluid solution, all four exhibit weak red-orange to red emission at 77 K in 3:1 ethanol:methanol glassy solution or in the solid-state (Figure 2.11). The emission profiles are characteristically broad and Gaussian in shape, with values for the emission band full-width at half-maximum (FWHM) between $3600-4000 \text{ cm}^{-1}$. The bands exhibit a large Stokes shift from the intense UV absorption features, and the onset of these emissions and their maxima shift to lower energy along the series: 5 > 2 > 3 > 4 (640-765 nm). This ordering is entirely consistent with the relative positions of the monodentate ligands in the spectrochemical series: imine > CI > Br > I. The emission decays for solid samples of 2 are adequately modeled with a single-exponential function (average τ , 1.9 µs, Figure 2.12). Taken together, these data suggest the emissions originate from a lowest predominantly spin-forbidden ligand field excited state, most likely having $d\pi(xy,xz,yz) \rightarrow d\sigma^*(x^2-y^2)$ character.⁵² The emission maxima (640-765 nm) and

FWHM values are similar to the broad ligand field emissions reported for other platinum(II) complexes: cis-Pt(NH₃)₂Cl₂ (78 K, 590),⁴⁵ trans-Pt(NH₃)₂Cl₂ (78 K, 610 nm),⁴⁵ Pt(bpy)Cl₂ (250 K, 641 nm),⁵⁰ Pt(bpy)I₂ (300 K, 694 nm),⁵⁰ K₂PtCl₄ (5 K, 777 nm),⁵³ and K₂PtBr₄ (5 K, 804 nm).⁵³ The observed variation in emission energies for **2-5** also is consistent with relative ligand field strengths. For example, the energy difference between the emission maxima of the imine (5) and chloride (2) complexes (1400 cm^{-1}) is somewhat less than that of *trans*-Pt(NH₃)₂Cl₂ and K₂PtCl₄ (3600 cm⁻¹). Similarly, the emission energy difference between the chloride (2) and bromide (3) complexes (~260 cm⁻¹) is less than that of K₂PtCl₄ and K₂PtBr₄ (430 cm⁻¹).⁵³ The corresponding 77 K excitation spectra are in good agreement with the solution absorption spectra. Notably, a weak band near 370 nm gradually shifts to lower energy with decreasing ligand field strength (Figure 2.11). For solid samples of 2 and 4, a spin-forbidden ligand field transition occurs near 460 nm in the 77 K excitation spectra (Figure 2.13), falling between the lowest energy absorptions reported for *trans*-Pt(NH₃)₂Cl₂ (407 nm)⁴⁵ and [NBu₄]₂PtCl₄ (560 nm).^{42,52}

It is noteworthy that the emissions from the imine (5) and chloride (2) complexes occur at longer wavelengths than those of *cis*- and *trans*-Pt(NH₃)₂Cl₂. This result seemingly contradicts the notion that phenyl anion is a significantly stronger field ligand than imine and chloride.⁵⁴ However, it is evident that the orientation of the phenyl group in 2-5 is not optimized for π -backbonding with the d_{xy} level, and therefore, favors low-energy d_{xy} \rightarrow d σ * excited states. This interpretation accounts for the preference of π -acceptor ligands to adopt a geometry favoring



Figure 2.11. (a) 77 K corrected emission ($\lambda_{ex} = 300 \text{ nm}$) and excitation spectra in 3:1 ethanol:methanol glassy solution for compounds **2** (- - - -), **3** (.. - -), **4** (_____), and **5** (.....).



Figure 2.12. 77 K solid-state emission decay (—), single exponential fit (—), and calculated residuals (……) of 2 excited at 355 nm.



Figure 2.13. 77 K excitation spectra of solid samples of 2 and 5. Spectra have been arbitrarily scaled, and excitation spectra are offset for the purposes of comparison.

interaction with the high-lying d_{xy} level in Pt(II) complexes with NCN⁻ ligands,^{8,26} such as 5.²¹ The orientation of the phenyl group also favors relatively low-energy Pt→phenyl charge-transfer excited states (270-285 nm). The lowest spin-allowed MLCT transitions occur at somewhat shorter wavelengths for Pt(COD)(Ph)₂ (<270 nm) and Pt(PEt₃)₂PhCl (<260 nm),^{43,55,56} in which the phenyl rings are likely to be significantly tilted with respect to the coordination plane.⁵⁷ Nevertheless, the lowest MLCT states of 2-5 are still significantly less stable than those found in related Pt(II) complexes with cyclometallating ligands having more extended π -systems (300-450 nm). For example, the lowest spin-allowed MLCT bands occur near 400 and 380 nm for $Pt(ppy)_2$ (ppyH=2-phenyl-pyridine)⁵⁸ and $Pt(bph)(CH_3CN)_2$ (bph²⁻=biphenyl dianion),⁵⁹ respectively. The emissions from those complexes are believed to originate from triplet MLCT or ligand-centered excited states.^{58,59} These considerations suggest the feasibility of tuning the orbital character of the lowest emissive states of Pt(pip₂NCN)L complexes by varying the donor properties of the monodentate ligand (L), as discussed in Chapter 3.

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CHAPTER 3:

Tuning the Electronic Structures of Platinum(II) Complexes with a Cyclometallating Aryldiamine Ligand[†]

Introduction.

Platinum complexes with tridentate cyclometallating aryldiamine ligands, such as the 2,6-bis(dimethylaminomethyl)phenyl anion (Me₄NCN⁻), have attracted increasing interest, in part because of their potential utility in gas sensing devices,²⁻⁴ catalytic systems,⁵⁻⁷ and the preparation of organometallic supramolecular structures and materials.⁸⁻¹²



In an effort to better understand the electronic structures of platinum(II) complexes with NCN⁻ ligands, we recently undertook an investigation of the emissive properties of a series of complexes with the pip₂NCN⁻ pincer ligand, as described in Chapter 2.¹³ It was found that compounds with the general formula Pt(pip₂NCN)X (X=Cl, Br, I), as well as Pt(pip₂NCN)(CH₃N=C(CH₃)₂)⁺, exhibit weak, red emissions originating from a lowest

[†] Most of the contents of Chapter 3 appeared in a manuscript in *Inorganic Chemistry*.¹

predominantly spin-forbidden ligand field (${}^{3}LF$) excited state. More recently, a series of related complexes were prepared with monodentate pyridyl ligands. In the course of these studies, it was noted that Pt(pip₂NCN)(py)⁺ (py=pyridine) exhibits red emission characteristic of a lowest ${}^{3}LF$ excited state. In contrast, Pt(pip₂NCN)(4-phpy)⁺ (4-phpy=4-phenylpyridine) exhibits intense yellow-green emission. In this chapter, we report the synthesis and characterization of a series of complexes with pyridyl ligands, and examine the influence of the pyridyl ligand on the orbital character of the lowest emissive state.

Experimental Section

All reagents were purchased from Acros (Pittsburg, PA). Tetrahydrofuran (THF) was distilled from Na(s)/benzophenone, ethanol was distilled from zinc metal and potassium hydroxide, and methylene chloride was distilled over CaH₂. All other chemicals were used as received. For the synthesis of Pt(COD)Cl₂¹⁴ and 2,6-bis(piperdylmethyl)-1-bromobenzene (pip₂NCNBr)¹³ see Chapter 2 or the published procedures. Tetrabutylammonium hexafluorophosphate (TBAPF₆) was recrystallized twice from boiling methanol and dried under vacuum prior to use. Argon was pre-dried using activated sieves and trace impurities of oxygen were removed with activated R3-11 catalyst from Schweizerhall (New Jersey).

¹H NMR spectra were recorded at room temperature, unless otherwise noted, using a Bruker AC 250 MHz spectrometer. Deuterated chloroform (0.03 % tetramethylsilane (TMS)), methanol and acetonitrile were purchased from Cambridge Isotope Laboratories (Andover, MA). Absorption spectra were recorded using a HP8453 UV-visible absorption spectrometer. Cyclic voltammetry was carried out using a standard three-electrode cell and a CV50w potentiostat from Bioanalytical Systems (West Lafayette, IN). Scans were collected in methylene chloride solution containing 0.1 M TBAPF₆. All scans were recorded using a platinum wire auxiliary electrode, a Ag/AgCl (3.0 M NaCl) reference electrode and a 0.79 mm² gold working electrode. Between scans, the working electrode was polished with 0.05 μ m alumina, rinsed with distilled water and wiped dry using a Kimwipe. 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*°'. Reported potentials are referenced against Ag/AgCl. Peak currents (*i*_p) were estimated with respect to the extrapolated baseline current as described elsewhere.¹⁵ Under these conditions, the ferrocene/ferrocenium (FcH/FcH⁺) couple occurs at 0.45 V. Irreversible oxidation potentials are reported as the potential of the cathodic wave (*i*_{pc}).

Emission spectra were recorded as previously described.¹³ Emission samples for lifetime measurements at 77 K were excited using the third harmonic (355 nm) of a Continuum Surelite Nd:YAG with 4-6 ns pulse widths. Emission transients were detected using a modified PMT connected to a Tektronix TDS580D oscilloscope and modeled using in-house software on a Microsoft Excel platform. Under these conditions, the emission decay of $[Ru(bpy)_3]Cl_2$ in a 4:1 EtOH:MeOH 77 K glassy solution was single exponential corresponding to a 5.1 µs lifetime, as expected.¹⁶ Peak intensities for the Huang-Rhys ratios $(I_{1,0}/I_{0,0})$ were measured with a ruler.

 $Pt(pip_2NCN)Cl$ (1). All glassware and compounds were rigorously dried prior to use because this reaction was found to be extremely sensitive to moisture. Under an Ar(g) atmosphere, 1.84 ml (3.0 mmol) of *N*-butyllithium (1.6 M in hexanes) was added to a stirred solution of pip_NCNBr (1.13 g, 3.2 mmol) in 50 ml of THF at -70° C. After 30

minutes, the solution of lithiated ligand was cannula transferred into a mixture of Pt(COD)Cl₂ (1.0 g, 2.7 mmol) in 200 ml THF at -70° C. The mixture was stirred for 1 hour at -70° C, and subsequently allowed to warm to room temperature and stirred for 12 hours. The filtrate was rotary-evaporated to dryness. Water was added to the solid, and the product was extracted with CH₂Cl₂. The organic layer was dried over MgSO₄ and rotary-evaporated to dryness. After addition of hexanes to the precipitate, the mixture was sonicated, and the white solid was collected and dried. Yield: 1.1 g, 82%. Anal. Calcd. for C₁₈H₂₇N₂PtCl: C, 43.08; H, 5.42; N, 5.58. Found: C, 42.98; H, 5.44; N, 5.43. ¹H NMR (CDCl₃, δ): 1.43 (4H, m, CH₂), 1.54-1.79 (8H, m, CH₂), 3.25 (4H, m, CH₂), 3.95 (4H, m, CH₂), 4.25 (4H, s with Pt satellites, J_{H-Pt}=47 Hz, benzylic CH₂), 6.80 (2H, d, CH), and 6.98 (1H, t, CH).

[Pt(pip₂NCN)(py)](CF₃SO₃) (2(CF₃SO₃⁻)). A mixture of silver triflate (0.052 g, 0.20 mmol) and **1** (0.10 g, 0.20 mmol) in 15 ml of acetone was stirred for 30 minutes at room temperature. The resulting AgCl precipitate was removed by vacuum filtration through celite. After addition of pyridine (15 µl, 0.20 mmol), the filtrate was stirred for three hours, and the solvent was removed by rotary-evaporation. The white solid was dissolved in CH₂Cl₂, and hexanes were added to induce precipitation. The product was washed with ether and dried. Yield: 0.095 g, 82%. Anal. Calcd. for [C₂₃H₃₂N₃Pt](CF₃SO₃): C, 41.50; H, 4.64; N, 6.05. Found: C, 41.65; H, 4.77; N, 6.12. ¹H NMR (CDCl₃, *δ*): 1.17-1.24 (4H, m, CH₂), 1.60-1.83 (8H, m, CH₂), 2.90 (4H, m, CH₂), 3.27 (4H, m, CH₂), 4.39 (4H, s with Pt satellites, J_{H-Pt}=54 Hz, benzylic CH₂), 6.91 (2H, d, CH), 7.05 (1H, t, CH), 7.85 (2H, dd, CH), 8.04 (1H, t, CH), and 9.01 (2H, d, CH).

[Pt(pip₂NCN)(4-phpy)](CF₃SO₃) (3(CF₃SO₃⁻)). Prepared by the same procedure as **2**, substituting the appropriate starting materials: **1** (0.050 g, 0.10 mmol), silver triflate (0.026 g, 0.10 mmol) and 4-phenylpyridine (0.016 g, 0.10 mmol). Yield: 0.045g, 58%. Anal. Calcd. for [C₂₉H₃₆N₃Pt](CF₃SO₃) • H₂O: C, 45.68; H, 4.85; N, 5.33. Found: C, 45.66; H, 4.67; N, 5.34. ¹H NMR (CDCl₃, δ): 1.26-1.31 (4H, m, CH₂), 1.62-1.78 (8H, m, CH₂), 2.98 (4H, m, CH₂), 3.32 (4H, m, CH₂), 4.40 (4H, s with Pt satellites, J_{H-Pt}=50 Hz, benzylic CH₂), 6.92 (2H, d, CH), 7.54 (3H, m, CH), 7.85 (2H, m, CH), 8.05 (2H, d, CH), and 9.05 (2H, d, CH).

 $[Pt(pip_2NCN)(4-phpy)](BF_4)$ (3(BF₄)). Prepared by the same procedure as for the triflate salt, substituting AgBF₄ for silver triflate. Yield: 74%. Anal. Calcd. for $[C_{29}H_{36}N_3Pt](BF_4) \cdot H_2O: C, 47.94; H, 5.27; N, 5.78.$ Found: C, 47.99; H, 4.94; N, 5.54.

 $[(Pt(pip_2NCN))_2(\mu-4,4'-bpy)](CF_3SO_3)_2 (4(CF_3SO_3)_2).$ Prepared by the same procedure as for **2**, substituting the appropriate starting materials: **1** (0.10 g, 0.20 mmol), silver triflate (0.052 g, 0.20 mmol), and 4,4'-bipyridine (4,4'-bpy, 0.0155 g, 0.10 mmol) Yield: 0.078 g, 57%. Anal. Calcd. for $[C_{46}H_{62}N_6Pt_2](CF_3SO_3)_2$: C, 41.55; H, 4.50; N, 6.06. Found: C, 41.89; H, 4.51; N, 6.31. ¹H NMR (CDCl₃, ∂): 1.25-1.35 (8H, m, CH₂), 1.58-1.1.80 (16H, m, CH₂), 2.95 (8H, m, CH₂), 3.30 (8H, m, CH₂), 4.41 (8H, s with Pt satellites, J_{H-Pt}=47 Hz, benzylic CH₂), 6.93 (4H, d, CH), 7.07 (2H, t, CH), 8.63 (4H, d, CH), and 9.10 (4H, d, CH).

[Pt(pip₂NCN)(2,6-pydiol)](CF₃SO₃) (5(CF₃SO₃⁻)). Prepared by the same procedure as for 2, except stirring for 12 hours and substituting the appropriate starting materials: 1 (0.078 g, 0.15 mmol), silver triflate (0.040 g, 0.15 mmol) and 2,6pyridinedimethanol (2,6-pydiol, 0.022 g, 0.15 mmol). Yield: 0.100 g, 89%. Anal. Calcd. for [C₂₅H₃₆N₃O₂Pt](CF₃SO₃): C, 41.37; H, 4.81; N, 5.57. Found: C, 41.12; H, 4.61; N, 5.46. ¹H NMR (CDCl₃, δ, 242 K): 1.75 (4H, m, CH₂), 1.27 (8H, m, CH₂), 2.76 (4H, m, CH₂), 3.35 (4H, m, CH₂), 4.42 (4H, s, benzylic CH₂), 5.33 (2H, t, OH), 5.80 (4H, d, benzylic CH₂), 6.96 (2H, d, CH), 7.11 (1H, t, CH), 7.94 (2H, d, CH), and 8.05 (1H, t, CH).

X-ray Crystallography. Yellow rods of $2(CF_3SO_3)$ were grown by slow evaporation of an acetone solution. Colorless rectangular plates of $3(CF_3SO_3)$ were grown by slow evaporation of a CH₂Cl₂-hexanes solution. Colorless plates of $4(CF_3SO_3)_2 \cdot 1/2(CH_3)_2CO$ were grown by slow evaporation of an acetone-hexanes solution. Colorless rods of $5(CF_3SO_3) \cdot 3/2CHCl_3$ were grown by slow evaporation of a chloroform solution. Diffraction data were collected at 150 K using a Siemens SMART 1K CCD diffractometer (Mo K α radiation and graphite monochromater, λ =0.71073 Å). Data frames were processed using the Siemens SAINT program.¹⁷ Intensities were corrected for Lorentz, polarization and decay effects. Absorption and beam corrections based on the multi-scan technique were applied using SADABS.¹⁸ The structures were solved using SHELXTL¹⁹ and refined by full-matrix least squares on F^2 . For all compounds non-hydrogen atoms were located directly by successive Fourier calculations and refined anisotropically. Ligand H atoms were calculated based on geometric criteria and were treated with a riding model in subsequent refinements for 2, 3 and 4. For $5(CF_3SO_3) \cdot 3/2CHCl_3$, the hydroxyl H atoms were located directly and held fixed at that location. The remaining H atoms were either located directly or calculated based on geometric criteria and were treated with a riding model in subsequent refinements. The isotropic displacement parameters for the H atoms were defined as a times U_{eq} of the

	$2(CF_3SO_3)$	$3(\mathrm{CF}_3\mathrm{SO}_3^-)$
Formula	$[C_{23}H_{32}N_3Pt](CF_3SO_3)$	$[C_{29}H_{36}N_3Pt](CF_3SO_3)$
Fw, g/mol	694.68	770.77
Space group	Pī	<i>P</i> 2 ₁ /c
a, Å	9.7518(6)	15.550(2)
b, Å	12.0132(8)	9.7386(11)
<i>c</i> , Å	12.6718(9)	18.965(3)
<i>α</i> , °	114.190(2)	90
<i>β</i> , °	100.745(3)	92.559(7)
γ, °	103.545(2)	90
$V, Å^3$	1247.895(14)	2869.1(6)
Ζ	2	4
$\rho_{\rm calc}, {\rm g \ cm^{-3}}$	1.849	1.784
<i>Т</i> , К	150(2)	150(2)
radiation, Å	0.71073	0.71073
Reflns collected	13294	18166
ind reflns	6024	7016
GOF on F^2	1.090	0.961
$R_1/wR_2 [I \ge 2\sigma(I)]^a$	0.0262/0.0704	0.0273/0.0528
R_1/wR_2 (all data) ^a	0.0289/0.0711	0.0430/0.0566

Table 3.1. Crystallographic Data and Structural Refinement Details for Compounds $2(CF_3SO_3^{-})$ and $3(CF_3SO_3^{-})$.

^a $R_1 \Sigma || F_o |$ - $|F_c || \Sigma |F_o|$, $wR_2 = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2]^{\frac{1}{2}}$.

	$4(CF_3SO_3)_2 \cdot 1/2(CH_3)_2CO$	5 (CF ₃ SO ₃ ⁻) • 3/2CHCl ₃
Formula	$\frac{[C_{46}H_{62}N_6Pt_2](CF_3SO_3)_2}{1/2(CH_3)_2CO} \bullet$	$[C_{25}H_{36}N_{3}O_{2}Pt](CF_{3}SO_{3}) \bullet 3/2CHCl_{3}$
Fw, g/mol	1387.34	933.78
Space group	I2/a	$P2_{1}/n$
<i>a</i> , Å	21.3316(5)	17.1236(10)
b, Å	9.6526(2)	9.3591(5)
<i>c</i> , Å	26.1800(6)	21.3189(11)
α , °	90	90
β, °	96.4930(10)	96.11(3)
γ, °	90	90
V, Å ³	5356.0(2)	3397.2(3)
Ζ	4	4
$ ho_{\rm calc}$, g cm ⁻³	1.720	1.826
<i>Т</i> , К	150(2)	150(2)
radiation, Å	0.71073	0.71073
Reflns collected	26659	34572
ind reflns	6614	8379
GOF on F^2	1.143	1.006
$R_1/wR_2 [I \ge 2\sigma(I)]^a$	0.0451/0.0776	0.0210/0.0468
R_1/wR_2 (all data) ^a	0.0758/0.0860	0.0293/0.0486

Table 3.2. Crystallographic Data and Structural Refinement Details for Compounds $4(CF_3SO_3)_2 \cdot 1/2(CH_3)_2CO$ and $5(CF_3SO_3) \cdot 3/2CHCl_3$.

 $\frac{1}{a} R_{1} \Sigma ||F_{o}| - |F_{c}|| \Sigma |F_{o}|, wR_{2} = [\Sigma w (F_{o}^{2} - F_{c}^{2})^{2} / \Sigma w (F_{o}^{2})^{2}]^{\frac{1}{2}}.$

adjacent atom, where a=1.5 for -CH₃ and 1.2 for all others. For **2**(CF₃SO₃⁻), the anion is disordered, and a suitable model could not be constructed. Its contribution was subtracted from the data using the program SQUEEZE.²⁰ The final difference Fourier map showed a highest residual electron density peak (1.79 eÅ⁻³) within 1 Å of the Pt.

Compound 4(CF₃SO₃⁻)₂ crystallizes with a badly disordered solvent molecule, which appears to be acetone (~50% occupancy). A suitable disorder model was not obtained, and the solvent contribution was subtracted from the reflection data using the program SQUEEZE.²⁰ The 58.2 electrons/unit cell were applied to the molecular weight, F(000) and density values reported. Compound $5(CF_3SO_3^-)$ crystallizes with 3/2 CHCl₃ in the lattice. The fully occupied CHCl₃ refines normally, but the partially occupied molecule of CHCl₃ is disordered about a center of symmetry. The refined occupancy for the chlorine atoms was approximately 50%, and rounded to 0.5 in subsequent refinements. The carbon atom adopts two positions with occupancies of 0.3 and 0.2. Crystallographic data are summarized in Tables 3.1 and 3.2.

Results and Discussion

Synthesis. The synthesis of **1**, **2**, **3**, **4** and **5** is illustrated in Scheme 3.1, and the pyridyl complexes were isolated as triflate salts. The colorless compounds were characterized by ¹H NMR spectroscopy and elemental analysis. Previously we reported the preparation of **1** from Pt(SMe₂)₂Cl₂, using chromatography to obtain product in low yields (~40%).¹³ Here we report a slightly modified procedure for the conversion of Pt(COD)Cl₂ to product in much higher yields (75-82%) without chromatography. Isolation of salts of **2**, **3**, **4**, and **5** also is straightforward, giving good yields. Metathesis was accomplished by allowing compound **1** to react with a silver salt (*e.g.*, AgCF₃SO₃) at

room temperature. After removal of silver chloride by filtration, one equivalent of pyridine, 4-phenylpyridine or 2,6-pyridinedimethanol was added to give **2**, **3** or **5**, respectively. In the case of **4**, 0.5 equivalents of 4,4'-bipyridine were used



(i) AgCF₃SO₃, pyridine, acetone; *(ii)* AgCF₃SO₃, 4-phenylpyridine, acetone; *(iii)* AgCF₃SO₃, 4,4'-bipyridine, acetone; *(iv)* AgCF₃SO₃, 2,6-pydiol, acetone.

Scheme 3.1. Synthesis of 2-5.

Crystal Structures. The structures of the triflate salts of **2**, **3**, **4**, and **5** were confirmed by single-crystal X-ray diffraction studies. ORTEP diagrams of the cations are shown in Figures 3.1-3.4, and relevant data are summarized in Tables 3.1, 3.2, 3.3 and 3.4. No unusual intermolecular interactions are present, and there is no evidence of water molecules in any of the crystals. For each complex, the pip_2NCN^{-1} ligand is

tridentate, bonded to the approximately square planar platinum center. Each piperidyl ring adopts a chair conformation with the Pt atom occupying an equatorial site. As a

	$2(CF_3SO_3)$	3 (CF ₃ SO ₃ ⁻)
Pt-C(1)	1 920(4)	1 917(3)
Pt-N(1)	2.104(3)	2.103(3)
Pt-N(2)	2.092(3)	2.099(3)
Pt-N(3)	2.159(3)	2.143(3)
N(1)-C(7)	1.531(5)	1.528(4)
N(2)-C(13)	1.536(5)	1.528(4)
C(6)-C(7)	1.493(6)	1.499(6)
C(2)-C(13)	1.503(5)	1.510(5)
C(1)-Pt-N(2)	82.7(2)	81.68 (13)
C(1)-Pt-N(1)	83.1(2)	82.54 (13)
C(1)-Pt-N(3)	176.67(13)	177.34(12)
N(2)-Pt-N(1)	164.45(12)	164.12(11)
C(7)-N(1)-Pt	109.5(2)	106.0(2)
C(13)-N(2)-Pt	108.5(2)	108.1(2)
C(6)-C(7)-N(1)	111.3(3)	109.8(3)
C(2)-C(13)-N(2)	110.1(3)	109.9(3)
N(2)-Pt-N(3)	97.17(12)	96.47(10)
N(1)-Pt-N(3)	96.73(12)	99.36(10)

Table 3.3. Selected Distances (Å) and Angles (°) for Compounds $2(CF_3SO_3)$ and $3(CF_3SO_3)$.

$5(CF_3SO_3) \cdot 3/2CHCl_3.$				
	4(CF ₃ SO ₃ ⁻) ₂ • 1/2(CH ₃) ₂ CO	5 (CF ₃ SO ₃ ⁻) • 3/2CHCl ₃		
Pt-C(1)	1.926(5)	1.930(2)		
Pt-N(1)	2.107(5)	2.124(2)		
Pt-N(2)	2.098(5)	2.117(2)		
Pt-N(3)	2.138(4)	2.201(2)		
N(1)-C(7)	1.534(7)	1.529(3)		
N(2)-C(13)	1.534(7)	1.523(3)		
C(6)-C(7)	1.500(8)	1.507(3)		
C(2)-C(13)	1.513(8)	1.502(3)		
C(1)-Pt-N(2)	81.5(2)	80.45(9)		
C(1)-Pt-N(1)	80.8(2)	81.23(9)		
C(1)-Pt-N(3)	178.4(2)	177.15(8)		
N(2)-Pt-N(1)	162.4(2)	161.20(8)		
C(7)-N(1)-Pt	105.2(3)	105.36(13)		
C(13)-N(2)-Pt	106.1(3)	106.06(14)		
C(6)-C(7)-N(1)	109.1(5)	109.0(2)		
C(2)-C(13)-N(2)	109.2(5)	108.6(2)		
N(2)-Pt-N(3)	97.0 (2)	98.16(7)		
N(1)-Pt-N(3)	100.6(2)	100.32(7)		

Table 3.4. Selected Distances (Å) and Angles (°) for $4(CF_3SO_3)_2 \cdot 1/2(CH_3)_2CO$ and



Figure 3.1. ORTEP diagram of 2(CF₃SO₃⁻). Anion and H-atoms are omitted for clarity.



Figure 3.2. ORTEP diagram of 3(CF₃SO₃⁻). Anions and H-atoms are omitted for clarity.



Figure 3.3. ORTEP diagram of $4(CF_3SO_3)_2 \cdot 1/2(CH_3)_2CO$. Anions, solvent and H-atoms are omitted for clarity.



Figure 3.4. ORTEP diagram of **5**(CF₃SO₃⁻) • 3/2CHCl₃. H-atoms, with the exception of hydroxyl groups, anion and solvents are omitted for clarity.

result, the piperidyl rings are splayed away from the pyridyl ligands and do not appear to interfere with coordination to platinum. The pyridyl groups adopt an approximately perpendicular orientation to the platinum coordination plane. It is intriguing to note that this orientation should position potential binding groups built off the α -carbons of the pyridyl ligand (C19 and C23) above and below the platinum coordination plane. Thus, upon two-electron oxidation the groups are expected to bind to the platinum center, stabilizing the resulting octahedral platinum(IV) species.

The Pt-C and Pt-N(piperidyl) distances for 2 (1.920(4); 2.104(3), 2.092(3) Å), 3 (1.917(3); 2.103(3), 2.099(3) Å), 4 (1.926(5); 2.107(5), 2.098(5) Å), and 5 (1.930(2); 2.124(2), 2.117(2) Å) are consistent with those of related complexes with the same tridentate ligand, Pt(pip₂NCN)Cl (1.910(4), 1.899(5); 2.094(3), 2.099(3), 2.101(4), 2.115(4) Å) and Pt(pip_NCN)(CH_3N=C(CH_3)_2)][CF_3SO_3] (1.919(5); 2.108(3)/2.104(3)) Å).¹³ The Pt-N(pyridyl) distances (2, 2.159(3); 3, 2.143(3); 4, 2.138(4) Å) are significantly longer than the distances for pyridyl ligands trans to a weaker transdirecting ligand such as ethylenediamine ($[(Pt(ethylene-1,2-diamine)(4,4'-bpy))_4]^{8+}$, 2.012, 2.013, 2.041, 2.044 Å),²¹ but agree with those observed when the pyridyl ligand is trans to a relatively strong *trans*-directing group such as an aryl group ($[(Pt(PEt_3)_2)_4(4,4'$ $bpy_{2}(anthracenyl)_{2}^{4+}, 2.132(5), 2.138(6) \text{ Å};^{22} Pt((2,6-CH_{2}PPh_{2})_{2}C_{6}H_{3})(8$ acetamidoquinolinato)⁺, 2.150(4) Å).²³ For **5**, the Pt-N(pyridyl) distance (2.201(2) Å) is significantly longer than those found for 2-4 and the N(pyridyl)-Pt-N(piperidyl) angles are smaller, suggesting the steric demands of the piperidyl and pyridine dimethanol groups interfere with coordination to the metal center.

The N(piperidyl)-Pt-N(piperidyl) angles (2, 164.45(12); 3, 164.12(11); 4, 162.4(2); 5, 161.20(8)°) substantially deviate from ideal *trans*-coordination, with 5 exhibiting the smallest value. This deviation has been ascribed to the geometric preferences of the two five-membered chelate rings.^{24,25} For **2-5**, the rings are slightly puckered, resulting in displacement of the benzylic carbons above and below (2, 0.113, 0.321 Å; **3**, 0.603, 0.537 Å; **4**, 0.744, 0.677 Å; **5**, 0.701, 0.693 Å) the platinum coordination plane, defined by the four atoms directly bonded to platinum center. The displacements for 2 lie outside the range of observed values for related compounds (0.492-0.702 Å).¹³ To accommodate this puckering, the planar phenvl ring is rotated slightly about the Pt-C bond, forming dihedral angles (2, 7.6; 3, 11.6; 4, 15.6; 5, 14.41°) with the Pt coordination plane. These twist angles are similar to those found for other complexes with the pip₂NCN⁻ ligand, Pt(pip₂NCN)Cl (10.3, 9.2°) and $Pt(pip_2NCN)(CH_3N=C(CH_3)_2 (11.4^\circ))^{13}$ The variability in these displacements (0.1-0.7) Å) and twist angles $(7.6-15.6^{\circ})$ suggests the conformational energies of the complexes are not strongly influenced by variation of these parameters over modest ranges.

In the four crystal structures, the planar pyridyl ligands lie nearly perpendicular to the platinum coordination plane, forming dihedral angles of 89.5° (2), 84.5° (3), 86.0° (4), and 89.0° (5). These values are consistent with those observed for related complexes with a bulky tridentate ligand bonded to the platinum center, such as Pt((2,6-CH₂PPh₂)₂C₆H₃)(8-acetamidoquinolinato)⁺ (87.3°).²³ For complexes with less sterically hindered tridentate ligands, such as 2,6-bis(methylthiomethyl)pyridine (SNS), the dihedral angle shows greater variability, ranging from 55.0 to 89.3° : Pt(SNS)(4-CNpy)²⁺, $63.0, 89.3^{\circ}$; Pt(SNS)(4-COOHpy)²⁺, 55.0° ; Pt(SNS)(4-NH₂-py)²⁺, 81.3° ; Pt(SNS)(4-
$Clpy)^{2+}$, 61.7°; Pt(SNS)(4-CH₃py)²⁺, 79.4°.²⁶ Similar variation is observed for a series of Pt(phbpy)(L)⁺ complexes (phbpyH=6-phenyl-2,2'-bipyridine), where L=pyridine (61.7°), 4-aminopyridine (88°), 2-aminopyridine (65.5°), 2,6-diaminopyridine (68°).²⁷ In the latter systems, the orientation of the pyridyl ligand may be influenced by well-known agostic interactions between the NH₂ groups and the platinum center.^{23,27,28} In contrast, there is no indication of interaction between the Pt center and the benzylic or hydroxyl H atoms of **5**, supporting the notion that the metal center is not strongly basic.²⁹ The hydroxyl groups of **5** are directed away from the metal center, forming hydrogen bonds with a triflate O atom and an adjacent complex (O(1)-H(1)···O(4), 2.752(3);

O(2)-H(2)···O(4), 2.777(2) Å). Kaim *et. al.* have suggested that a dihedral angle of approximately 70° between the pyridine and phenyl rings in Pt(diimine)(Ph)₂ provides optimal overlap between the phenyl rings and the π -system of the diimine ligand.³⁰ The nearly perpendicular orientation of the pyridyl and phenyl groups in crystals of **2-5** is consistent with steric considerations, as well as electronic effects since the Pt-pyridine π -interactions do not directly compete with the Pt-phenyl π -interactions.^{13,28,31}

¹**H NMR spectroscopy.** The ¹H NMR spectra of **2** (Figure 3.5), **3** (Figure 3.6) and **4** (Figure 3.7) in CDCl₃ are qualitatively similar to that reported previously for compound **1** (Figure 2.5).¹³ A general labeling scheme for non-equivalent protons (A-F) is shown in Scheme 3.1. The spectra of **1-4** exhibit a doublet and triplet between 6.8 and 7.1 ppm due to the protons on the phenyl ring (A, B). The resonances near 4.3 ppm, arising from the benzylic protons (C), exhibit well-resolved ¹⁹⁵Pt satellites with $J_{\text{H-Pt}}$ values of 47, 54, 50, and 47 Hz for **1-4**, respectively. Two characteristic multiplets between 2.9 and 4.1 ppm are attributable to the diastereotopic protons (D' and D'') of the

 α -carbons of the piperidyl rings. Similarly, the aliphatic protons E and F are diastereotopic, accounting for the complexity of the splitting patterns further upfield. The aromatic resonances of the pyridyl ligands occur downfield of 7.50 ppm. Notably, the doublet resonance attributable to the α -protons of the pyridyl group (9.0-9.1 ppm) is shifted downfield of the corresponding free ligand resonance, confirming that the pyridyl ligands are bonded to the platinum center. In the case of the 4,4'-bipyridine bridged dimer (4), the pyridyl resonances appear as two doublets at 8.63 and 9.10 ppm, indicating that the two halves of the ligand are equivalent.



Figure 3.5. ¹H NMR spectrum of $2(CF_3SO_3)$ in CDCl₃. Solvent and TMS resonances are labeled with *.



Figure 3.6. ¹H NMR spectrum of $3(CF_3SO_3)$ in CDCl₃. Solvent and TMS resonances are labeled with *.



Figure 3.7. ¹H NMR spectrum of $4(CF_3SO_3)_2$ in CDCl₃. Solvent and TMS resonances are labeled with *.



Figure 3.8. ¹H NMR spectra of 5(CF₃SO₃⁻) in CDCl₃ at (A) 298 K, (B) 272 K and (C) 242 K. Identifiable resonances are labeled for Pt(pip₂NCN)(2,6-pydiol)⁺ (a), 2,6-pydiol (b) and Pt(pip₂NCN)(H₂O)⁺ (c), as well as for chloroform, water and TMS (*).

In CD₃OD solution, the ¹H NMR spectrum of **2** is qualitatively similar to that observed in chloroform. However, the spectra of **3** and **4** indicate that the pyridyl ligands are partially dissociated (<10%) at room temperature. In CD₃CN solution, the dissociation is enhanced, and the NMR spectra of **2-4** exhibit resonances associated with the pyridyl complexes, free pyridyl ligand and Pt(pip₂NCN)(H₂O)⁺,³² as well as the monomeric Pt(pip₂NCN)(4,4'-bpy)⁺ adduct in the case of **4**. These results are consistent with van Koten and van Eldik's assessment of the strong *trans*-labilizing properties of the NCN⁻ ligand.²⁴

At room temperature, resonances in the ¹H NMR spectrum of **5** in CDCl₃ solution are broad, as expected for ligand exchange occurring in the slow-to-intermediate exchange regime (Figure 3.8). All available evidence points to substitution of the pydiol ligand by water that is present as a solvent impurity. At room temperature, compound **5** is the major component in solution. Upon cooling, the resonances sharpen, and those corresponding to compound **5** gain intensity at the expense of the others. At 272 K, resonances attributable to **5**, free pydiol and Pt(pip₂NCN)(H₂O)⁺ are well-resolved. These assignments are confirmed by variable temperature studies of free pydiol and Pt(pip₂NCN)(H₂O)⁺.³² Taken together with the crystallographic data for **5**, these observations suggest that the bond between the pydiol and the Pt is weakened because of the steric demands of the benzylic groups and the *trans*-labilizing properties of the NCN⁻ ligand. In support of this view, the ligand is fully dissociated in CD₃CN solution at room temperature.

These findings have important implications for the design of two-electron reagents with two potentially *mer*-coordinating ligands. If pip₂NCN⁻ and a pyridyl ligand

(*e.g.*, terpyridine) are to be incorporated into the design of a two-electron reagent, these data suggest that the pyridyl ligand has to be tridentate. A tridentate pyridyl ligand is expected to discourage pyridyl ligand exchange, and yield a Pt(II) complex that is stable both in the solid state and solution.

Electronic Structures. To investigate their electronic structures, cyclic voltammograms of **1-4** were recorded in methylene chloride solution (0.1 M TBAPF₆). As discussed in Chapter 2, compound **1** exhibits an irreversible oxidation near 1.1 V vs. Ag/AgCl (Figure 2.9), similar to that observed for Pt(Me₄NCN)Cl (0.76 V vs. FcH/FcH⁺, THF, 0.1 M TBAPF₆).^{33,34} This behavior is characteristic of metal-centered oxidation of platinum(II) complexes, resulting in large structural reorganization.^{35,36} Similar irreversible waves have been reported for related complexes with NCN⁻ pincer ligands.^{33,34} At present, no definitive mechanistic information is available for these systems, and a two-electron ECE mechanism is as likely as any other. Nevertheless, the electrochemical behavior of these compounds is markedly different than that observed for nearly reversible cooperative two-electron reagents, such as Pt(2,2':6',2"-terpyridine)(pip>NCN)⁺ discussed in Chapter 8.²⁹

None of the pyridyl complexes (2-4) undergoes oxidation at potentials <1.3 V, suggesting this process is shifted to more positive potentials, as predicted for neutral donor groups bonded the metal center. As previously noted for 1,²⁹ neither 2 nor 3 is reduced at potentials more positive than -1.8 V. However, complex 4 (Figure 3.9) undergoes a nearly reversible one-electron reduction at -1.22 V ($\Delta E_p=61 \text{ mV}, i_{pc}/i_{pa}=1.4$, 0.25 V/s). A similar process has been assigned to a bipyridine-centered reduction in the cyclic voltammogram of [(Pt(PEt_3)_2)_4(\mu-4,4'-bpy)_2(anthracenyl)_2]^{4+} (-1.44 \text{ V}, \Delta E_p=69



Figure 3.9. Cyclic Voltammogram of **4**(CF₃SO₃⁻)₂ in CH₂Cl₂/0.1 M TBAPF₆ vs. Ag/AgCl.

Cmpd (L)	absorption λ_{max} , nm (ϵ , cm ⁻¹ M ⁻¹)	Emission λ_{max} , nm (fwhm, cm ⁻¹)		<i>E</i> °', V
		Glassy Solution ^a	Solid-State	
1 (Cl ⁻)	270, (7800) 281 (8000), 305sh (2600)	705 (3500)	740	_
2 (py)	259 (13000), 272sh (8300), 292sh (3050)	650 (3700)	680	_
3 (4-phpy)	262sh (23800), 280 (32100), 286sh (30700)	444, 474, 498, 535sh	450, 477, 508, 546sh ^b	_
4 (4,4'- bpy)	260 (30750), 277 (30100), 291sh (24800), 305sh (15800)	433, 458, 485sh, 520sh	449, 479, 507, 550sh	-1.44

Table 3.5. Room Temperature UV-Visible Absorption (CH2Cl2) Spectra, 77 K EmissionData and Reduction Potentials^c for 1-4.

^a 4:1 EtOH:MeOH glassy solution; ^b solid-state maxima of BF₄⁻ salt; ^c cyclic voltammograms were recorded in 0.1 M TBAPF₆/CH₃CN at 0.25 V/s and referenced vs. Ag/AgCl.

mV, 0.2 V/s, 0.1 M TBAPF₆, CH₃CN).³⁷ Reduction of **4** at potentials more positive than **2** or **3** is in keeping with the relative reduction potentials of the free pyridyl ligands, and the cathodic shift of this process with respect to free 4,4'-bpy is consistent with coordination to the acidic metal centers stabilizing the LUMO of the bridging diimine ligand.

The colorless solids dissolve to give colorless methylene chloride solutions that absorb strongly in the UV region (Figure 3.10, Table 3.5). As noted previously for the

chloride complex (1) and related compounds, 13,38 the UV spectrum in CH₂Cl₂ is dominated by two intense features (270 nm, 7800 M⁻¹cm⁻¹; 281 nm, 8000 M⁻¹cm⁻¹) tentatively assigned as having partial metal-to-ligand charge-transfer (MLCT) character involving the piperidyl ligand.^{13,38,39} As expected for decreased electron density on the metal center, the MLCT bands in the spectrum of the pyridyl complex (2) are shifted to shorter wavelengths, and an absorption maximum occurs at 259 nm (13000 M⁻¹cm⁻¹). The overall absorption profile is remarkably similar to that of the imine analog, $Pt(pip_2NCN)(CH_3N=C(CH_3)_2)^+$ in methanol solution (258 nm, 11000 M⁻¹cm⁻¹; 273 nm, 7600 $M^{-1}cm^{-1}$, 290sh nm, 3350 $M^{-1}cm^{-1}$),¹³ as expected for ligands with similar donor properties. The enhanced intensity of the 259 nm absorption for 2 is consistent with an overlapping pyridyl-centered transition that appears in the spectra of free pyridine (252 nm, 2000 $M^{-1}cm^{-1}$) and protonated pyridine (256 nm, 5360 $M^{-1}cm^{-1}$, acidic ethanol),⁴⁰ as well as other pyridyl metal complexes.⁴¹⁻⁴⁵ Though it is reasonable to expect the MLCT transitions involving the pyridyl ligand to lie between the lowest energy MLCT bands of Pt(py)₂Cl₂ (*cis*, 300 nm; *trans*, 310 nm)⁴⁴ and those of complexes with neutral donor ligands (*e.g.*, $Pt(NH_3)_3(py)^{2+}$, $Pt(NH_3)_2(py)_2^{2+}$, and $Pt(py)_4^{2+}$, <240 nm),⁴¹ the remarkable similarity of the spectra of **2** and the imine analog¹³ suggests these bands occur at $\lambda < 260$ nm for **2**.

The UV spectra of **3** (280 nm, 32100 $M^{-1}cm^{-1}$) and **4** (260 nm, $M^{-1}cm^{-1}$, 30750 $M^{-1}cm^{-1}$; 277 nm, 30100 $M^{-1}cm^{-1}$) are dominated by bands with significantly greater intensity than observed for **2**, suggesting the presence of additional transitions. Free 4-phpy exhibits a broad π - π * absorption near 255 nm (16600 $M^{-1}cm^{-1}$) that shifts to 285 nm (~17,000 $M^{-1}cm^{-1}$) on protonation.⁴⁶ Similar ligand-centered transitions have been



Figure 3.10. Room temperature UV-visible absorption spectra in methylene chloride solution for compounds **1** (- - - -), **2** (... - -), **3** (.....), and **4** (_____).

identified in the spectra of $Ru(NH_3)_5(4-phpy)^{2+}$ (289 nm, 18600 M⁻¹cm⁻¹),⁴⁷ fac- $Re(CO)_3(Cl)(4-phpy)_2$ (268 nm, 36500 M⁻¹cm⁻¹)⁴³ and $Cu_4Cl_4(4-phpy)_4$ (286 nm),⁴⁸ and a significant fraction of the intensity of the 280 nm feature in the spectrum of **3** is reasonably attributed to a 4-phpy-centered transition. The spectrum of free 4,4'-bpy exhibits an intense π - π * absorption band and shoulder (239 nm, 15400 M⁻¹cm⁻¹; 270sh nm, $\sim 6000 \text{ M}^{-1} \text{cm}^{-1}$) that also shift slightly to longer wavelengths and gain intensity on double protonation (248 nm, 16000 $M^{-1}cm^{-1}$; 275sh nm, ~10000 $M^{-1}cm^{-1}$).⁴⁹ The shorter wavelength band has been identified in the spectra of $Ru(NH_3)_5(4,4'-bpy)^{2+}$ (250) nm, 25700 M⁻¹cm⁻¹),⁴⁷ fac-Re(CO)₃(Cl)(4,4'-bpy)₂ (238 nm, 35000 M⁻¹cm⁻¹), fac- $\text{Re(CO)}_{3}(\text{Cl})(4,4'-\text{bpyH})_{2}^{+}$ (~250 nm),⁴³ and [(Ru(NH₃)₅)₂(μ -4,4'-bpy)]⁴⁺ (249 nm, 15000 $M^{-1}cm^{-1}$),⁵⁰ and the 260 nm band in the spectrum of **4** is reasonably attributed to a 4,4'bpy centered transition. Interestingly, an intense longer wavelength π - π * feature has not been identified in spectra of the aforementioned complexes; it is conceivable that the broad 280 nm feature in the spectrum of 4 is comprised of several transitions, including a MLCT involving 4,4'-bpy. Though the MLCT bands involving the pyridyl ligands cannot yet be firmly identified for **2-4**, the accumulated data suggest that these transitions occur at $\lambda < 300 \text{ nm}$ (>33,300 cm⁻¹). Assuming singlet-triplet splittings comparable to those reported for other platinum(II) complexes (3000-5000 cm-1),^{51,52} the lowest spinforbidden MLCT absorption band is expected to occur at wavelengths $\lambda < 360$ nm (>27,800 cm-1) in fluid solution and even shorter wavelengths in rigid matrices. Thus, given the relatively low energies of the lowest triplet $\pi - \pi^*$ states of the free pyridyl ligands (py, 29650; 4-phpy, 23800; 4,4'-bpy, 24400 cm-1)⁵³⁻⁵⁶ and of the 3LF states of



Figure 3.11. 77 K emission spectra in 4:1 ethanol:methanol glassy solution for 1-4,
4-phenylpyridine (.....) and 4,4'-bipyridine (- - -). Spectra have been arbitrarily scaled.

related complexes,¹³ it is unlikely that spin-forbidden MLCT emissions will be observed from these complexes.

Solid-state samples of **2** exhibit weak red emissions under UV irradiation at roomtemperature, reminiscent of the 3LF emissions observed for **1** and related complexes, Pt(pip2NCN)X (X=Br, I).¹³ In contrast, solid-state samples of **3** and **4** exhibit bright yellow-green emission. To investigate the origin of this behavior, the emission spectra of solid and glassy solution samples (4:1 EtOH:MeOH and 2-methyl-tetrahyrofuran) of **2-4** were recorded at 77 K (Figure 3.11, Table 3.5). Solid samples of **2** and **3** showed evidence of contamination consistent with pyridyl ligand substitution.⁵⁷ Though dissociation also is expected for solution samples, this chemistry appears to be minimized at low temperatures (Figure 3.11). In addition, the frozen solution emission profiles are concentration independent and in good agreement with solid-state data, indicating that aggregates are not responsible for the observed spectra.

Excitation of glassy solutions of the triflate salt of **2** at 300 or 355 nm results in characteristically broad, low-energy and Gaussian-shaped emissions centered near 650 nm with a full-width at half-maximum (fwhm) of 3700 cm-1. The emission band exhibits a large Stokes shift from the intense absorption features, and the emission maximum is blue-shifted with respect to that observed for the chloride complex (**1**, 705 nm). Taken together, these observations are consistent with emission originating from a lowest 3LF excited state, as previously reported for **1**.¹³ The large Stokes shift and broadness are consistent with an excited state having a very different optimum geometry than the ground state, as expected for population of the Pt(dx_2 -y_2) antibonding level. Consequently, the onset of the emission near 515 nm does not necessarily mark the 3LF



Figure 3.12. 77 K solid-state emission (630 nm) decay (—), single exponential fit (—, $\tau = 5 \ \mu s$) and calculated residuals (……) of **2** excited at 355 nm.



Figure 3.13. 77 K solid-state emission (630 nm) decay (—), double exponential fit (—, $\tau_1 = 3 \ \mu s, \tau_2 = 10 \ \mu s$) and calculated residuals (……) of **2** excited at 355 nm.

0-0 transition, and we can only conclude from these data that the energy of the lowest ligand field state for 2 must be $\geq 19,400$ cm-1 (≤ 515 nm). The 77 K excitation spectra are in good agreement with solution absorption spectra, and at longer wavelengths, a weak band is resolved near 370 nm (1, 373 nm; 2, 365 nm). In the case of 2, the emission maximum is near that observed for $Pt(pip_2NCN)(CH_3N=C(CH_3)_2)^+$ (640 nm), as expected for ligands with comparable donor properties. In the solid state, the emission maxima for $1 (740 \text{ nm})^{13}$ and 2 (680 nm) are shifted to longer wavelengths from the frozen solution maxima by $\sim 700 \text{ cm}^{-1}$. However, in contrast to 1, the emissions from solid salts of **2** are weakly excitation dependent (*e.g.*, λ_{ex} =355 nm, λ_{max} =694 nm), indicating some contamination, presumably from a product of pyridine ligand substitution.⁵⁷ In addition, whereas the emission decays for solid samples of **1** (Figure 2.12) are adequately modeled with a single-exponential function (τ , 1.9 µs), the emission decays from repeatedly recrystallized samples of the triflate salt of 2 (Figures 3.12 and 3.13) in glassy solution or the solid state required a biexponential function to obtain a reasonable fit (τ , 3, 11 µs).^{57,58} Nevertheless, the microsecond lifetimes are within the expected range for d-d emissions from platinum(II) complexes.^{44,59,60}

The intense emissions from glassy solution samples of **3** and **4** excited at 300 nm are strongly blue-shifted with respect to the previous compounds. The sharply structured emissions clearly originate from the lowest pyridyl-centered π - π * excited-states of the respective 4-phpy and 4,4'-bpy ligands. The ~1000 and ~1400 cm⁻¹ spacings in the vibronic progressions are in excellent agreement with those of the free ligands (Figure 3.11). However, the origin of the bands for **3** and **4** are shifted by ~1300 cm⁻¹ and ~1000 cm⁻¹, respectively, from those of the free ligands, confirming that the observed emissions

do not arise from either protonated⁶¹ or free pyridyl ligands (Figure 3.11). Similarly, the bandshapes and Franck-Condon factors, as indicated by the Huang-Rhys ratios⁶² ($I_{1.0}/I_{0.0}$): **3**, 1.4; **4**, 1.3), are distinctly different from those of the free ligands (0.8, 0.9) and indicative of metal coordination.^{51,60,63} The emission spectra of the complexes excited at 355 nm also are several orders of magnitude more intense than those obtained by exciting similar concentrations of 4-phpy and 4,4'-bpy. The excitation spectra are in good agreement with absorption spectra, and in the case of 4, the emission spectra of solid samples are very similar to those observed for frozen solutions. However, the emissions from salts of **3** show considerable variation depending on counterion and excitation wavelength; it also is likely that sample aging influences these spectra, however this parameter was not extensively investigated. The emission decay for 4 (Figure 3.14) in the solid state is adequately modeled by a single-exponential function (τ , 0.16 ms), whereas the decay for **3** is not (τ , 0.1, 0.6 ms). Nevertheless, as expected for a lowest triplet excited state centered on the pyridyl ligands, the observed lifetimes are significantly shorter than those of the free ligands (4-phpy, 2.1 s; 4.4'-bpy, 0.8 s),⁵⁶ but considerably longer than observed for 1 and 2.

The accumulated data indicate that substitution of pyridine with 4-phenylpyridine in Pt(pip₂NCN)L⁺ complexes results in a dramatic change in the orbital character of the emissive state. To a reasonable approximation, the donor properties of the two pyridyl ligands are simlar, and the crossover from a lowest, ³LF state to a ${}^{3}\pi$ - π * state can be largely attributed to the ~5900 cm⁻¹ stabilization^{53,54,56} of the triplet π - π * state of 4-phpy with respect to that of py. (Similarly, the lowest triplet state of 4,4'-bpy lies ~5300 cm⁻¹ below that of py.)^{55,56} Though the large Stokes shift of ³LF emissions makes difficult the



Figure 3.14. 77 K 2-MeTHF glassy solution emission (475 nm) decay (—), single exponential fit (—, $\tau_1 = 0.16$ ms) and calculated residuals (……) of 4 excited at 355 nm.

evaluation of the 0-0 energy of the emitting state of **2**, the preceding results effectively bracket this energy between the emission onset for compounds **3** and **4** (~425 nm, 23500 cm⁻¹) and the lowest triplet state of py (337 nm, 29650 cm⁻¹).

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CHAPTER 4:

Tuning the Lowest Excited States of Pyridyl Bridged Platinum(II) Dimeric Complexes.

Introduction

During the past fifteen years, there has been increasing interest in using pyrazine (pyz),¹⁻⁵ *trans*-1,2-bis(4-pyridyl)ethylene (bpe),⁶⁻¹⁴ 1,2-bis(4-pyridyl)ethane (bpa),^{15,16} and 4,4'-bipyridine (bpy)^{8,10-13,16-23} as building blocks for supramolecular platinum



complexes. Complexes with these ligands tend to self-assemble^{4,6-8,20-22} and have potentially useful medicinal,^{2,3,13-16} photochemical^{10,23,24} and electrochemical^{10,11,23,24} properties. While supramolecular structures, such as $(Pt(PMe_3)_2(\mu-bpe))_4^{8+}$, $(Pt(PMe_3)_2(\mu-bpe))_3^{6+}$, and $(Pt(PMe_3)_2(\mu-pyz))_3^{6+}$ prepared by Stang's group,^{4,7} have received increasing attention, platinum(II) dimers bridged by $pyz^{1,2,5}$ and bpy^{23-26} are rare, and there are no previously reported examples of platinum(II) dimers with bpa and bpe bridging ligands.



In this chapter we report a series of platinum(II) dimers with the tridentate ligand pip₂NCN⁻. The X-ray crystal structures of three of these complexes are reported, and their chemical, electrochemical and spectroscopic properties are discussed.



Experimental Section. Tetrahydrofuran (THF) was distilled from Na(s)/benzophenone, ethanol was distilled from zinc metal/potassium hydroxide, and methylene chloride was distilled from CaH₂. Anhydrous 2-methyltetrahydrofuran (2-MeTHF) was purchased from Aldrich Chemical Company (Milwaukee, WI) and used as received. All other reagents were purchased from Acros (Pittsburg, PA) and used as received. Pt(pip₂NCN)Cl^{27,28} and [Pt(pip₂NCN)(μ -bpy)][CF₃SO₃]₂²⁸ were prepared according to literature procedures (Chapters 2 & 3). Tetrabutylammonium hexafluorophosphate (TBAPF₆) was recrystallized twice from boiling methanol and dried under vacuum prior to use. Argon was pre-dried using activated sieves and trace impurities of oxygen were removed with activated R3-11 catalyst from Schweizerhall (New Jersey).

¹H NMR spectra were recorded at room temperature, unless otherwise noted, using a Bruker AC 250 MHz spectrometer. Deuterated chloroform (0.03 % tetramethylsilane (TMS)), methanol and acetonitrile were purchased from Cambridge Isotope Laboratories (Andover, MA). UV-visible absorption spectra were recorded using a HP8453 UV-visible spectrometer. Cyclic voltammetery was carried out using a standard three-electrode cell and a CV50w potentiostat from Bioanalytical Systems. Scans were collected in methylene chloride solution containing 0.1 M TBAPF₆. All scans were recorded using a platinum wire auxiliary electrode, a Ag/AgCl (3.0 M NaCl) reference electrode and a 0.79 mm² gold working electrode. Between scans, the working electrode was polished with 0.05 µm alumina, rinsed with distilled water and wiped dry using a Kimwipe. Reported potentials are referenced against Ag/AgCl (3.0 M NaCl). Peak currents (*i*_p) were estimated with respect to the extrapolated baseline current as

described elsewhere.²⁹ Under these conditions, the ferrocene/ferrocenium (FcH/FcH⁺) couple occurs at 0.45 V.

Emission spectra were recorded with a SPEX Fluorolog-3 fluorimeter equipped with a double emission monochromator and a single excitation monochromator. 77 K glassy solutions were prepared by inserting a quartz EPR tube containing either a 4:1 EtOH:MeOH or a 2:1 MeOH:2-MeTHF solution of the complex into a quartz-tipped finger dewar. Emission spectra were corrected for instrumental response. Emission samples for lifetime measurements at 77 K were excited using the third harmonic (355 nm) of a Continuum Surelite II Nd:YAG with 4-6 ns pulse widths or with 4-6 ns pulses from a Continuum Panther Optical Parametric Oscillator (420 nm) pumped with the third harmonic (355 nm) of a Continuum Surelite II Nd:YAG laser. Emission transients were detected using a modified PMT connected to a Tektronix TDS580D oscilloscope and modeled using in-house software on a Microsoft Excel platform. Under these conditions, the emission decay of [Ru(2,2'-bpy)₃]Cl₂ in 4:1 EtOH:MeOH 77 K glassy solution was single exponential corresponding to a 5.1 µs lifetime as expected.³⁰

 $[(Pt(pip_2NCN))_2(\mu-pyz)](CF_3SO_3)_2$. A mixture of silver triflate (0.026 g, 0.1 mmol) and Pt(pip_2NCN)Cl (0.05 g, 0.1 mmol) in 15 ml of acetone was stirred for 30 minutes at room temperature. The resulting AgCl precipitate was removed by vacuum filtration through celite. After addition of pyz (0.004 g, 0.1 mmol), the filtrate was stirred for 5 hours, and the solvent was removed by rotary-evaporation. The yellow solid was dissolved in CH₂Cl₂, and diethyl ether was added to induce precipitation. The product was washed with ether and dried. Yield: 0.037 g, 57%. Anal. Calcd. for $[C_{40}H_{58}N_6Pt_2](CF_3SO_3)_2$: C, 38.47; H, 4.46; N, 6.41. Found: C, 38.24; H, 4.51; N, 6.28.

¹H NMR (CDCl₃, *δ*): 1.25-1.80 (24H, m, CH₂), 3.03 (8H, m, CH₂), 3.32 (8H, m, CH₂), 4.40 (8H, s with Pt satellites, J_{H-Pt}=52 Hz, benzylic CH₂), 6.93 (4H, d, CH), 7.08 (2H, t, CH), 9.49 (4H, s, CH).

The BF₄ salt ([(Pt(pip₂NCN))₂(μ -pyz)](BF₄)₂) was prepared by the same procedure as [(Pt(pip₂NCN))₂(μ -pyz)](CF₃SO₃)₂, substituting silver tetrafluoroborate for silver triflate. Yield: 0.034 g, 58%. Anal. Calcd. for [C₄₀H₅₈N₆Pt₂](BF₄)₂: C, 40.49; H, 4.93; N, 7.08. Found: C, 40.05; H, 4.83; N, 6.97.

 $[(Pt(pip_2NCN))_2(\mu$ -bpe)](CF₃SO₃)_2. Prepared by the same procedure as for $[(Pt(pip_2NCN))_2(\mu$ -pyz)](CF₃SO₃)_2, substituting the appropriate starting materials: Pt(pip_2NCN)Cl (0.110 g, 0.22 mmol), silver triflate (0.056 g, 0.22 mmol) and bpe (0.020 g, 0.22 mmol). Yield: 0.085 g, 55%. Anal. Calcd. for $[C_{48}H_{64}N_6Pt_2](CF_3SO_3)_2$: C, 42.49; H, 4.57; N, 5.95. Found: C, 42.56; H, 4.59; N, 6.07. ¹H NMR (CDCl₃, δ): 1.25-1.35 (16H, m, CH₂), 1.60-1.80 (8H, m, CH₂), 2.94 (8H, m, CH₂), 3.28 (8H, m, CH₂), 4.39 (8H, s, benzylic CH₂), 6.92 (4H, d, CH), 7.07 (2H, m, CH), 7.97 (2H, s, bridging CH), 8.31 (4H, d, CH), and 8.82 (4H, d, CH).

[(Pt(pip₂NCN))₂(μ -bpa)](CF₃SO₃)₂. Prepared by the same procedure as for [(Pt(pip₂NCN))₂(μ -pyz)](CF₃SO₃)₂, substituting the appropriate starting materials: Pt(pip₂NCN)Cl (0.100 g, 0.2 mmol), silver triflate (0.051 g, 0.2 mmol) and bpa (0.018 g, 0.2 mmol). Yield: 0.107 g, 76%. Anal. Calcd. for [C₄₈H₆₆N₆Pt₂](CF₃SO₃)₂ • H₂O: C, 41.43; H, 4.73; N, 5.80. Found: C, 41.26; H, 4.75; N, 5.82. ¹H NMR (CDCl₃, δ): 1.25-1.35 (16H, m, CH₂), 1.60-1.80 (8H, m, CH₂), 2.93 (8H, m, CH₂), 3.27 (12H, m, piperidyl and bridging CH₂), 4.38 (8H, s, benzylic CH₂), 6.91 (4H, d, CH), 7.06 (2H, t, CH), 8.01 (4H, d, CH), 8.77 (4H, d, CH).

X-ray Crystallography. Yellow plates of $[(Pt(pip_2NCN))_2(\mu-pyz)](CF_3SO_3)_2$ were grown by slow evaporation of a CH₂Cl₂/CHCl₃ solution. Marginal-quality single crystals of $[(Pt(pip_2NCN))_2(\mu-bpe)](CF_3SO_3)_2 \cdot 2CH_2Cl_2$ were obtained as colorless rods from CH₂Cl₂/hexanes/Et₂O. Diffraction data for $[(Pt(pip_2NCN))_2(\mu-pyz)](CF_3SO_3)_2$ were collected at 150K using a SMART6000 CCD diffractometer, and data for $[(Pt(pip_2NCN))_2(\mu-bpe)](CF_3SO_3)_2 \cdot 2CH_2Cl_2$ were collected at 150K using a standard Siemens SMART 1K CCD diffractometer (Mo Kα radiation and graphite monochromater, λ =0.71073 Å). For $[(Pt(pip_2NCN))_2(\mu-bpe)](CF_3SO_3)_2 \cdot 2CH_2Cl_2$ weakly diffracting data beyond 50° in 2θ were truncated. Data frames were processed using the Siemens SAINT program.³¹ Intensities were corrected for Lorentz, polarization and decay effects. Absorption and beam corrections based on the multi-scan technique were applied using SADABS.³² The structures were solved using SHELXTL³³ and refined by full-matrix least squares on F².

For all compounds non-hydrogen atoms were located directly by successive Fourier calculations and refined anisotropically. Ligand H atoms were either located directly or calculated based on geometric criteria and were treated with a riding model in subsequent refinements. The isotropic displacement parameters for the H atoms were defined as *a* times U_{eq} of the adjacent atom, where *a*=1.5 for -CH₃ and 1.2 for all others.

For $[(Pt(pip_2NCN))_2(\mu-pyz)](CF_3SO_3)_2$, one triflate anion is severely disordered, and the geometry of the disordered anion was restrained to be similar to the triflate that was well-behaved.³⁴ The highest residual electron density peaks are near the badly disordered triflate. Compound $[(Pt(pip_2NCN))_2(\mu-bpe)](CF_3SO_3)_2$ crystallizes with two

	[(Pt(pip ₂ NCN)) ₂ (µ-pyz)] (CF ₃ SO ₃) ₂	$[(Pt(pip_2NCN))_2(\mu-bpe)]$ $(CF_3SO_3)_2 \bullet 2CH_2Cl_2$
Formula	$[C_{40}H_{58}N_6Pt_2][CF_3SO_3]_2$	$[C_{48}H_{64}N_6Pt_2](CF_3SO_3)_2 \bullet 2CH_2Cl_2$
fw, g/mol	1311.24	1583.22
Space group	Pī	$P2_{1}/c$
<i>a</i> , Å	12.5240(5)	10.1288(6)
b, Å	14.1570(6)	16.3346(9)
<i>c</i> , Å	14.2928(6)	17.4764(10)
<i>α</i> , °	106.458(1)	90
<i>β</i> , °	92.527(1)	90.882(2)
γ, °	106.880(1)	90
V, Å ³	2303.46(17)	2891.1(3)
Ζ	2	2
$\rho_{\rm calc}, {\rm g \ cm}^{-3}$	1.891	1.819
<i>T</i> , K	150(2)	150(2)
radiation, Å	0.71073	0.71073
no reflens colled	31588	14728
no indpt reflens	11310	5083
GOF on F^2	1.059	1.028
$R_1/wR_2 \left[I \ge 2\sigma(I)\right]^a$	0.0341/0.0900	0.0697/0.1139
R_1/wR_2 (all data) ^a	0.0428/0.0959	0.1474/0.1369

Table 4.1. Crystallographic Data and Structural Refinement Details for[(Pt(pip2NCN))2(μ-pyz)](CF3SO3)2 and [(Pt(pip2NCN))2(μ-bpe)](CF3SO3)2 •

 $2CH_2Cl_2$.

^a $R_1 \Sigma || F_o || - |F_c| |/\Sigma || F_o |, wR_2 = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2]^{\frac{1}{2}}.$

CH₂Cl₂ molecules in the lattice. For $[(Pt(pip_2NCN))_2(\mu-bpe)](CF_3SO_3)_2 \cdot 2CH_2Cl_2$, attempts at resolving potential twinning (β angle near 90°) failed, causing refinements and metrical parameters to substantially worsen. In the structure of $[(Pt(pip_2NCN))_2(\mu$ $bpe)](CF_3SO_3)_2 \cdot 2CH_2Cl_2$, one benzylic carbon (C13) is disordered, and the occupancies for C13A and C13B were set at 0.5. The anisotropic displacement parameters for piperidyl atoms, N2 and C13B, were set equivalent to the better behaved N1 and C13A, respectively.

Results and Discussion

Synthesis. The synthesis of $(Pt(pip_2NCN))_2(\mu-pyz)^{2^+}$, $(Pt(pip_2NCN))_2(\mu-bpe)^{2^+}$, $(Pt(pip_2NCN))_2(\mu-bpa)^{2^+}$, and $(Pt(pip_2NCN))_2(\mu-bpy)^{2^+}$ is illustrated in Scheme 4.1. The platinum dimers were isolated in good yields (55-80%) as triflate or tetrafluoroborate salts and fully characterized by ¹H NMR spectroscopy and elemental analysis. Metathesis was accomplished by allowing Pt(pip_2NCN)Cl to react with a silver salt (*e.g.*, AgCF₃SO₃) at room temperature. After removal of silver chloride by filtration, 0.5 equivalents of pyz, bpe, bpa, or bpy were added to give $(Pt(pip_2NCN))_2(\mu-pyz)^{2^+}$, $(Pt(pip_2NCN))_2(\mu-bpe)^{2^+}$, $(Pt(pip_2NCN))_2(\mu-bpe)^{2^+}$, $(Pt(pip_2NCN))_2(\mu-bpe)^{2^+}$, $(Pt(pip_2NCN))_2(\mu-bpe)^{2^+}$, respectively.

The ¹H NMR spectra of $(Pt(pip_2NCN))_2(\mu-pyz)^{2+}$ (Figures 4.1), $(Pt(pip_2NCN))_2(\mu-bpe)^{2+}$ (Figures 4.2), $(Pt(pip_2NCN))_2(\mu-bpa)^{2+}$ (Figures 4.3), and $(Pt(pip_2NCN))_2(\mu-bpy)^{2+}$ (Figures 3.7) in CDCl₃ are qualitatively similar to those reported previously for platinum complexes with the pip₂NCN⁻ ligand.^{27,28} A general labeling scheme for non-equivalent protons (A-I) is shown for the bpe dimer in



(*i*) AgCF₃SO₃, pyrazine, acetone; (*ii*) AgCF₃SO₃, *trans*-1,2-bis(4-pyridyl)ethylene, acetone; (*iii*) AgCF₃SO₃, 1,2-bis(4-pyridyl)ethane, acetone; (*iv*) AgCF₃SO₃, 4,4'-bipyridine, acetone.

Scheme 4.1. Synthesis of
$$(Pt(pip_2NCN))_2(\mu-pyz)^{2+}$$
, $(Pt(pip_2NCN))_2(\mu-bpe)^{2+}$, $(Pt(pip_2NCN))_2(\mu-bpa)^{2+}$, and $(Pt(pip_2NCN))_2(\mu-bpy)^{2+}$.

Scheme 4.1. The ¹H NMR spectra of the dimers exhibit a doublet and triplet between 6.9 and 7.1 ppm due to the phenyl protons (A, B). The resonances near 4.4 ppm, arising from the benzylic protons (C), exhibit ¹⁹⁵Pt satellites with J_{H-Pt} values of 52 and 47 Hz for $(Pt(pip_2NCN))_2(\mu-pyz)^{2+}$ and $(Pt(pip_2NCN))_2(\mu-bpy)^{2+}$, respectively. The satellites appear as shoulders in the spectra of $(Pt(pip_2NCN))_2(\mu-bpe)^{2+}$ and $(Pt(pip_2NCN))_2(\mu-bpa)^{2+}$. Two characteristic multiplets between 2.9 and 4.1 ppm are attributable to the diastereotopic protons (D' and D'') of the α -carbons of the piperidyl

rings. Similarly, the aliphatic protons E and F are diastereotopic, accounting for the complexity of the splitting patterns further upfield. A set of pyridyl doublet resonances with equal intensities occurs downfield of 8.0 ppm (G, F) for $(Pt(pip_2NCN))_2(\mu-bpe)^{2+}$, $(Pt(pip_2NCN))_2(\mu-bpa)^{2+}$ and $(Pt(pip_2NCN))_2(\mu-bpy)^{2+}$, indicating that the two halves of the ligand are equivalent. In the case of the pyrazine bridged dimer,

 $(Pt(pip_2NCN))_2(\mu-pyz)^{2+}$, the bridging resonances appear as a singlet at 9.5 ppm. The bpe dimer exhibits a singlet at 8.0 ppm (I) attributable to the protons of the aliphatic bridge, and the bpa dimer exhibits a singlet at 3.27 ppm (I) attributable the protons of the olefin bridge. In CDCl₃, the latter resonance overlaps with a piperidyl CH₂ resonance (D).



Figure 4.1. ¹H NMR spectrum of $[(Pt(pip_2NCN))_2(\mu-pyz)](CF_3SO_3)_2$ in CDCl₃. Solvent and TMS resonances are labeled with *.



Figure 4.2. ¹H NMR spectrum of $[(Pt(pip_2NCN))_2(\mu-bpe)](CF_3SO_3)_2$ in CDCl₃. Solvent and TMS resonances are labeled with *.



Figure 4.3. ¹H NMR spectrum of $[(Pt(pip_2NCN))_2(\mu-bpa)](CF_3SO_3)_2$ in CDCl₃. Solvent and TMS resonances are labeled with *.

In CD₃OD solution, the ¹H NMR spectra of the dimers are qualitatively similar to those observed in deuterated chloroform. However, the ¹H NMR spectra of all four complexes indicate that the pyridyl ligands are partially dissociated (<10%) at room temperature. In CD₃CN solution, the dissociation is enhanced, and the NMR spectra clearly exhibit resonances associated with the dimers, $Pt(pip_2NCN)(L)^+$ (L=pyz, bpe, bpa, or bpy) and $Pt(pip_2NCN)(H_2O)^+$.³⁵ These results are consistent with strong the *trans*labilizing properties of the NCN⁻ ligand,^{28,36} which have recently been exploited in the design of main-chain reversible polymers.³⁷

Crystal Structures. The structures of the triflate salts of $(Pt(pip_2NCN))_2(\mu-pyz)^{2+}$ and $(Pt(pip_2NCN))_2(\mu-bpe)^{2+}$ were confirmed by single-crystal X-ray diffraction studies. ORTEP diagrams of the cations are shown in Figures 4.4 and 4.5, and relevant data are summarized in Tables 4.1 to 4.3. We previously reported the structure of [(Pt(pip_2NCN))_2(μ -bpy)](CF₃SO₃)₂ • $\frac{1}{2}$ (CH₃)₂CO (Figure 3.3) in Chapter 3.²⁸ To our knowledge, only a few platinum(II) pyrazine bridged dimer are structurally characterized.^{1,2,5} However, a monomer, a molecular triangle and a molecular square have been reported by Stang and coworkers.^{4,7,21,22} No unusual intermolecular interactions are present in crystals of the triflate salt of $(Pt(pip_2NCN))_2(\mu-pyz)^{2+}$, $(Pt(pip_2NCN))_2(\mu-bpe)^{2+}$ or $(Pt(pip_2NCN))_2(\mu-bpy)^{2+}$, and there is no evidence of water molecules in any of the crystals. For each complex, the pip_2NCN^2 ligand is tridentate. Each piperidyl ring adopts a chair conformation with the Pt atom occupying an equatorial site. As a result, the piperidyl rings are splayed away from the bridging ligands and do not appear to interfere with coordination to platinum. The plane of the pyridyl groups is approximately perpendicular to the platinum coordination plane, defined by the platinum


Figure 4.4. ORTEP diagram of [(Pt(pip₂NCN))₂(μ-pyz)](CF₃SO₃)₂. Anion and Hatoms are omitted for clarity.



Figure 4.5. ORTEP diagram of [(Pt(pip₂NCN))₂(μ-bpe)](CF₃SO₃)₂ • 2CH₂Cl₂. Anion, solvent, and H-atoms are omitted for clarity.

	[(Pt(pip ₂ NCN)) ₂ (µ-pyz)] (CF ₃ SO ₃) ₂	$[(Pt(pip_2NCN))_2(\mu-bpe)] \\ (CF_3SO_3)_2 \bullet 2CH_2Cl_2$
Pt(1)-C(1)	1 936(5)	1 910(12)
Pt(1)-N(1)	2.094(4)	2.096(11)
Pt(1)-N(2)	2.126(4)	2.132(10)
Pt(1)-N(3)	2.132(4)	2.164(10)
N(1)-C(7)	1.523(6)	1.550(15)
N(2)-C(13) ^a	1.526(6)	1.63(5)/1.56(5)
C(6)-C(7)	1.518(7)	1.460(19)
C(2)-C(13) ^a	1.516(7)	1.52(6)
Pt(2)-C(23)	1.922(5)	
Pt(2)-N(5)	2.099(4)	
Pt(2)-N(6)	2.098(4)	
Pt(2)-N(4)	2.144(4)	
N(5)-C(29)	1.523(6)	
N(6)-C(35)	1.530(6)	
C(24)-C(35)	1.519(7)	
C(28)-C(29)	1.503(7)	

Table 4.2. Selected Distances (Å) for $[(Pt(pip_2NCN))_2(\mu-pyz)](CF_3SO_3)_2$ and $[(Pt(pip_2NCN))_2(\mu-bpe)](CF_3SO_3)_2 \cdot 2CH_2Cl_2.$

^a C(13) is disordered for [(Pt(pip_2NCN))_2(μ -bpe)](CF₃SO₃)₂ • 2CH₂Cl₂.

	[(Pt(pip ₂ NCN)) ₂ (µ-pyz)] (CF ₃ SO ₃) ₂	$[(Pt(pip_2NCN))_2(\mu-bpe)] \\ (CF_3SO_3)_2 \bullet 2CH_2Cl_2$
C(1)-Pt(1)-N(1)	81 36(19)	81 7(5)
C(1)-Pt(1)-N(2)	80.77(19)	84.2(5)
C(1)-Pt(1)-N(3)	177.76(18)	178.3(5)
N(1)-Pt(1)-N(2)	162.07(16)	164.8(4)
C(7)-N(1)-Pt(1)	106.8(3)	106.5(7)
$C(13)-N(2)-Pt(1)^{a}$	104.7(3)	104.8(19)/108(2)
C(6)-C(7)-N(1)	109.0(4)	111.3(10)
C(2)-C(13)-N(2) ^a	108.9(4)	108(4)/108(3)
N(1)-Pt(1)-N(3)	96.45(16)	97.1(4)
N(2)-Pt(1)-N(3)	101.41(16)	97.1(4)
C(23)-Pt(2)-N(5)	82.71(19)	
C(23)-Pt(2)-N(6)	81.76(19)	
C(23)-Pt(2)-N(4)	178.70(19)	
N(5)-Pt(2)-N(6)	164.47(16)	
C(29)-N(5)-Pt(2)	107.4(3)	
C(35)-N(6)-Pt(2)	108.6(3)	
C(28)-C(29)-N(5)	110.4(4)	
C(24)-C(35)-N(6)	108.9(4)	
N(5)-Pt(2)-N(4)	97.96(16)	
N(6)-Pt(2)-N(4)	97.55(16)	

Table 4.3. Selected Angles (°) for $[(Pt(pip_2NCN))_2(\mu-pyz)](CF_3SO_3)_2$ and

 $[(Pt(pip_2NCN))_2(\mu-bpe)](CF_3SO_3)_2 \bullet 2CH_2Cl_2.$

^a C(13) is disordered for [(Pt(pip₂NCN))₂(µ-bpe)](CF₃SO₃)₂ • 2CH₂Cl₂.

and the four bonded ligand atoms, suggesting that potential binding groups built off the α -carbons of the pyridyl groups will be positioned above and below the platinum coordination plane. Thus, upon two-electron oxidation of the complexes, these groups are expected to bind to the metal, stabilizing the resulting octahedral platinum(IV) center.

The Pt-C and Pt-N(piperidyl) distances for $(Pt(pip_2NCN))_2(\mu-pyz)^{2+}$ (1.936(5), 1.922(5); 2.094 (4), 2.098(4), 2.099(4), 2.126(4)) and (Pt(pip2NCN))2(u-bpe)²⁺ (1.910(12); 2.096(11), 2.132(10) Å) are consistent with those of related complexes with the same tridentate ligand, Pt(pip₂NCN)Cl (1.910(4), 1.899(5); 2.094(3), 2.099(3), 2.101(4), 2.115(4) Å),²⁷ [Pt(pip₂NCN)(py)](CF₃SO₃) (1.920(4); 2.104(3), 2.092(3) Å), $[Pt(pip_2NCN)(4-phenylpyridine)](CF_3SO_3)(1.917(3); 2.103(3), 2.099(3) Å), and$ [(Pt(pip₂NCN))₂(µ-bpy)] (CF₃SO₃)₂ • ¹/₂(CH₃)₂CO (1.930(2); 2.124(2), 2.117(2) Å).²⁸ The Pt-N(pyz) distances for $(Pt(pip_2NCN))_2(\mu-pyz)^{2+}$ (2.132(4), 2.144(4)) agree with the distances observed for the structurally characterized triangle $(Pt(PMe_3)_2(\mu-pyz))_3^{6+}$ $(2.109-2.144 \text{ Å}).^4$ The Pt-N(bpe) distance for $(Pt(pip_2NCN))_2(\mu-bpe)^{2+}(2.164(10) \text{ Å})$ is longer than the Pt-N(bpe) distances observed for the triangle $(Pt(PMe_3)_2(\mu-bpe))_3^{6+}$ $(2.091-2.123 \text{ Å})^7$ or the square $(Pt(PMe_3)_2(\mu-bpe))_4^{8+} (2.092-2.138 \text{ Å}).^4$ The Pt-N(pyz or bpe) distances for $(Pt(pip_2NCN))_2(\mu-pyz)^{2+}$ and $(Pt(pip_2NCN))_2(\mu-bpe)^{2+}$ are significantly longer than the Pt-N(pyridyl) distances observed for pyridyl ligands trans to a weaker *trans*-directing ligand such as ethylenediamine ([(Pt(ethylene-1,2-diamine)(μ -bpy))₄]⁸⁺, 2.012, 2.013, 2.041, 2.044 Å),³⁸ but similar to those observed for a pyridyl ligand trans to the pip₂NCN⁻ ligand ([Pt(pip₂NCN)(py)](CF₃SO₃), 2.159 (3); [Pt(pip₂NCN)(4phenylpyridine)](CF₃SO₃), 2.143 (3); [(Pt(pip₂NCN))₂(µ-bpy)](CF₃SO₃)₂ • ¹/₂(CH₃)₂CO, 2.138 (4) Å)²⁸ or other relatively strong trans-directing groups such as phenyl anion

 $([(Pt(PEt_3)_2)_4(\mu-bpy)_2(anth)_2]^{4+}$ (anth=anthracene-1,8-diyl), 2.132(5), 2.138(6) Å;¹²

Pt((2,6-CH₂PPh₂)₂C₆H₃)(8-acetamidoquinolinato)⁺, 2.150(4) Å).³⁹ The bpe C=C distance (1.32(2) Å) is similar to those observed for the free ligand (bpe, 1.32 Å),⁴⁰ protonated bpe (bpeH₂²⁺, 1.33/1.34 Å),⁴¹ and *N*-methyl bpe (*N*-Me₂-bpe, 1.32 Å).⁴⁰

The N(piperidyl)-Pt-N(piperidyl) angles $((Pt(pip_2NCN))_2(\mu-pyz)^{2+}: 162.07(16),$ $164.47(16)^{\circ}$; (Pt(pip_NCN))₂(u-bpe)²⁺: 164.8(4)^o) substantially deviate from ideal *trans*coordination but are characteristic of platinum complexes with the pip₂NCN⁻ ligand $(Pt(pip_2NCN)(py)^+, 164.45(12); Pt(pip_2NCN)(4-phpy)^+, 164.12(11);$ $[(Pt(pip_2NCN))_2(\mu-bpy)](CF_3SO_3)_2 \cdot \frac{1}{2}(CH_3)_2CO, 162.4(2)^\circ)$. This deviation is attributed to the geometric preferences of the two five-membered chelate rings formed by the platinum and the pincer ligand.^{27,28,36,42} For $(Pt(pip_2NCN))_2(\mu-pyz)^{2+}$ and $(Pt(pip_2NCN))_2(\mu-bpe)^{2+}$, these five member rings are slightly puckered, resulting in displacement of the benzylic carbons above and below $((Pt(pip_2NCN))_2(\mu-pyz)^{2+}: 0.758,$ 0.646, 0.508, 0.530 Å; (Pt(pip₂NCN))₂(µ-bpe)²⁺: 0.603, 0.537 Å) the platinum coordination plane. These displacements are similar to those observed values for related compounds (0.113-0.744 Å).^{27,28} To accommodate this puckering, the planar phenyl ring is rotated slightly about the Pt-C bond, forming dihedral angles of 7.9/14.7° $((Pt(pip_2NCN))_2(\mu-pyz)^{2+})$ and 5.4° $((Pt(pip_2NCN))_2(\mu-bpe)^{2+})$ with the Pt coordination plane. As previously discussed in Chapter 2, the variability in these displacements (0.1-0.75 Å) and twist angles (5.4-14.7°) suggests the conformational energies of the complexes are not strongly influenced by variation of these parameters over modest ranges.^{27,28}

In crystals of $(Pt(pip_2NCN))_2(\mu-pyz)^{2+}$ and $(Pt(pip_2NCN))_2(\mu-bpe)^{2+}$, the planar pyz and pyridyl groups lie nearly perpendicular to the platinum coordination plane, forming dihedral angles of 83.3/89.8° and 85.2°, respectively. These angles are consistent with those observed for monomeric platinum pyridyl complexes with the pip_2NCN⁻ ligand (Chapters 2 and 3).^{27,28} Similar dihedral angles have been observed for the triangles $(Pt(PMe_3)_2(\mu-pyz))_3^{6+}$ (86.3-89.1°)⁴ and $(Pt(PMe_3)_2(\mu-bpe))_3^{6+}$ (77.5-87.0°),⁷ and the square $(Pt(PMe_3)_2(\mu-bpe))_4^{8+}$ (84.2-89.9°).⁴ The nearly perpendicular orientation of the pyridyl and phenyl groups is consistent with steric considerations, as well as electronic effects since the Pt-pyridine π -interactions do not directly compete with the Ptphenyl π -interactions.^{27,43,44}

Electrochemical Properties. To investigate the electronic structures of $(Pt(pip_2NCN))_2(\mu-pyz)^{2+}$, $(Pt(pip_2NCN))_2(\mu-bpa)^{2+}$, $(Pt(pip_2NCN))_2(\mu-bpa)^{2+}$, and $(Pt(pip_2NCN))_2(\mu-bpy)^{2+}$, cyclic voltammograms were recorded in methylene chloride solution (0.1 M TBAPF₆). As previously noted for $Pt(pip_2NCN)(py)^+$, the dimers do not oxidize at potentials less than 1.6 V. As also noted for $Pt(pip_2NCN)(py)^+$, $(Pt(pip_2NCN))_2(\mu-bpa)^{2+}$ does not reduce at potentials > -1.8 V. In contrast, the other three dimers undergo a nitrogen heterocycle ligand-centered reduction at potentials >-1.8 V. For example, $(Pt(pip_2NCN))_2(\mu-bpy)^{2+}$ is reversibly reduced at -1.22 V ($\Delta E_p=61 \text{ mV}$, $i_{pc}/i_{pa}=1.4$, 0.25 V/s, Figure 3.9).²⁸ A similar process has been assigned to a bipyridine-centered reduction in the cyclic voltammogram of $[(Pt(PEt_3)_2)_4(\mu-bpy)_2(anth)_2]^{4+}$ (-1.44 V vs. FcH/FcH⁺, $\Delta E_p=69 \text{ mV}$, 0.2 V/s, 0.1 M TBAPF₆ in CH₃CN).⁴⁵ In the case of $(Pt(pip_2NCN))_2(\mu-pyz)^{2+}$, a nearly reversible one-electron reduction is observed at -0.88 V ($\Delta E_p=66 \text{ mV}$, $i_{pc}/i_{pa}=1.4$, 0.25 V/s, Figure 4.6), and a second irreversible reduction



Figure 4.6. Cyclic Voltammogram of [(Pt(pip₂NCN))₂(μ-pyz)](CF₃SO₃)₂ in CH₂Cl₂/0.1 M TBAPF₆ vs. Ag/AgCl.



Figure 4.7. Cyclic Voltammogram of [(Pt(pip₂NCN))₂(μ-pyz)](CF₃SO₃)₂ in CH₂Cl₂/0.1 M TBAPF₆ vs. Ag/AgCl.

occurs at -1.5 V. For $(Pt(pip_2NCN))_2(\mu-bpe)^{2+}$, a nearly reversible one-electron bpecentered reduction is observed at -1.11 V ($\Delta E_p=80 \text{ mV}$, $i_{pc}/i_{pa}=1.3$, 0.25 V/s, Figure 4.7). In accord with this assignment, a bpe-centered reduction has previously been reported for $[(Pt(PEt_3)_2)_4(\mu-bpe)_2(anth)_2]^{4+}$ near -1.36 V vs. FcH/FcH⁺ ($\Delta E_n=67$ mV, 0.2 V/s, 0.1 M TBAPF₆ in CH₃CN).⁴⁵ The ligand-centered reduction potentials of the dimers follow the order: $(Pt(pip_2NCN))_2(\mu-pyz)^{2+}(-0.88 \text{ V}) > (Pt(pip_2NCN))_2(\mu-bpe)^{2+}(-1.11 \text{ V})$ > $(Pt(pip_2NCN))_2(\mu-bpy)^{2+}(-1.44 \text{ V}) > (Pt(pip_2NCN))_2(\mu-bpa)^{2+}(<-2.0 \text{ V})$. The relative potentials of the complexes with bpe, bpy and bpa are consistent with the free ligand reduction potentials of -1.80, -2.10, and >-2.3 V vs SCE (CH_2Cl_2 , 0.1 M TBAClO₄), respectively.⁴⁶ In contrast, the pyz-bridged complex is more easily reduced than expected from the free ligand reduction potential, indicating that the unoccupied lowest π^* level is strongly stabilized by the two acidic metal centers. Zulu and Lees observed a similar trend in the reduction potentials of a series of occurs at -1.5 V. For $(Pt(pip_2NCN))_2(\mu-bpe)^{2+}$, a nearly reversible one-electron bpe-centered reduction is observed at -1.11 V ($\Delta E_p = 80 \text{ mV}$, $i_{pc}/i_{pa} = 1.3$, 0.25 V/s, Figure 4.7). In accord with this assignment, a bpe-centered reduction has previously been reported for $[(Pt(PEt_3)_2)_4(\mu$ $bpe_{2}(anth)_{2}^{4+}$ near -1.36 V vs. FcH/FcH⁺ (ΔE_{p} =67 mV, 0.2 V/s, 0.1 M TBAPF₆ in CH₃CN).⁴⁵ The ligand-centered reduction potentials of the dimers follow the order: $(Pt(pip_2NCN))_2(\mu-pyz)^{2+}(-0.88 V) > (Pt(pip_2NCN))_2(\mu-bpe)^{2+}(-1.11 V) >$ $(Pt(pip_2NCN))_2(\mu-bpy)^{2+}(-1.44 \text{ V}) > (Pt(pip_2NCN))_2(\mu-bpa)^{2+}(<-2.0 \text{ V})$. The relative potentials of the complexes with bpe, bpy and bpa are consistent with the free ligand reduction potentials of -1.80, -2.10, and >-2.3 V vs SCE (CH₂Cl₂, 0.1 M TBAClO₄), respectively.⁴⁶ In contrast, the pyz-bridged complex is more easily reduced than expected from the free ligand reduction potential, indicating that the unoccupied lowest π^* level is strongly stabilized by the two acidic metal centers. Zulu and Lees observed a similar trend in the reduction potentials of a series of bridged tungsten carbonyl complexes ((OC)₅W(L)W(CO₅) in methylene chloride (0.1 M TBAClO₄): L = bpa (>-2.3 V) < bpy (-1.30 V) < bpe (-1.20 V) ~ pyz (-1.21 V vs SCE).⁴⁶ The relative stabilization is presumably greater for the platinum(II) dimers because of the relative π -acidities of the Pt(II) and W(0) metal centers.

Absorption Spectroscopy. Salts of $(Pt(pip_2NCN))_2(\mu-bpe)^{2+}$,

 $(Pt(pip_2NCN))_2(\mu-bpy)^{2+}$, and $(Pt(pip_2NCN))_2(\mu-bpa)^{2+}$ are colorless and dissolve in methylene chloride to give colorless solutions that absorb strongly in the UV region (Figure 4.8, Table 4.4). Salts of $(Pt(pip_2NCN))_2(\mu-pyz)^{2+}$ are yellow and dissolve to give vellow solutions. The UV absorption spectra of $(Pt(pip_2NCN))_2(\mu-bpe)^{2+}$, $(Pt(pip_2NCN))_2(\mu-bpa)^{2+}$ and $(Pt(pip_2NCN))_2(\mu-bpy)^{2+}$, in methylene chloride exhibit an intense feature near 280 nm (18000-32000 cm⁻¹M⁻¹). A similar but less intense absorption band was observed for Pt(pip₂NCN)X (X=Cl⁻, Br⁻, or I⁻; 8000-10000 cm⁻¹M⁻¹) and has been assigned to a spin-allowed transition with charge-transfer character involving the pip₂NCN ligand.²⁷ The absorptions bands for the dimers between 240 and 300 nm are more than twice the intensity of the halide complexes.²⁷ This result is consistent with the occurrence of pyridyl ligand-centered transitions in this region, as observed for the free bridging ligands (Table 4.4). Similar ligand-centered absorption bands have been identified in the spectra of rhenium and ruthenium dimers.⁴⁷⁻⁴⁹ Notably, $(Ru(NH_3)_5)_2(\mu-bpe)^{6+}$ exhibits an intense ligand-centered absorption at 324 nm (27500 $\text{cm}^{-1}\text{M}^{-1}$).⁴⁸ similar to that observed for (Pt(pip_2NCN))₂(µ-bpe)²⁺ (320 nm, 25000

Table 4.4. Reduction Potentials,^a Room-Temperature UV-Visible Absorption (CH₂Cl₂)data and 77 K Emission Data for $(Pt(pip_2NCN))_2(\mu-pyz)^{2+}$, $(Pt(pip_2NCN))_2(\mu-bpe)^{2+}$, $(Pt(pip_2NCN))_2(\mu-bpa)^{2+}$, and $(Pt(pip_2NCN))_2(\mu-bpy)^{2+}$.

Compound	Absorption λ_{max} , nm (ϵ , cm ⁻¹ M ⁻¹)	Emission λ_{max} , nm (fwhm, cm ⁻¹)		
		Glassy Solution	Solid-State ^d	' <i>E</i> °', V
$(Pt(pip_2NCN))_2(\mu-pyz)^{2+}$	258, 270, 315, ~368sh, ~410sh ^e	$\sim 510^{b,f}$	~550	-0.88
$(Pt(pip_2NCN))_2(\mu-bpe)^{2+}$	259 (24300), 276 (20400), 292sh (19500), 320 (25000)	580, 638, 706, 780 ^b	584, 642, 707, 780sh	-1.11
$(Pt(pip_2NCN))_2(\mu-bpy)^{2+}$	260 (30750), 277 (30100), 291sh (24800), 305sh (15800)	433, 458, 485sh, 520sh ^c	449, 479, 507, 550sh	-1.44
$(Pt(pip_2NCN))_2(\mu-bpa)^{2+}$	259 (31800), 276sh (18800), 292sh 8950)	638 (3600) ^b	650 (3800)	<-2.0
bpe	288 (31000), 298 (30200), 313 (18000), 335sh (~1600)	380, 405, 430sh ^b		
bpy	239 (15400), 270 (~6000)	410, 430, 455, 485sh ^c		
bpa	257 (3920), 264 (3050)	425 ^b		
pyz	256 (4400), 262 (4950), 267 (3300), 313 (650), 318 (600), 324 (550)	390, 400, 410, 420 ^b		

^a cyclic voltammograms were recorded in 0.1 M TBAPF₆/ CH₂Cl₂ at 0.25 V/s and referenced vs. Ag/AgCl; ^b 2:1 MeOH:2-MeTHF glassy solution; ^c 4:1 EtOH:MeOH glassy solution; ^d 77 K solid-state maxima for CF₃SO₃⁻ salts. ^e absorption maxima are reported for a 0.177 mM solution; maxima and intensities are concentration dependent. ^f $\lambda_{ex} = 300$ nm; the emission profiles are excitation wavelength dependent (see text).



Figure 4.8. Room temperature UV-visible absorption spectra in methylene chloride solution of (Pt(pip₂NCN))₂(μ-bpe)²⁺ (.....), (Pt(pip₂NCN))₂(μ-bpa)²⁺ (.....), (Pt(pip₂NCN))₂(μ-bpy)²⁺ (-...), and Pt(pip₂NCN)(py)⁺ (....).

cm⁻¹M⁻¹); (Ru(NH₃)₅)₂(μ -bpy)⁶⁺ exhibits an intense band at 290 nm (13500 cm⁻¹M⁻¹),⁴⁸ and a related transition may account for some of the intensity of the 277 nm band (30750 cm⁻¹M⁻¹) in the spectrum of (Pt(pip₂NCN))₂(μ -bpy)²⁺. Overall, the absorption profile of (Pt(pip₂NCN))₂(μ -bpa)⁺ is remarkably similar to that of Pt(pip₂NCN)(py)⁺,²⁸ with twice the molar absorptivity, as expected for only weak communication between the two Pt(pip₂NCN)(py)⁺ units. A similar observation has been made for (W(CO)₅)₂(μ -bpa) and W(CO)₅(4-Mepy) (4-Mepy=4-methylpyridine).⁵⁰⁻⁵²

At wavelengths longer than the pyridyl ligand bands, the complexes exhibit tailing absorption profiles, attributable to LF and spin-forbidden charge-transfer transitions. It also seems reasonable to anticipate relatively low-lying metal-to-ligand (pyridyl) charge –transfer (MLCT) transitions in the spectra of these complexes because of the low-lying pyridyl π^* level. Electrochemical measurements suggest the MLCT charge transfer energies should decrease along the ligand series: bpa > bpy > bpe. However, the ligand-centered π - π^* charge-transfer energies also decrease along this series and may obscure the MLCT bands.

While recording UV-visible absorption spectra of $(Pt(pip_2NCN))_2(\mu-pyz)^{2+}$, we noticed that the absorption profile is concentration dependent (Figure 4.9). These results prompted us to undertake a more detailed investigation. The UV/visible spectrum of a 0.177 mM CH₂Cl₂ solution of $(Pt(pip_2NCN))_2(\mu-pyz)^{2+}$ exhibits a pair of intense absorptions at 258 and 270 nm, with apparent molar absorptivities of 24900 and 20800 cm⁻¹M⁻¹, respectively. Similar features are observed in the spectra of the other dimer complexes. An absorption band also occurs at 315 nm with apparent molar absorptivity of 9500 cm⁻¹M⁻¹, and shoulders at 368 and 410 nm. These bands cannot be reasonably

attributed to ligand-centered transitions, since the free and protonated bridging ligand (Table 4.4; $pyzH_2^{2^+}$ in EtOH: ~305 nm, ~1000 cm⁻¹M⁻¹, H₂O/H₂SO₄, pH=0.6)⁵³ only absorbs weakly in this region. A more reasonable interpretation is that these transitions have considerable metal-to-ligand (pyz) charge-transfer character in keeping with the notion of a low-lying pyz π^* level. The blue shift of these transitions with respect to that observed for (Ru(NH₃)₅)₂(μ -pyz)⁴⁺ (547 nm, 30000 cm⁻¹M⁻¹)⁵⁴ is consistent with the relative energies of MLCT states in Pt(II) and Ru(II) complexes. For example, the lowest spin-allowed MLCT band for Pt(2,2'-bipyridine)Cl₂ (390 nm, DMF),⁵⁵ is shifted by 7600 cm⁻¹ to the blue of that observed for Ru(2,2'-bipyridine)Cl₂ (553 nm, DMF).⁵⁶ In the case of (Pt(pip₂NCN))₂(μ -pyz)²⁺, there are four possible 5d- π^* spin-allowed MLCT transitions, though only three are formally allowed by symmetry.⁵⁷

Whereas $(Pt(pip_2NCN))_2(\mu$ -bpe)²⁺, $(Pt(pip_2NCN))_2(\mu$ -bpa)²⁺, and

 $(Pt(pip_2NCN))_2(\mu-pyz)^{2+}$ are dimers in the solid state and in methylene chloride solution, $(Pt(pip_2NCN))_2(\mu-pyz)^{2+}$ partially dissociates in CH₂Cl₂, as indicated by non-Beer's law behavior. Figure 4.9 shows UV-visible absorption spectra of $(Pt(pip_2NCN))_2(\mu-pyz)^{2+}$ for concentrations ranging from 0.177 mM to 0.007 mM. As the Pt concentration decreases, the apparent molar absorptivity of the 315 nm band decreases and that of the 258 nm band increases (Figure 4.9). The data are consistent with the reaction of $(Pt(pip_2NCN))_2(\mu-pyz)^{2+}$ with adventitious water to form $Pt(pip_2NCN)(pyz)^+$ and $Pt(pip_2NCN)(H_2O)^+$ (equation 1):

$(Pt(pip_2NCN))_2(\mu-pyz)^{2+} \longrightarrow Pt(pip_2NCN)(pyz)^{+} + Pt(pip_2NCN)(H_2O)^{+}$ (1)

At low concentrations dissociation is enhanced.⁵⁸ The intensity of the 315 nm band associated with the dimer decreases, whereas the intensity of the 260 nm band increases,



Figure 4.9. Apparent molar absorbtivity of [(Pt(pip₂NCN))₂(μ-pyz)](BF₄)₂ in CH₂Cl₂ recorded with decreasing concentration: 1.77x10⁻⁴, 8.85x10⁻⁵, 3.54x10⁻⁵, 1.77x10⁻⁵, and 7.08x10⁻⁶ M. Inset: titration of [(Pt(pip₂NCN))₂(μ-pyz)](BF₄)₂ (100 ml of 8.85 x10⁻⁵ M) with 45 μL aliquots (~0.5 equivalents) of pyrazine (0.1 M) bridging ligand. Free pyrazine only absorbs very weakly at λ > 275 nm (ε≤600 cm⁻¹M⁻¹).

presumably because of the hypsochromic shift of the metal-to-ligand(pyz) charge-transfer transitions. In support of this analysis, titration of a solution of $(Pt(pip_2NCN))_2(\mu-pyz)^{2+}$ with pyz increased dissociation, as indicated by a gradual decrease in intensity of the 315 nm band and an increase in the intensity of the 260 nm band (Figure 4.9 inset).

Emission Spectroscopy. Solid samples of salts of $(Pt(pip_2NCN))_2(\mu-bpy)^{2+}$ exhibit yellow-green emission when irradiated with UV light at room temperature, whereas salts of $(Pt(pip_2NCN))_2(\mu-bpa)^{2+}$ and $(Pt(pip_2NCN))_2(\mu-bpe)^{2+}$ exhibit weak red emission. In contrast, salts of $(Pt(pip_2NCN))_2(\mu-pyz)^{2+}$ exhibit remarkably intense yellow emission at room temperature. To investigate the origin of these different colored emissions, spectra of solid and dilute glassy solution samples (4:1 EtOH:MeOH and/or 2:1 MeOH:2-MeTHF) of the dimers were recorded at 77 K (Figure 4.10, Table 4.4). Dilute and concentrated frozen solution and solid-state emission profiles of $(Pt(pip_2NCN))_2(\mu-bpe)^+$, $(Pt(pip_2NCN))_2(\mu-bpa)^+$, and $(Pt(pip_2NCN))_2(\mu-bpy)^+$ are in good agreement and excitation independent, indicating that monomeric complexes or aggregates are not responsible for the observed spectra. However, frozen solution and solid-state emission profiles of $(Pt(pip_2NCN))_2(\mu-pyz)^{2+}$ are excitation dependent.

The intense structured emission from glassy solution samples of $(Pt(pip_2NCN))_2(\mu-bpy)^+$ is characteristic of a lowest ligand centered $\pi-\pi^*$ excited state (Figures 4.10 and 3.11) as previously discussed.²⁸ The vibronic spacings are in excellent agreement with those of the free ligand emission, however the origin of the band is shifted to lower energy by about 1000 cm⁻¹ (Figure 3.11). Similarly, the bandshape and Frank-Condon Factors, as indicated by the Huang-Rhys ratio⁵⁹ (I_{1,0}/I_{0,0} = 1.3) are distinctively different from those of the free ligands (0.9) and indicative of metal

coordination.⁶⁰⁻⁶² The excitation spectrum of $(Pt(pip_2NCN))_2(\mu$ -bpy)⁺ is in good agreement with the absorption spectrum, and the emission decay for $(Pt(pip_2NCN))_2(\mu$ -bpy)⁺ in the solid state is adequately modeled as a single exponential decay (τ , 1600 µs).

Excitation of glassy solutions of $(Pt(pip_2NCN))_2(\mu-bpa)^{2+}$ at 300 nm results in a broad, low energy and Gaussian-shaped emission centered near 640 nm with a full-width at half maximum (fwhm) of 3600 cm^{-1} . In the solid state, the emission maximum (650 nm) is shifted to slightly longer wavelength. The band exhibits a large Stokes shift from the intense absorption features. Overall, the emission is very similar to that observed for $Pt(pip_2NCN)(py)^+$ (650 nm, fwhm=3700 cm⁻¹, 4:1 EtOH:MeOH) which has previously been assigned to a lowest ³LF state, ²⁸ and a similar assignment is made here. In the excitation spectrum, a weak band is resolved at 367 nm, similar to that observed for $Pt(pip_2NCN)(py)^+$ (365 nm).²⁸ In the case of solid samples of $Pt(pip_2NCN)(py)^+$, the emission maximum was found to be slightly excitation dependent (λ_{ex} =300 λ_{max} =680; λ_{ex} =355, λ_{max} =694) due to pyridine ligand substitution.²⁸ In contrast, emission from $(Pt(pip_2NCN))_2(\mu-bpa)^{2+}$ is not discernibly excitation dependent under these conditions. Since partial ligand dissociation is expected for the dimer, the apparent absence of excitation dependence is likely related to formation of a relatively weakly emitting solvated complex, as well as $Pt(pip_2NCN)(\mu-bpa)^+$, which is expected to exhibit an emission similar to the dimer. The emissions from $(Pt(pip_2NCN))_2(\mu-bpa)^{2+}$ in the solid state and 77 K glassy solution (excitation at 355 and 420 nm) were too weak for lifetime measurements.



Figure 4.10.77 K emission spectra in 2:1 MeOH:2-MeTHF $((Pt(pip_2NCN))_2(\mu-pyz)^{2+}$ $(---), (Pt(pip_2NCN))_2(\mu-bpe)^{2+} (\dots), (Pt(pip_2NCN))_2(\mu-bpa)^{2+} (\dots))$ or 4:1 ethanol:methanol $((Pt(pip_2NCN))_2(\mu-bpy)^{2+} (---))$ glassy solution.Intensities have been arbitrarily scaled.

Excitation of glassy solutions of $(Pt(pip_2NCN))_2(\mu-bpe)^{2+}$ at 300 or 375 nm results in a low energy structured emission with maxima at 580, 638, 706, and 780 nm. The structured emissions clearly originate from the lowest bpe-centered π - π * excitedstate of the bridging ligand. The 1300-1600 cm⁻¹ spacings of the vibronic progression are in excellent agreement with those of free ligand emission, however the maxima are shifted to lower energy by approximately 600 cm⁻¹ (77 K butyronitrile; 558, 608, 666 nm).⁶³ The emission occurs at the same energy with similar Frank-Condon Factors, as indicated by the Huang-Rhys ratio⁵⁹ (I_{1,0}/I_{0,0} = ~1), when 77 K solid state or 77 K glassy solution samples (2:1 MeOH:2-MeTHF and 4:1 EtOH:MeOH) are excited at 300, 350, or 375 nm. The emissions from (Pt(pip_2NCN))₂(μ -bpe)²⁺ in the solid state and 77 K glassy solution (excitation at 355 and 420 nm) were too weak for lifetime measurements.

Excitation of 77 K glassy solutions samples of $[Pt(pip_2NCN))_2(\mu-pyz)^{2+}](BF_4)_2$ at 300 nm results in a broad and very intense emission at ~510 nm (Figure 4.12). The solidstate emission maximum is shifted to longer wavelengths (Figure 4.11). In both cases the emission maximum is excitation dependent. For example, the 77 K solid-state emission maximum occurs at 550 and 568 nm for excitation wavelengths of 300 and 430 nm, respectively (Figure 4.11). For 430 nm excitation, the resulting emission band can be adequately fit with one Gaussian function (λ_{max} =565 nm, FWHM=2250 cm⁻¹); however for 300 nm excitation, two Gaussian functions are required to model the emission (λ_{max} =549 nm, FWHM=1900 cm⁻¹, λ_{max} =640 nm, FWHM=2200 cm⁻¹). When 77 K glassy solution (2:1 MeOH:2-MeTHF) samples of [(Pt(pip_2NCN))_2(\mu-pyz)](BF_4)_2, are excited at 375 nm, the emission can be reasonably modeled with one Gaussian function



Figure 4.11. 77 K solid state emission spectra of [(Pt(pip₂NCN))₂(μ-pyz)](BF₄)₂ showing dependence on excitation wavelength. At excitation wavelengths of 300 (— —), 380 (……) and 430 nm (——), the emission maxima are 550, 561, and 568 nm, respectively. Intensities have been arbitrarily scaled.

 $(\lambda_{max}=505 \text{ nm}, \text{FWHM}=5200 \text{ cm}^{-1})$. As the excitation wavelength is tuned from 375 to 300 nm, a low energy shoulder emerges (Figure 4.12), and two Gaussian functions are required to fit the resulting spectrum ($\lambda_{max}=502 \text{ nm}, \text{FWHM}=5200 \text{ cm}^{-1}, \lambda_{max}=640 \text{ nm}, \text{FWHM}=3800 \text{ cm}^{-1}$; Figure 4.13). In addition, excitation between 300 and 325 nm results in a weak, highly structured emission near 400 nm (Figure 4.12). The accumulated data are suggestive of three different emitting species. One absorbs at wavelengths as long as 430nm, whereas the other two absorb comparatively weakly at wavelengths \geq 375 and \geq 325 nm, respectively. The dependence of the emission maximum on excitation wavelength is consistent with variations in the contributions of the two emitting species to the overall spectrum.

The excitation dependence of the 77 K glassy solution emission spectrum is consistent with the tendency of the pyrazine dimer to dissociate in solution, most likely forming Pt(pip₂NCN)(pyz)⁺ and Pt(pip₂NCN)(H₂O)⁺ (eqn 1). The long wavelength component of the emission from glassy solution samples of (Pt(pip₂NCN))₂(μ -pyz)²⁺, is almost coincident with the ³LF emissions of Pt(pip₂NCN)(py)⁺ (650 nm, FWHM=3700 cm⁻¹) and Pt(pip₂NCN)(H₂O)⁺ (λ_{max} =634 nm, FWHM=3700 cm⁻¹). Though we have not been able to prepare pure samples of Pt(pip₂NCN)(pyz)⁺ and directly characterize its emission properties, we anticipate that the crystal field splitting for this complex will be similar to that of Pt(pip₂NCN)(py)⁺. Therefore, the observed long-wavelength emission most likely originates from the dissociation products (Pt(pip₂NCN)(pyz)⁺ and Pt(pip₂NCN)(H₂O)⁺). In support of this assignment, the lowest energy feature in the excitation spectra of Pt(pip₂NCN)(H₂O)⁺ and Pt(pip₂NCN)(py)⁺ occur at 365 and 370 nm, respectively. On the other hand, the weak, structured emission at 400 nm that results



Figure 4.12. 77 K glassy solution emission (2:1 MeOH:2-MeTHF) spectra of $(Pt(pip_2NCN))_2(\mu-pyz)^{2+}$ showing the dependence of the emission on excitation wavelength: $\lambda_{ex}=300$ (.....), 325 (---), 350 (---), and 375 nm (----). Intensities have been arbitrarily scaled. * denotes emission maxima for free pyrazine.



Figure 4.13. 77 K glassy solution emission (2:1 MeOH:2-MeTHF) spectrum of $(Pt(pip_2NCN))_2(\mu-pyz)^{2+}, \lambda_{ex} = 300 \text{ nm} (----), \text{ fitted spectrum (-----)},$ Gaussian fit of 500 nm component (----) and Gaussian fit of 640 nm component (----) emission. Intensities have been arbitrarily scaled. * denotes emission maxima for free pyrazine.

from 300-325 nm excitation is characteristic of free pyrazine, indicating that $Pt(pip_2NCN)(pyz)^+$ further dissociates as observed for $Pt(pip_2NCN)(py)^+$ (Figure 3.12).²⁸ Upon excitation at longer wavelengths where pyrazine does not strongly absorb (*e.g.*, 350 nm), the structured pyrazine emission is no longer observed.

The broad intense emission centered near 510 nm arises from the $(Pt(pip_2NCN))_2(\mu-pyz)^{2+}$ dimer, which absorbs at wavelengths as long as 430 nm. The predominantly spin-forbidden character of the emission was confirmed by luminescence decay measurements. Emission decay traces from 77 K solid-state samples of the BF₄⁻ and CF₃SO₃ salts excited at 355 nm could not be adequately modeled with a single exponential function, but required a biexponential function to obtain a reasonable fit (2, 4 μ s). This result is consistent with partial ligand substitution in the solid state, as previously suggested for [Pt(pip₂NCN)(py)](CF₃SO₃);²⁸ therefore, in addition to the dimer, $Pt(pip_2NCN)(pyz)^+$ and $Pt(pip_2NCN)(H_2O)^+$ likely contribute to the emission decay. Interestingly, decay traces for solid $[(Pt(pip_2NCN))_2(\mu-pyz)](CF_3SO_3)_2$ excited at 420 nm were adequately modeled by a single-exponential function (3 µs), as would be expected for selective excitation of the dimer. Qualitatively, the emission is much more intense than the ³LF and ³ π - π * emissions previously observed for this class of complexes. and neither of these assignments is appealing. The emission maximum ($\sim 20000 \text{ cm}^{-1}$) occurs at significantly higher energies than those observed for complexes with lowest ³LF excited states (e.g., Pt(pip_2NCN)Cl, 14200 cm⁻¹; Pt(pip_2NCN)(py)⁺, 15400 cm⁻¹).^{27,28} In addition, the emission onset is shifted by ~2000 cm⁻¹ to lower energy of the free ligand n- π^* emission, and the band lacks the structure expected for a ${}^{3}\pi$ - π^* pyrazine-centered emission.^{64,65} The lifetime also is significantly shorter than observed for related

complexes with the lowest pyridyl-centered those with lowest ${}^{3}\pi$ - π * excited states (*e.g.*, Pt(pip₂NCN))(μ -bpy)²⁺, 0.16 ms).²⁸ These data are consistent with a significantly faster rate of excited-state radiative decay (k_r) for the pyz dimer, as expected for increased involvement of the heavy metal center in the transition. For these reasons and bearing in mind that both electrochemical and UV-visible absorption measurements point to stabilization of the pyrazine π * level as compared to the pyridyl complexes, we tentatively assign the 510 nm emission of the dimer as having significant MLCT character.

The emission properties of this series of dimers suggest the intriguing notion that it is possible to tune between the lowest ${}^{3}LF$, ${}^{3}\pi$ - π *, and ${}^{3}MLCT$ states of $((Pt(pip_2NCN))_n(L)^{n+})$ complexes (n = 1,2) by careful selection of L. The observation of ³MLCT emission from the pyrazine dimer suggest the lowest ³LF and ³ π - π * states for this complex lie at higher energies than the emission onset ($\sim 25000 \text{ cm}^{-1}$). This conclusion is in reasonable agreement with our previous suggestion that the lowest ³LF state for $Pt(pip_2NCN)(4-phpy)^+$ is >23500 cm⁻¹. At present, the orbital character of the emissive MLCT state is uncertain. However, it is noteworthy that this emission is more intense than the relatively weak pyridyl ${}^{3}\pi$ - π * emissions observed for related complexes. This situation contrasts with observations for platinum(II) diimine and terpyridyl complexes, which tend to exhibit π - π * and MLCT emissions with comparable intensities and lifetimes within roughly an order of magnitude of one another.^{60,61,66} In the case of the platinum(II) pip₂NCN⁻ complexes with lowest pyridyl-centered excited states, the emissions are only weakly perturbed from those of the free ligand, and the lifetimes tend to be longer than those of platinum(II) diimine and terpyridyl complexes. These results

are consistent with complexes such as $(Pt(pip_2NCN))_2(\mu-bpy)^{2+}$, $(Pt(pip_2NCN))_2(\mu-bpe)^{2+}$ and $Pt(pip_2NCN)(phpy)^+$ having relatively pure lowest intraligand excited states. The relatively intense emission from the pyrazine dimer is consistent with an orbitally allowed excited state, possibly associated with a lowest $d_{xy} \rightarrow \pi^*$ transition, which is expected to have a large transition dipole from overlap considerations (Figure 4.14).



Figure 4.14. Diagram showing orientation of x, y and z axes with respect to the pyrazine dimer.

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with dilution. Also, $Pt(pip_2NCN)(H_2O)^+$ exhibits absorption maxima at 258, 277, and 294 nm, and only absorbs weakly near 315 nm. Thus, these data are consistent with the 315 nm charge transfer band of $(Pt(pip_2NCN))_2(\mu-pyz)^{2+}$ occurring at longer wavelengths than that of $Pt(pip_2NCN)(pyz)^+$ (<315 nm).

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CHAPTER 5:

Synthesis and Structural Characterization of Platinum(II) Terpyridyl Complexes with Aryl Ligands.

Introduction

Since the synthesis of Pt(tpy)Cl⁺ by Morgan and Burstall,¹ the spectroscopic and photophysical properties of platinum(II) terpyridyl complexes have received considerable attention.²⁻¹⁸



It is well established that these complexes have a tendency to associate in fluid solution, frozen solution, and the solid state by intermolecular ligand...ligand and/or metal...metal interactions.⁸⁻¹⁸ These interactions often dramatically affect the electrochemical properties of these complexes^{19,20} and their spectroscopy, as indicated by variations in the orbital character of the lowest emissive excited state. For example, the first reduction process for Pt(tpy)Cl⁺ appears as a broadened wave in the cyclic voltammogram because of the presence of monomers and (Pt(tpy)Cl)₂²⁺ dimers in solution.¹⁹ In addition it has been suggested that the short fluid solution lifetimes of platinum(II) terpyridyl complexes are, in part, a consequence of exciplex formation, involving attack of Lewis bases (*e.g.*, solvent) at the open axial coordination sites of a complex having significant metal-to-

ligand charge-transfer character.⁵ For example, $Pt(tpy)Cl^+$ exhibits exceedingly week emission in room temperature fluid solution ($\lambda_{max} = 500 \text{ nm}$ in CH_2Cl_2 , $\tau < 10 \text{ ns}$).²¹ McMillin and coworkers have recently shown that 4' substitution of the terpyridyl ligand or replacement with the php ligand can dramatically increase the emission lifetime,^{3,4,22} presumably because of increased intraligand charge-transfer character of the lowest excited state and concomitant decreased electrophilicity of the metal center.^{5,23}

To investigate the influence of intermolecular interactions on the properties of platinum(II) terpyridyl complexes, we have prepared eight platinum(II)-terpyridyl complexes with aryl ligands (L) and having the general formula $Pt(R-tpy)(L)^+$ (R=H, Ph). The synthesis and characterization of these complexes are described in this chapter, whereas their electrochemical and spectroscopic properties are discussed in Chapters 6 and 7, respectively. For four of these complexes (L=2,6-dimethylphenyl (2,6-dmph) or mesitlyene (mes)), methyl groups directed above and below the platinum square plane are expected to hinder intermolecular interactions that occur through the axial sites. For the remaining four complexes (L=Ph or 3,5-dimethylphenyl (3,5-dmph)), the platinum center is relatively exposed. Therefore, these eight complexes present the opportunity to gauge the significance of open coordination sites on the electronic properties of platinum(II) terpyridyl complexes.

Experimental: K₂PtCl₄ was obtained from Pressure Chemical. 1,5cyclooctadiene (COD), 2-mesitylmagnesium bromide (MesMgBr), 2,6dimethylphenylmagnesium bromide (2,6-dmphMgBr), 3,5-dimethylphenylmagnesium bromide (3,5-dmphMgBr), 2,2':6',2"-terpyridine (tpy), and SnMe₃Ph were obtained from Aldrich. Spectroscopic grade methanol and all other reagents were purchased from Acros. Ethanol was distilled from zinc metal and potassium hydroxide, and THF was distilled from sodium and benzophenone. Pt(COD)Cl₂ was prepared as reported in Chapter 2.²⁴ Argon was dried using activated sieves and trace oxygen was removed with activated R3-11 catalyst from Schweizerhall.

¹H NMR spectra were recorded at room temperature using a Bruker AC 250 MHz instrument. Deuterated solvents, CDCl₃ (0.03 % tetramethylsilane (TMS) (v/v)) and d₆-DMSO, were purchased from Cambridge Isotope Laboratories. Proton resonances were assigned with the aid of decoupling experiments. Mass spectra were recorded using a Micromass Q-TOF hybrid quadropole time of flight mass spectrometer with electrospray ionization. Elemental analysis was performed by Atlantic Microlabs (Norcross, GA).

3-phenyl-1,5-bis(2-pyridyl)-1,5-pentanedione. The synthesis of this compound was originally reported by Constable and coworkers.^{25,26} Solutions of 2-acetylpyridine (4.2 ml, 0.037 mol) and benzaldehyde (2.0 ml, 0.019 mol) were each dissolved in 30 ml of a NaOH solution (2 g NaOH dissolved in 25 ml H₂O and 35 mL EtOH). The two colorless solutions were combined and the resulting light orange solution was stirred for two hours. The white precipitate was collected and washed with ethanol (100 ml). Additional crops can be obtained by adding distilled water to the deep orange filtrate.

4-phenyl-2,2':6',2''-terpyridine (phtpy). The synthesis of this compound was originally reported by Whitesides and coworkers.^{25,26} A sample of 3-phenyl-1,5-bis(2-pyridyl)-1,5-pentanedione (1 g, 3.0 mmol) was dissolved in ethanol (30 ml), and $NH_4CH_3CO_2$ (2.30 g, 30 mmol) was added to the solution. After refluxing for 2 hours, the yellow solution was cooled to -25°C, and the resulting pale yellow precipitate was
collected by vacuum filtration. Distilled water was added to the filtrate to precipitate additional crops of the product. ¹H NMR (CDCl₃): 7.35 (2H, m, CH); 7.47 (3H, m, CH); 7.88 (4H, m, CH); 8.70 (6H, m, CH).

Pt(COD)(Ph)Cl. The synthesis of this compound was originally reported by Eaborn and coworkers.²⁷ A sample of Pt(COD)Cl₂ (1.0 g, 2.7 mmol) was dissolved in CH₂Cl₂ (40 ml), and bubbled degassed with Ar for ~5 minutes. SnMe₃Ph (0.5 ml, 2.7 mmol) was added to the solution before refluxing for ~18 hours. The solvent was removed by roto-evaporation. The oily residue was dissolved in CHCl₃, and hexanes were added to induce precipitation. Yield: 0.72 g, 61 %. ¹H NMR (CDCl₃): 2.3-2.7 (8H, m, CH₂); 4.61 (2H, m with Pt satellites, J_{H-Pt} =78 Hz, CH); 5.82 (2H, m with Pt satellites, J_{H-Pt} =34 Hz, CH); 6.94 (1H, t, CH); 7.09 (2H, m, CH): 7.25 (2H, m, CH).

Pt(COD)(mes)Cl. The synthesis of this compound was originally reported by Whitesides and coworkers.²⁸ A solution of MesMgBr (16 ml of a 1.0 M solution in THF, 16.0 mmol) was added to a -70°C mixture of Pt(COD)Cl₂ (1.0 g, 2.7 mmol) in THF (150 ml). The cloudy mixture was allowed to slowly warm to room temperature over 4 hours, during which the solid dissolved and the solution turned yellow. The reaction was quenched with concentrated aqueous NH₄Cl (50 ml). The THF layer was collected, and the water layer was extracted with diethyl ether (2 x 75 ml). The combined organic layers were dried over MgSO₄, filtered and roto-evaporated to dryness. The yellow residue was dissolved in CHCl₃, and hexanes were added to induce precipitation. Yield: 1.0 g, 89 %. ¹H NMR (CDCl₃): 2.20-2.50 (17H, m, CH₂ and CH₃); 4.44 (2H, m with Pt satellites, J_{H-Pt} =72 Hz, CH); 5.78 (2H, m with Pt satellites, J_{H-Pt} =39 Hz, CH); 6.69 (2H, s, CH).

Pt(COD)(**3,5-dmph**)₂. A solution of 3,5-dmphMgBr (32 ml of a 0.5 M solution in THF, 16.2 mmol) was added to a -70°C mixture of Pt(COD)Cl₂ (1.0 g, 2.7 mmol) in THF (80 ml), and the mixture was allowed to slowly warm to room temperature over 4 hours. The reaction was quenched with concentrated aqueous NH₄Cl (15 ml). The THF layer was collected, and the water layer was extracted with diethyl ether (2 x 50 ml). The combined organic layers were dried over MgSO₄, filtered and roto-evaporated to dryness. The yellow residue was dissolved in CHCl₃, and hexanes were added to induce precipitation. Yield: 1.20 g, 87 %. Anal. Calcd. for C₂₄H₃₀Pt: C, 56.13; H, 5.89. Found: C, 56.06; H, 5.90; ¹H NMR (CDCl₃): 2.17 (12H, s, CH₃); 2.50 (8H, m, CH₂); 5.06 (4H, m with Pt satellites, J_{H-Pt} =38 Hz, CH); 6.46 (1H, s, CH); 6.89 (2H, s with Pt satellites, J_{H-Pt} =70 Hz, CH).

Pt(COD)(**3,5-dmph)Cl**. Concentrated HCl (16 μl, 0.19 mmol) was added to a solution of Pt(COD)(3,5-dmph)₂ (0.1 g, 0.19 mmol) in acetone (30 ml). After stirring for 30 min, the solution was roto-evaporated to dryness. The white solid was dissolved in CH₂Cl₂, and hexanes were added to induce precipitation. Yield: 0.080 g, 93%. Anal. Calcd. for C₁₆H₂₁PtCl: C, 43.29; H, 4.77. Found: C, 42.68; H, 4.70; ¹H NMR (CDCl₃): 2.23 (6H, s, CH₃); 2.30-2.73 (8H, m, CH₂); 4.61 (2H, m with Pt satellites, J_{H-Pt} =76 Hz, CH); 5.79 (2H, m with Pt satellites, J_{H-Pt} =25 Hz, CH); 6.59 (1H, s, CH); 6.84 (2H, s, with Pt satellites, J_{H-Pt} =40 Hz, CH).

Pt(COD)(2,6-dmph)Cl. Prepared by the same procedure as Pt(COD)(3,5-dmph)₂, substituting the appropriate starting materials. 16 ml of 1.0 M 2,6-dmphMgBr in THF (16.2 mmol). Yield: 0.936 g, 79%. Anal. Calcd. for $C_{16}H_{21}$ PtCl • ¹/₂ CHCl₃: C, 39.43; H, 4.11. Found: C, 39.55; H, 4.34; ¹H NMR (CDCl₃): 2.20-2.70 (14H, m, CH₂ and CH₃); 4.43 (2H, m with Pt satellites, $J_{\text{H-Pt}}$ =74 Hz, CH); 5.79 (2H, m with Pt satellites, $J_{\text{H-Pt}}$ =31 Hz, CH); 6.83 (3H, m, CH).

[Pt(tpy)(Ph)](BF₄) (1a(BF₄⁻)). A mixture of silver tetrafluroborate (0.054 g, 0.229 mmol) and Pt(COD)(Ph)Cl (0.10 g, 0.229 mmol) in 30 mL of acetone was allowed to stir for 30 minutes at room temperature. The resulting AgCl precipitate was removed by vacuum filtration through Celite. After addition of tpy (0.045 g, 0.229 mmol) the solution was allowed to stir overnight in the dark. The acetone solution was roto-evaporated to dryness, and the residue was dissolved in a minimum of CH₃CN (~ 20 ml). Diethyl ether (75 ml) was added to precipitate the product as a yellow solid. Yield: 0.094 g, 69%. Analytical samples were prepared by cooling an acetonitrile/ether mixture to – 25 °C. Anal. Calcd. for [C₂₄H₂₂N₃Pt](BF₄) • 2H₂O: C, 40.15; H, 3.21; N, 6.69. Found: C, 40.30; H, 2.87; N, 6.88. MS (ESI): m/z = 505.100 (1a). ¹H NMR (d₆-DMSO): 7.11 (1H, t, CH); 7.24 (2H, t, CH); 7.53 (2H, d, CH); 7.84 (2H, t, CH); 8.34 (2H, d with Pt satellites, *J*_{H-Pf}=49 Hz, CH); 8.47 (2H, t, CH); 8.66 (5H, m, CH).

[Pt(phtpy)(Ph)](BF₄) (1b(BF₄⁻)). Prepared by the same procedure as 1a(BF₄⁻), substituting the appropriate starting materials. Silver tetrafluroborate (0.054 g, 0.229 mmol), Pt(COD)(Ph)Cl (0.10 g, 0.229 mmol) and phtpy (0.071 g, 0.229 mmol). Yield: 0.112 g, 73%. Anal. Calcd. for [C₂₄H₂₂N₃Pt](BF₄) • 2H₂O: C, 46.04; H, 3.43; N, 5.97. Found: C, 46.32; H, 3.00; N, 6.25. MS (ESI): m/z = 581.127 (1b). ¹H NMR (d₆-DMSO): 7.11 (1H, t, CH); 7.23 (2H, t, CH); 7.50 (2H, m, CH); 7.65 (3H, m, CH); 7.81 (2H, t, CH); 8.16 (2H, d, CH); 8.30 (2H, d, CH); 8.45 (2H, t, CH); 8.85 (2H, d, CH); 9.05 (2H, s, CH).

[Pt(tpy)(3,5-dmph)](BF₄) (2a(BF₄⁻)). Prepared by the same procedure as 1a(BF₄⁻), substituting the appropriate starting materials. Silver tetrafluroborate (0.044 g, 0.225 mmol), Pt(COD)(3,5-dmph)Cl (0.10 g, 0.225 mmol) and tpy (0.053 g, 0.225 mmol). Yield: 0.110 g, 79%. Anal. Calcd. for [C₂₃H₂₀N₃Pt](BF₄) • $\frac{1}{2}$ H₂O: C, 43.90; H, 3.36; N, 6.68. Found: C, 43.85; H, 3.26; N, 6.69. MS (ESI): *m*/*z* = 533.1 (2a). ¹H NMR (d₆-DMSO): 2.27 (6H, s, CH₃); 6.73 (1H, s, CH); 7.04 (2H, s with Pt satellites, *J*_{H-Pt}=31 Hz, CH); 7.83 (2H, m, CH); 8.33 (2H, d with Pt satellites, *J*_{H-Pt}=51 Hz, CH); 8.45 (2H, m, CH); 8.53-8.71 (5H, m, CH).

[Pt(phtpy)(3,5-dmph)](BF₄) (2b(BF₄⁻)). Prepared by the same procedure as 1a(BF₄⁻), substituting the appropriate starting materials. Silver tetrafluroborate (0.044 g, 0.225 mmol), Pt(COD)(3,5-dmph)Cl (0.10 g, 0.225 mmol) and phtpy (0.070 g, 0.225 mmol). Yield: 0.131 g, 84%. Anal. Calcd. for [C₂₉H₂₄N₃Pt](BF₄): C, 50.01; H, 3.47; N, 6.04. Found: C, 49.98; H, 3.48; N, 6.08. MS (ESI): m/z = 609.2 (2b). ¹H NMR (d₆-DMSO): 2.28 (6H, s, CH₃); 6.73 (1H, s, CH); 7.09 (2H, s, CH); 7.66 (2H, m, CH); 7.82 (2H, m, CH); 8.16 (2H, m, CH); 8.33 (2H, m, CH); 8.47 (2H, t, CH); 8.86 (2H, d, CH); 9.05 (2H, s, CH).

[Pt(tpy)(2,6-dmph)](BF₄) (3a(BF₄⁻)). Prepared by the same procedure as 1a(BF₄⁻), substituting the appropriate starting materials. Silver tetrafluroborate (0.044 g, 0.225 mmol), Pt(COD)(2,6-dmph)Cl (0.10 g, 0.225 mmol) and tpy (0.053 g, 0.225 mmol). Yield: 0.120 g, 86%. Anal. Calcd. for [C₂₃H₂₀N₃Pt](BF₄): C, 44.53; H, 3.25; N, 6.78. Found: C, 44.49; H, 3.19; N, 6.92. MS (ESI): m/z = 533.2 (3a). ¹H NMR (CDCl₃): 2.52 (6H, s, CH₃); 7.05 (3H, m, CH); 7.47 (2H, m, CH); 8.15 (2H, d with Pt satellites, $J_{H-Pt}=54$ Hz, CH); 8.31 (2H, t, CH); 8.47-8.60 (3H, m, CH); 8.68 (2H, d, CH). [Pt(phtpy)(2,6-dmph)](BF₄) (3b(BF₄⁻)). Prepared by the same procedure as 1a(BF₄⁻), substituting the appropriate starting materials. Silver tetrafluroborate (0.044 g, 0.225 mmol), Pt(COD)(2,6-dmph)Cl (0.10 g, 0.225 mmol) and phtpy (0.070 g, 0.225 mmol). Yield: 0.132 g, 84%. Anal. Calcd. for [C₂₉H₂₄N₃Pt](BF₄): C, 50.01; H, 3.47; N, 6.04. Found: C, 49.63; H, 3.36; N, 5.91. MS (ESI): m/z = 609.2 (3b). ¹H NMR (CDCl₃): 2.65 (6H, s, CH₃); 7.06-7.15 (6H, m, CH); 7.49 (2H, t, CH); 7.80 (2H, m, CH); 8.17 (2H, d with Pt satellites, $J_{H-Pt}=55$ Hz, CH); 8.32 (2H, t, CH); 8.51 (2H, s, CH); 8.72 (2H, d, CH).

[Pt(tpy)(mes)](BF₄) (4a(BF₄⁻)). Prepared by the same procedure as 1a(BF₄⁻), substituting the appropriate starting materials. Silver tetrafluroborate (0.042 g, 0.218 mmol), Pt(COD)(mes)Cl (0.10 g, 0.218 mmol) and tpy (0.051 g, 0.218 mmol). Yield: 0.105 g, 76%. Anal. Calcd. for [C₂₄H₂₂N₃Pt](BF₄) • H₂O: C, 44.19; H, 3.71; N, 6.44. Found: C, 44.34; H, 3.61; N, 6.73. MS (ESI): m/z = 547.146 (4a). ¹H NMR (CDCl₃): 2.34 (3H, s, CH₃); 2.47 (6H, s, CH₃); 6.86 (2H, s, CH); 7.46 (2H, m, CH); 8.19 (2H, d with Pt satellites, $J_{H-Pt}=51$ Hz, CH); 8.30 (2H, t, CH); 8.53 (3H, m, CH); 8.66 (2H, d, CH).

[**Pt(phtpy)(mes)](BF₄) (4b(BF₄⁻))**. Prepared by the same procedure as **1a**(BF₄⁻), substituting the appropriate starting materials. Silver tetrafluroborate (0.042 g, 0.218 mmol), Pt(COD)(mes)Cl (0.10 g, 0.218 mmol) and phtpy (0.067 g, 0.218 mmol). Yield: 0.113 g, 73%. Anal. Calcd. for [C₂₄H₂₂N₃Pt](BF₄): C, 50.72; H, 3.69; N, 5.92. Found: C, 50.45; H, 3.67; N, 6.04. MS (ESI): m/z = 623.1773 (**4b**). ¹H NMR (CDCl₃): 2.38 (3H, s, CH₃); 2.60 (6H, s, CH₃); 6.92 (2H, s, CH); 7.10 (3H, m, CH); 7.46 (2H, m, CH); 7.80 (2H, m, CH); 8.19 (2H, d with Pt satellites, $J_{H-Pt}=52$ Hz, CH); 8.35 (2H, t, CH); 8.51 (2H,

s, CH); 8.70 (2H, d, CH). The triflate salt ($4b(CF_3SO_3^-)$) was prepared by the same procedure, substituting AgCF₃SO₃ (0.056 g, 0.218 mmol) for AgBF₄. Anal. Calcd. for [C₂₄H₂₂N₃Pt](CF₃SO₃): C, 48.19; H, 3.39; N, 5.44. Found: C, 48.03; H, 3.28; N, 5.46. MS (ESI): m/z = 623.177 (**4b**).

X-ray Crystallography. Yellow rod-shaped crystals of $1b(BF_4)$ were grown by slow diffusion of Et₂O into a CH₃CN/MeOH solution. Orange rod-shaped crystals of $2a(BF_4)$ were grown by slow evaporation of acetonitrile solution. Single crystals of $4a(CF_3SO_3) \cdot CH_2Cl_2$ were obtained as orange-yellow rectangular plates from CH_2Cl_2 /hexanes solution. Single crystals of $4b(CF_3SO_3^-)$ were obtained as orange blocks from CH₂Cl₂/Et₂O solution. Diffraction data were collected using graphite monochromated Mo K α radiation (λ =0.71073 Å) and a Siemens SMART 1K CCD diffractometer (150 K: 2a(BF₄), 4a(CF₃SO₃) • CH₂Cl₂) or a standard Siemens SMART 6000 CCD diffractometer (150 K: **1b**(BF₄⁻); 295 K: **4b**(CF₃SO₃⁻)). Data frames were processed using the Siemens SAINT program.²⁹ Intensities were corrected for Lorentz, polarization and decay effects. Absorption and beam corrections based on the multi- scan technique were applied using SADABS.³⁰ The structures were solved using SHELXTL³¹ and refined by full-matrix least squares on F^2 . For all compounds non-hydrogen atoms were located directly by successive Fourier calculations and refined anisotropically. Ligand H atoms were either located directly or calculated based on geometric criteria and were treated with a riding model in subsequent refinements. The isotropic displacement parameters for the H atoms were defined as a times U_{eq} of the adjacent atom where a=1.5for -CH₃ and 1.2 for all others. The triflate counter ion for $4b(CF_3SO_3)$ shows typical

	1b (BF ₄ ⁻)	$C_{23}H_{20}N_3Pt](BF_4)$)(2a (BF ₄)	$\begin{array}{c} \mathbf{4a}(\mathrm{CF}_3\mathrm{SO}_3^{-}) \bullet \\ \mathrm{CH}_2\mathrm{Cl}_2 \end{array}$	4b (CF ₃ SO ₃ ⁻)
Formula	$\begin{array}{c} [C_{27}H_{20}N_{3}Pt] \\ (BF_{4}) \end{array}$	$\begin{array}{c} [C_{23}H_{20}N_{3}Pt] \\ (BF_{4}) \end{array}$	$\begin{array}{c} [C_{24}H_{22}N_{3}Pt] \\ (CF_{3}SO_{3}) \bullet \\ CH_{2}Cl_{2} \end{array}$	$\begin{array}{c} [C_{30}H_{26}N_{3}Pt] \\ (CF_{3}SO_{3}) \end{array}$
Fw, g/mol	668.36	620.32	781.53	772.70
Space group	$P2_1/n$	$P2_1/n$	$P2_{1}/c$	Pī
a, Å	11.9163(6)	7.8557(4)	16.6693(10)	8.4394(3)
b, Å	9.3043(5)	13.3721(7)	11.4422(7)	12.9346(5)
c, Å	20.7567(10)	19.8308(11)	16.2158(10)	15.0962(6)
α, °	90	90	90	111.206(1)
<i>β</i> , °	94.149(1)	92.6710(10)	118.153 (1)	95.949(1)
γ, °	90	90	90	106.980(1)
V, Å ³	2295.3(2)	2080.91(19)	2727.0 (3)	1428.30(9)
Ζ	4	4	4	2
<i>Т</i> , К	150(2)	150(2)	150 (2)	295(2)
reflns collected	30761	13659	27926	18395
ind reflns	5720	5123	6726	7087
R _{int}	0.0325	0.0391	0.0375	0.0413
GOF on F^2	1.038	1.022	1.266	1.106
$\frac{R_1/wR_2}{\left[I > 2\sigma(I)\right]^a}$	0.0150/0.0360	0.0391/0.0678	0.0375/0.0639	0.0413/0.0967
$\frac{R_1/wR_2}{(\text{all data})^{\text{a}}}$	0.0191/0.0382	0.0608/0.0724	0.0459/0.0657	0.0469/0.0988

Table 5.1. Crystallographic Data for Salts of $1b(BF_4^-)$, $2a(BF_4^-)$, $4a(CF_3SO_3^-) \cdot CH_2Cl_2$ and $4b(CF_3SO_3^-)$.

^a $R_1 \Sigma || F_0 |- |F_c| |/\Sigma |F_0|, wR_2 = [\Sigma w (F_0^2 - F_c^2)^2 / \Sigma w (F_0^2)^2]^{\frac{1}{2}}.$

disorder, but no reasonable multi-component disorder model was obtained.

Crystallographic data are summarized in Table 5.1.

Results and Discussion.



Scheme 5.1. Eight $Pt(R-tpy)(Ar)^+$ complexes (R=H or Ph; Ar = Ph, 3,5-dmph, 2,6-dmph, or mes).

Synthesis and Characterization. Complexes 1-4 are shown in Scheme 5.1. Arena and co-workers previously prepared chloride salts of 1a and 1b in 75% and 72% yields, respectively, by taking advantage of the labilizing properties of sulfoxide and σ -donor phenyl ligands, of the Pt(DMSO)₂(Ph)Cl starting material.¹⁷ Here we report the synthesis of the BF₄⁻ salts of these and six new complexes, in comparably high yield (69-86%) from Pt(COD)(Ar)Cl, (Ar=Ph, 3,5-dmph, 2,6-dmph or mes; Schemes 5.1 and 5.2). The platinum containing starting reagents, Pt(COD)(Ar)Cl, were prepared from the reaction of Pt(COD)Cl₂ with trimethylphenyl tin (Ar = Ph),²⁷ mesitylmagnesium bromide (Ar = Mes)^{27,28} 3,5-dimethylphenylmagnesium bromide (Ar = 3,5-dmph), or 2,6-dimethylphenylmagnesium bromide (Ar = 2,6-dmph). Modifications of published procedures for the preparation of Pt(COD)(3,5-dmph)₂ and Pt(COD)(3,5-dmph)Cl resulted in significantly higher yields (79% and 93%, respectively) than previously reported (23%, 50%).²⁸ The chloride ion was displaced by stirring a solution of the appropriate starting material with a silver salt (*e.g.*, AgBF₄). After removal of the resultant silver chloride by filtration, the filtrate was stirred with one equivalent of tpy or phtpy overnight. The recrystallized yellow/orange products were fully characterized by elemental analysis, ¹H NMR spectroscopy and mass spectrometry. The triflate salts of **1**-**4** were prepared by substituting AgBF₄ with AgCF₃SO₃.



Scheme 5.2. Synthesis of $Pt(tpy)(Ar)^+$ (Ar = Ph, 3,5-dmph, 2,6-dmph, or mes).

Due to the low solubility of **1** and **2** in CHCl₃, their ¹H NMR spectra were recorded in d₆-DMSO (Figures 5.1 through 5.4) and the ¹H NMR spectra of the more soluble complexes (**3** and **4**) were recorded in CDCl₃ (Figures 5.5 through 5.8). Resonances were fully assigned with the aid of ¹H decoupling experiments and the presence of ¹⁹⁵Pt satellites associated with resonance H₆ and H₂["] (Scheme 5.1, Table 5.2). Coupling constants (J_{H-Pt}) of ~30 Hz were observed for H₂["] and 50-55 Hz for H₆. Singlet resonances were observed between 2.25 and 2.60 ppm for methyl protons in complexes **2-4**. The four complexes with methyl at the 2 and 6 positions of the aryl groups (**3-4**) are



Figure 5.1. ¹H NMR spectrum of $1a(BF_4)$ in d₆-DMSO. Solvent and TMS resonances are labeled with *.



Figure 5.2. ¹H NMR spectrum of $\mathbf{1b}(BF_4)$ in d₆-DMSO. Solvent and TMS resonances are labeled with *.



Figure 5.3. ¹H NMR spectrum of **2a**(BF₄⁻) in d₆-DMSO. Solvent and TMS resonances are labeled with *



Figure 5.4. ¹H NMR spectrum of $2b(BF_4)$ in d₆-DMSO. Solvent and TMS resonances are labeled with *.



Figure 5.5. ¹H NMR spectrum of **3a**(BF₄⁻) in CDCl₃. Solvent and TMS resonances are labeled with *.



Figure 5.6. ¹H NMR spectrum of **3b**(BF₄⁻) in CDCl₃. Solvent and TMS resonances are labeled with *.



Figure 5.7. ¹H NMR spectrum of **4a**(BF₄⁻) in CDCl₃. Solvent and TMS resonances are labeled with *.



Figure 5.8. ¹H NMR spectrum of **4b**(BF₄⁻) in CDCl₃. Solvent and TMS resonances are labeled with *.

IA^a ZA^a $3A^b$ $4A^b$ IB^a Me 2.27 2.52 $2.34/2.47$ H_4^a 1.4^a 2.52 $2.34/2.47$ H_4^a 1.52 1.52 1.65 H_3^a 1.4^a 7.65 1.65 H_4^a 7.12 6.73 7.05 1.65 H_4^a 7.12 6.73 7.05 7.11 H_3^a 7.51 (NR) ^d 7.09 1.05 6.86 7.23 H_4^a 8.55 8.51 8.50 7.50 (NR) ^d H_4^a 8.72 8.68 8.60 8.65 9.05 H_3 8.72 8.68 8.55 8.55 8.85 H_4 8.48 8.45 8.31 8.30 8.45 H_5 7.84 7.83 7.47 7.46 7.81							
\mathbf{Mc} $\mathbf{2A^a}$ $\mathbf{3A^b}$ $\mathbf{4A^b}$ $\mathbf{IB^a}$ $\mathbf{M_a}$ 2.27 2.52 $2.34/2.47$ $\mathbf{H_4^{m}}$ 1.5 1.5 7.65 $\mathbf{H_5^{m}}$ 1.5 1.5 1.65 $\mathbf{H_2^{m}}$ 7.12 6.73 7.05 8.16 $\mathbf{H_4^{m}}$ 7.12 6.73 7.05 7.51 $\mathbf{H_2^{m}}(\mathbf{H_{+P}})^c$ $7.51(\mathbf{NR})^d$ $7.09(31)^d$ $7.50(\mathbf{NR})^d$ $\mathbf{H_4^{m}}$ 8.55 8.51 8.50 $7.50(\mathbf{NR})^d$ $\mathbf{H_5}$ 8.72 8.68 8.60 8.55 8.85 $\mathbf{H_4}$ 8.48 8.45 8.55 8.51 8.50 $\mathbf{H_5}$ 7.84 7.84 7.46 7.46	32 (N	8.30 (NR) ^d 8.3	8.18 (51)	8.15 (54)	8.34 (51)	8.34 (55)	H ₆ (J _{H-Pt} Hz) ^c
\mathbf{Me} \mathbf{Aa}^{a} \mathbf{AA}^{b} \mathbf{AA}^{b} \mathbf{AA}^{b} \mathbf{Ba}^{a} $\mathrm{H_4m}$ 2.272.522.34/2.47 $\mathrm{H_4m}$ 7.125.55.5 $\mathrm{H_2m}$ 5.55.55.65 $\mathrm{H_2m}$ 7.126.735.5 $\mathrm{H_4m}$ 7.126.737.05 $\mathrm{H_2m}$ 7.257.057.11 $\mathrm{H_2m}$ 7.51 (NR) ^d 7.09 (31) ^d 7.50 (NR) ^d $\mathrm{H_4m}$ 8.558.518.507.50 (NR) ^d $\mathrm{H_4m}$ 8.728.688.608.659.05 $\mathrm{H_3}$ 8.728.688.558.518.518.51 $\mathrm{H_4}$ 8.488.458.308.458.45	7.82	7.81	7.46	7.47	7.83	7.84	H_{5}
\mathbf{Me} \mathbf{Aa}^{a} \mathbf{AA}^{b} $\mathbf{4A}^{\mathrm{b}}$ $\mathbf{1B}^{\mathrm{a}}$ $\mathrm{H}_{\mathrm{a}^{\mathrm{m}}}$ 2.27 2.52 $2.34/2.47$ $\mathrm{H}_{\mathrm{a}^{\mathrm{m}}}$ 1.2 1.52 $2.34/2.47$ $\mathrm{H}_{\mathrm{a}^{\mathrm{m}}}$ 1.51 1.51 1.51 $\mathrm{H}_{\mathrm{a}^{\mathrm{m}}}$ 7.12 6.73 1.51 $\mathrm{H}_{\mathrm{a}^{\mathrm{m}}}$ 7.12 6.73 7.05 $\mathrm{H}_{\mathrm{a}^{\mathrm{m}}}$ 7.51 7.09 7.05 $\mathrm{H}_{\mathrm{a}^{\mathrm{m}}}$ 8.55 8.51 8.50 $\mathrm{H}_{\mathrm{a}^{\mathrm{m}}}$ 8.72 8.68 8.65 9.05 $\mathrm{H}_{\mathrm{a}^{\mathrm{m}}}$ 8.72 8.68 8.55 8.55 8.55	8.45	8.45	8.30	8.31	8.45	8.48	H_4
\mathbf{Me} \mathbf{AA}^{a} $\mathbf{3A}^{b}$ $\mathbf{4A}^{b}$ $\mathbf{1B}^{a}$ \mathbf{Me} 2.27 2.52 $2.34/2.47$ \mathbf{H}_{4}^{n} \mathbf{X} \mathbf{X} \mathbf{X} \mathbf{H}_{3}^{n} \mathbf{X} \mathbf{X} \mathbf{X} \mathbf{H}_{2}^{n} \mathbf{X} \mathbf{X} \mathbf{X} \mathbf{H}_{4}^{n} 7.12 6.73 7.05 \mathbf{X} \mathbf{H}_{4}^{n} 7.12 6.73 7.05 7.11 \mathbf{H}_{3}^{n} 7.25 7.09 7.05 7.23 \mathbf{H}_{2}^{n} \mathbf{X} \mathbf{X} \mathbf{X} \mathbf{X} \mathbf{H}_{4}^{n} 8.55 8.51 8.50 \mathbf{X} \mathbf{H}_{3}^{n} 8.72 8.68 8.60 9.05	8.83	8.85	8.55	8.55	8.68	8.72	H_3
\mathbf{IA}^{a} $\mathbf{2A}^{a}$ $\mathbf{3A}^{b}$ $\mathbf{4A}^{b}$ \mathbf{IB}^{a} Me 2.27 2.52 $2.34/2.47$ H_4^m 2.27 2.52 $2.34/2.47$ H_4^m 1.51 1.52 1.52 H_2^m 7.12 1.52 1.52 H_2^m 7.12 6.73 7.05 H_2^m 7.25 7.05 7.11 H_2^m 7.51 (NR) ^d 7.09 (31) ^d 7.50 (NR) ^d H_4 8.55 8.51 8.50	9.03	9.05	8.65	8.60	8.68	8.72	$H_{3'}$
\mathbf{IA}^{a} $\mathbf{2A}^{a}$ $\mathbf{3A}^{b}$ $\mathbf{4A}^{b}$ \mathbf{IB}^{a} Me 2.27 2.52 $2.34/2.47$ H ₄ m 1.57 1.52 1.52 7.65 H ₂ m 1.51 1.51 1.51 1.05 1.05 H ₂ m 7.12 6.73 7.05 7.11 H ₃ m 7.25 $7.09(31)^{d}$ $7.50(NR)^{d}$			8.50	8.51	8.55	8.55	$H_{4'}$
\mathbf{IA}^a $\mathbf{2A}^a$ $\mathbf{3A}^b$ $\mathbf{4A}^b$ \mathbf{IB}^a Me 2.27 2.52 $2.34/2.47$ H_m -12 -12 -12 -165 H_m -12 -12 -12 -165 H_m -7.12 -6.73 -7.05 -7.65 H_3m -7.25 -7.05 -7.23	7.08(N	7.50 (NR) ^d			7.09 (31) ^d	7.51 (NR) ^d	$H_{2"}\left(J_{H-Pt}\right)^{c}$
\mathbf{IA}^a $\mathbf{2A}^a$ $\mathbf{3A}^b$ $\mathbf{4A}^b$ \mathbf{IB}^a Me 2.27 2.52 $2.34/2.47$ 1.65 H_4^m 1.2 1.2 1.2 1.65 H_2^m 1.12 1.05 1.05 1.11		7.23	6.86	7.05		7.25	H _{3"}
IA ^a 2A ^a 3A ^b 4A ^b IB ^a Me 2.27 2.52 2.34/2.47 7.65 H ₄ ^m 7.65 8.16 8.16 H ₂ ^m 7.65 7.65	6.73	7.11		7.05	6.73	7.12	$H_{4"}$
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	7.65	7.65					H ₂ ,,
$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	8.15	8.16					H _{3"}
$1A^{a}$ $2A^{a}$ $3A^{b}$ $4A^{b}$ $1B^{a}$ Me 2.27 2.52 2.34/2.47	7.65	7.65					H_{4} "
$1\mathbf{A}^{\mathrm{a}}$ $2\mathbf{A}^{\mathrm{a}}$ $3\mathbf{A}^{\mathrm{b}}$ $4\mathbf{A}^{\mathrm{b}}$ $1\mathbf{B}^{\mathrm{a}}$	2.28		2.34/2.47	2.52	2.27		Me
	2B [°]	1B ^a	$4A^{b}$	3A ^b	$2A^{a}$	$\mathbf{1A}^{\mathrm{a}}$	

 Table 5.2.
 ¹H NMR data for 1-4

much more soluble in halogenated solvents than **1-2** which have more exposed platinum centers. It is conceivable that the α -methyl groups of the aryl ligands somewhat interfere with intermolecular interactions including metal…metal, ligand…ligand, and cation…anion interactions, that can stabilize aggregates and favor precipitation.

Crystal Structures. The structures of **1b**(BF₄⁻), **2a**(BF₄⁻), **4a**(CF₃SO₃⁻) • CH₂Cl₂ and **4b**(CF₃SO₃⁻) were confirmed by single crystal X-ray diffraction. ORTEP diagrams are shown in Figures 5.9 through 5.12, and relevant data are summarized in Tables 5.1 and 5.3. The salts crystallize with one anion in the asymmetric unit, and the CF₃SO₃⁻ salt of **4a** crystallizes with a CH₂Cl₂ solvent molecule. Bond lengths and angles of the cations and anions are normal, though the CF₃SO₃⁻ counterion of **4b** is disordered.

As anticipated the complexes adopt distorted square planar structures that are qualitatively similar to those of other platinum(II) terpyridyl complexes.^{7-13,32-36} The Pt-C(phenyl) distances for **1b** (2.025 (2), **2a** (2.042(4)), **4a** (2.041(5)) and **4b** (2.023(6) Å) are similar to Pt-C distances reported for [Pt(tpy)(CH₃)](B(C₆H₅)₄) (2.039(6), 2.054(7) Å)¹¹ and Pt(bpy)(Mes)₂ (2.016(10), 2.032(9) Å) (bpy=2,2'-bipyridine).³⁷ The Pt-N1 and Pt-N3 distances (**1b**: 2.0405(17), 2.0387(16) Å; **2a**: 2.033(4), 2.029(3) Å; **4a**: 2.022(4), 2.030(4) Å; and **4b**: 2.029(4), 2.026(5) Å) are comparable to those of other platinum(II) terpyridine complexes, ^{7,8,11-13,33,34} including [Pt(phtpy)CI](BF₄) (2.008(9), 2.013(10), 2.023(9), 2.039(9) Å),¹² [Pt(tpy)CI](CF₃SO₃) (2.018(5), 2.030(5) Å),³⁴ and [Pt(4'-*o*-tolyl-tpy)CI](BF₄) (2.025(11), 2.025(11) Å).¹³ However, the central Pt-N(tpy) distances (**1b**: 1.9929(16), **2a**: 1.992(3), **4a**: 1.987(4), and **4b**: 1.998(4) Å) are significantly longer than reported for many Pt(II) terpyridine complexes, such as [Pt(4'-*o*-tolyl-tpy)CI](BF₄) (1.935(9)),¹³ [Pt(tpy)(1-methylimidazole)](CIO₄) (1.943(7)),¹⁰ and [Pt(4,4',4''-tri-*tert*-



Figure 5.9. ORTEP diagram of $1b(BF_4)$. Anion and H-atoms are omitted for clarity.



Figure 5.10. ORTEP diagram of **2a**(BF₄⁻). Anion and H-atoms are omitted for clarity.



Figure 5.11. ORTEP diagram of **4a**(CF₃SO₃⁻) • CH₂Cl₂. Anion, solvent, and H-atoms are omitted for clarity.



Figure 5.12. ORTEP diagram of **4b**(CF₃SO₃⁻). Anion and H-atoms are omitted for clarity.

	$\begin{array}{c} [C_{27}H_{20}N_{3}Pt] \\ (BF_{4}) \\ (\mathbf{1b}(BF_{4}\bar{})) \end{array}$	$\begin{array}{c} [C_{23}H_{20}N_{3}Pt] \\ [BF_{4}] \\ (\textbf{2a}(BF_{4}\)) \end{array}$	$\begin{array}{c} [C_{24}H_{22}N_{3}Pt] \\ [CF_{3}SO_{3}] \bullet CH_{2}Cl_{2} \\ (\textbf{4a}(CF_{3}SO_{3}^{-}) \bullet \\ CH_{2}Cl_{2}) \end{array}$	$\begin{array}{c} [C_{30}H_{26}N_{3}Pt] \\ [CF_{3}SO_{3}] \\ (\textbf{4b}(CF_{3}SO_{3}^{-})) \end{array}$
Pt-C(16)	2.025(2)	2.023(6)	2.042(4)	2.041(5)
Pt-N(1)	2.0405(17)	2.029(4)	2.033(4)	2.022(4)
Pt-N(2)	1.9929(16)	1.998(4)	1.992(3)	1.987(4)
Pt-N(3)	2.0387(16)	2.026(5)	2.029(4)	2.030(4)
N(1)-C(5)	1.374(3)	1.366(7)	1.377(5)	1.368(7)
N(3)-C(11)	1.381(2)	1.388(7)	1.374(5)	1.369(7)
N(2)-C(6)	1.342(2)	1.338(6)	1.338(6)	1.349(6)
N(2)-C(10)	1.341(2)	1.342(7)	1.344(5)	1.325(6)
C(5)-C(6)	1.482(3)	1.479(8)	1.479(6)	1.483(7)
C(10)-C(11)	1.475(3)	1.479(8)	1.477(6)	1.498(7)
C(16)-Pt-N(1)	100.29(7)	98.9(2)	99.69(15)	99.67(19)
C(16)-Pt-N(2)	177.04(7)	178.8(2)	1.344(5)	177.99(19)
C(16)-Pt-N(3)	100.16(7)	100.8(2)	100.06(15)	100.82(19)
N(1)-Pt-N(2)	79.74(7)	80.06(18)	80.11(14)	79.87(17)
N(2)-Pt-N(3)	79.80(7)	80.17(18)	80.15(14)	79.72(17)
N(1)-Pt-N(3)	159.54(7)	160.23(19)	160.25(14)	159.41(18)
C(5)-N(1)-Pt	113.55(13)	113.5(4)	113.6(3)	114.2(3)
C(11)-N(3)-Pt	113.47(12)	113.6(4)	113.6(3)	114.0(3)
C(6)-C(5)-N(1)	115.89(17)	116.2(5)	115.4(4)	115.7(4)
C(10)-C(11)-N(3)	115.60(16)	115.6(5)	115.8(4)	115.2(4)
C(6)-N(2)-Pt	118.60(13)	118.0(4)	118.0(3)	118.6(3)
C(10)-N(2)-Pt	118.41(13)	118.2(4)	118.0(3)	119.2(3)

Table 5.3. Selected Distances (Å) and Angles (°) for Salts of $1b(BF_4^-)$, $2a(BF_4^-)$, $4a(CF_3SO_3^-) \cdot CH_2Cl_2$ and $4b(CF_3SO_3^-)$.

butyl-tpy)Cl](ClO₄) (1.935(6) Å),⁹ and are consistent with the strong trans directing properties of a phenyl anion, as also noted for $[Pt(tpy)(pip_2NCNH_2)](PF_6)_3$ (2.005(6) Å).³⁵

As previously noted,^{10,13,32} the restricted bite angle of the tridentate terpyridine ligand precludes the 90° and 180° ligand-metal-ligand bond angles of an idealized square planar complex. The N1-Pt-N2 and N2-Pt-N3 bond angles (**1b**: 79.74(7), 79.80(7)°; **2a**: 80.06(18), 80.17(18)°; **4a**: 80.11(14), 80.15(14)°; and **4b**: 79.87(17), 79.72(17)°) are characteristically smaller than 90°. The strong trans directing phenyl groups might be expected to aggravate the situation, because the long Pt-N2 bond distances necessitate even smaller N1-Pt-N3 bond angles (**1b**, 159.54(7)°; **2a**, 160.25(14)°; **4a**, 159.41(18)°; and **4b**, 160.23(19)°). These angles are comparable to those observed for [Pt(tpy)(CH₃)](B(C₆H₅)₄) (160.6(3), 160.8(2)°),¹¹ and [Pt(tpy)(pip₂NCNH₂)](PF₆)₃ (160.2(3)),³⁵ but smaller than those observed for compounds with weaker trans directing groups, including [Pt(4'-o-tolyl-tpy)Cl](BF₄) (162.3(4))¹³ and [Pt(4,4',4"-tri-*t*-butyltpy)Cl](ClO₄) (161.8(3)).⁹

The dihedral angles formed by the Pt coordination plane, defined by the Pt and the four atoms bonded to the Pt center, and the plane of the mesityl or 2,6-dmph ring are 51.40(6), 54.7(1), 74.6(1), and 69.5(2)° for **1b**, **2a**, **4a**, and **4b**, respectively. Steric requirements most likely prohibit a coplanar configuration, and similar results are observed for platinum(II) complexes with monodentate pyridyl ligands. When bulky tridentate ligands are bonded to the platinum center, the plane of the ancillary pyridyl ligand is nearly perpendicular to the coordination plane:

Pt(pip2NCN)(pyridine)](CF3SO3), 89.5°,^{38,39} [Pt(pip2NCN)(4-phenylpyridine)](CF3SO3),

 $84.5;^{38,39}$ and Pt(PCP)(8-acetamidoquinolinato)⁺, $87.3^{\circ 40}$ (pip₂NCN⁻ = 2,6-

 $((C_5H_{10}N)CH_2)_2C_6H_3^{-}; PCP^- = 2,6-(((C_6H_5)_2PCH_2)_2C_6H_3^{-}).$ However, for less sterically demanding tridentate ligands, such as $[Pt(4'-bis-\{2-(hydroxyethyl)amino\}-tpy)(4-picoline)](BF_4)$ (70.8)³⁶ Pt(phbpy)(pyridine)⁺ (61.7°),⁴¹ Pt(phbpy)(4-aminopyridine)⁺ (88°),⁴¹ and Pt(SNS)(4-COOHpyridine)²⁺ (55.0°)⁴² (phbpy=6-phenyl-2,2'-bipyridine, SNS=2,6-bis(methylthiomethyl)pyridine), the dihedral angle ranges from 55.0 to 88°. In crystal of **1b** and **4b** the phenyl ring, attached to the 4' position of the tpy ligand, is rotated 19.05(8) and 11.9(3)°, respectively, from the platinum coordination plane. These angles are much smaller than observed for, $[Pt(phtpy)Cl](BF_4) (24.7/34.2°)$,¹² suggesting that weak packing forces may influence the ligand conformation.

In crystals of salts of **1b**, **2a** and **4b**, pairs of cations related by an inversion center are stacked in a head-to-tail orientation, resulting in relatively short intermolecular π - π interactions. However, there are no close Pt…Pt interactions (<4.0 Å), and the shortest Pt…Pt distances are 6.527 and 7.769 Å for **1b**, 5.563 and 5.875 Å for **2a**, and 7.919 and 7.878 Å for **4b**. In crystals of **1b**, the shortest intermolecular ligand…ligand contact of 3.473 Å (C6…C6') is between the central pyridyl rings of adjacent complexes. In crystals of **2a**, two pyridyl rings of one molecule overlap with two pyridyl rings of an adjacent molecule with a shortest contact of 3.387 Å (C6…C12'). In crystals of **4b**, there are short intermolecular contacts between the phenyl ring and a pyridyl ring of two molecules related by an inversion center, resulting in a shortest distance of 3.347 Å (C27…C10'). No close interactions are observed in crystals of **4a**.

Conclusions. This series of complexes (**1-4**) provides an opportunity to probe the factors that govern stacking interactions between platinum(II) terpyridyl complexes.

There is crystallographic evidence for both π - π and Pt-Pt interactions in previously reported systems.⁸⁻¹⁸ In the case of the four structurally characterized compounds in the present study, we find evidence of π - π interactions in crystals of 1b, 2a, and 4b. Intermolecular interactions between platinum(II) terpyridyl complexes have been corroborated by other experiments. For example, Gray and coworkers observed broadening of the first reduction wave in the cyclic voltammogram of Pt(tpy)Cl⁺ in 0.1 M TBAPF₆/DMF due to the presence of monomers and dimers in solution.¹⁹ UV-visible absorption measurements in 0.1 M NaCl/water suggest formation of two distinctly different dimers with dimerization constants of $1.3(1) \times 10^3$ and $1.0(1) \times 10^3$ M^{-1.8} Emission spectra in 77 K 5:5:1 ethanol:methanol:DMF glassy solutions also confirm the presence of two types of emissive aggregates.⁸ The variations in the steric properties of the platinum(II) terpyridyl aryl complexes discussed in this chapter are expected to aid in understanding the nature of stacking interactions in this class of compounds. In Chapter 6, a series of cyclic voltammetry and differential pulse voltammetry experiments are used to investigate the compounds 1-4 and their tendency to aggregate in solution. Chapter 7 focuses on the room temperature and 77 K absorption and emission spectroscopy of these complexes. The accumulated data suggest that steric effects can dramatically influence aggregation in fluid and frozen solutions.

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CHAPTER 6:

Electrochemical Properties of Platinum(II) Terpyridyl Complexes with Aryl Ligands.

Introduction

Platinum(II) terpyridyl complexes often exhibit intermolecular metal…metal and/or ligand…ligand interactions in the solid state.¹⁻¹¹ It is reasonable to expect that similar interactions will occur in fluid solution, and previous studies have shown that the spectroscopy and electrochemistry of these compounds in solution are very sensitive to their tendency to aggregate.^{1-5,12-19} However, the details of this behavior are still not fully understood.

For example, Hill *et al.*¹³ have observed that $Pt(tpy)CI^+$ in 0.1 M TBAPF₆/DMF exhibits three one-electron reduction processes at -0.745, -1.30 and -2.1 V vs. Ag/AgCl (1.0 M KCl), respectively. Through a combination of UV-visible absorption spectroscopic and electrochemical measurements, the dimerization constants for $Pt(tpy)CI^+$ and Pt(tpy)Cl were found to be 80(10) and 100(40) M⁻¹, respectively.¹³ Subsequently, Liu *et al.*⁴ used cyclic and differential pulse voltammetry to show that the first and third reductions of $Pt(4'-OCH_2CH_2CH_3-tpy)CI^+$ in room temperature 0.1 M TBABF₄/DMF consist of two closely overlapping processes, which further separate at -40°C. The authors assigned these processes to the reduction of monomeric and dimeric species in solution. However, the nature of the interactions stabilizing the dimer(s) remains uncertain. It also was noted that the second reduction peak does not appear split, even at low temperatures.⁴ Therefore, it was suggested that the second process involves addition of an electron to the $d_{x^2x^2}$ (Pt) orbital, whose energy is argued to be only weakly

affected by dimerization. However, there is open disagreement surrounding this assignment and others have proposed that the second reduction of platinum(II) terpyridyl complexes is centered on the terpyridyl ligand.^{9,28} The third reduction process was assigned by Liu *et al.*⁴ as a terpyridyl ligand-centered reduction.

In Chapter 5 we reported the synthesis and characterization of a series of platinum(II) terpyridyl complexes with ancillary aryl ligands (Scheme 6.1). These compounds provide an opportunity to probe the effect of stacking interactions on the electrochemical properties of platinum(II) terpyridyl complexes. For complexes **3** and **4**, the ancillary aryl ring is substituted with methyl groups directed above and below the platinum center. In **2**, the methyl groups are directed away from the platinum center. In **1**, the platinum center also is relatively exposed. Therefore, intermolecular metal…metal interactions, as well as ligand…ligand interactions to a lesser extent, should be hindered



Scheme 6.1. Eight $Pt(R-tpy)(Ar)^+$ complexes (R=H or Ph; Ar = Ph, 3,5-dmph, 2,6-dmph, or mes).

in **3** and **4**, as compared to **1** and **2**. To test this hypothesis, we have undertaken an electrochemical investigation of this series of compounds. The results provide evidence that steric effects can be used to control aggregation of platinum(II) terpyridyl complexes.

Experimental: $[Pt(tpy)(Ph)](BF_4)(1a(BF_4)), [Pt(phtpy)(Ph)](BF_4)(1b(BF_4)),$ $[Pt(tpy)(3,5-dmph)](BF_4)$ (2a(BF₄⁻)), $[Pt(phtpy)(3,5-dmph)](BF_4)$ (2b(BF₄⁻)), $[Pt(tpy)(2,6-dmph)](BF_4)$ (**3a**(BF₄⁻)), $[Pt(phtpy)(2,6-dmph)](BF_4)$ (**3b**(BF₄⁻)), $[Pt(tpy)(mes)](BF_4)$ (4a(BF₄)), and $[Pt(phtpy)(mes)](BF_4)$ (4b(BF₄)) were prepared as reported in Chapter 5. Acetonitrile was distilled from CaH₂. Tetrabutylammonium hexafluorophosphate (TBAPF₆) was recrystallized twice from boiling methanol and dried under vacuum prior to use. Cyclic and differential pulse voltammetry was carried out using a standard three-electrode cell and a CV50w potentiostat from Bioanalytical Systems. Scans were collected on 1 mM samples of 1-4 in acetonitrile solution containing 0.1 M TBAPF₆. However, at -40°C some complexes began to precipitate (especially 1 and 2) and the concentrations were less than 1 mM. All scans were recorded using a platinum wire auxiliary electrode and a 0.79 mm² gold working electrode. Between scans, the working electrode was polished with 0.05 µm alumina, rinsed with distilled water and wiped dry using a Kimwipe. Room temperature potentials are referenced against Ag/AgCl (3.0 M NaCl), and low temperature values are referenced against a Ag wire immersed in a CH₃CN/0.1 M TBAPF₆ solution. 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° . Wherever possible, peak-to-peak separations (ΔE_{p}) were determined by scanning the potential from $E^{\circ} \pm 300 \text{ mV}$ for each reduction. Averaged values are

reported as the average with the standard deviation (σ) in parentheses. Peak currents (i_p) where estimated with respect to the extrapolated baseline current as described elsewhere.²⁰ Under these conditions, the ferrocene/ferrocenium (FcH/FcH⁺) couple occurs at E^o=0.44 V with ΔE_p =69 mV. Typical parameters for differential pulse voltammetry experiments were 50 mV pulse amplitude, 10 msec sample width, 25 msec pulse width, 200 msec pulse period, and 2 sec quiet time. Room temperature was 23°C.

Electrochemical Properties

Cyclic Voltammetry. For the following discussion, the eight complexes are divided into two groups. In complexes **3** and **4**, the platinum center is protected by methyl groups in the 2 and 6 positions of the ancillary phenyl ring. Kaim and coworkers²¹⁻²⁴ has shown that reversible one-electron platinum-centered oxidation is observed for $Pt(bpy)(mes)_2$ and related complexes. The two methyl groups protect each axial site of the metal center preventing axial ligation or disproportionation to give a two-electron oxidized platinum(IV) product.²¹⁻²⁴ However, Pt(bpy)(mes)Cl undergoes irreversible platinum-centered oxidation, indicating that a single mesityl group is unable to fully protect the metal center.²² Therefore, reversible oxidation of the platinum center is not expected for **3** and **4**. Nevertheless, the single methyl group protecting each axial site of the platinum center is expected to hinder metal---metal and possibly ligand---ligand stacking interactions, such as those proposed for $Pt(tpy)Cl^+$ in solution.^{2,13} In contrast, the axial sites of **1** and **2** are exposed and stacking interactions are expected to be more favorable.

Cyclic voltammograms for compounds **1-4** were recorded in acetonitrile solution containing 0.1 M TBAPF₆, and data are summarized in Tables 6.1 and 6.2. As expected,

Compound	E °' (V)	$\Delta E_{p} \left(mV \right)$	$i_{ m pc}/i_{ m pa}$
1a (BF ₄ ⁻)	-0.91	72	1.04
	-1.42	57	1.07
	-2.09	152	3.25
1b (BF ₄ ⁻)	-0.88	91	1.01
	-1.37	56	1.15
	-2.00	163	7.99
2a (BF ₄ ⁻)	-0.92	61	0.94
	-1.43	58	1.01
	-2.08	126	4.92
$2b(BF_4)$	-0.90	77	1.32
	-1.38	57	1.07
	-2.00	152	3.29

Table 6.1. Cyclic voltammetry data for salts of 1 and 2 at room temperature.^a

^a Cyclic voltammograms were recorded in 0.1 M TBAPF₆/CH₃CN at 250 mV/s; potentials are referenced against aqueous Ag/AgCl. E°' and ΔE_p were calculated from waves recorded between -0.6 and -1.2 V for the first reduction, -1.1 and -1.7 V for the second reduction, and +1.1 and -2.4 V for the third reduction.

Compound	E °' (V)	$\Delta E_{p}\left(mV ight)$	$i_{ m pc}/i_{ m pa}$
3a (BF ₄ ⁻)	-0.93	62	1.03
	-1.45	68	1.13
	-2.10	116	1.99
$3b(BF_4)$	-0.90	60	1.00
	-1.41	62	1.01
	-2.03	138	2.37
4a (BF ₄ ⁻)	-0.93	61	1.08
	-1.45	60	1.17
	-2.10	102	4.69
4b (BF ₄ ⁻)	-0.91	60	1.13
	-1.41	66	1.09
	-2.01	106	2.68

Table 6.2. Cyclic voltammetry data for salts of 3 and 4 at room temperature.^a

^a Cyclic voltammograms were recorded in 0.1 M TBAPF₆/CH₃CN at 250 mV/s; potentials are referenced against aqueous Ag/AgCl. E°' and ΔE_p were calculated from waves recorded between -0.6 and -1.2 V for the first reduction, -1.1 and -1.7 V for the second reduction, and +1.1 and -2.4 V for the third reduction. none of these complexes is oxidized at potentials <1.3 V vs. Ag/AgCl; however, each exhibits two chemically reversible reduction waves near $E^{\circ r} = -0.9$ V and $E^{\circ r} = -1.4$ V. Qualitatively these reductions are similar to the two one-electron reductions observed for other platinum(II) terpyridyl complexes,^{4,9,13,19,25-27} including [Pt(tpy)Cl](PF₆) ($E^{\circ r} = -0.74$ V, $E^{\circ r} = -1.30$ V, 0.1 M TBAPF₆/DMF, vs. Ag/AgCl),¹³ [Pt(phtpy)Cl](B(2,6-(CF₃)₂C₅H₃)₄) ($E^{\circ r} = -1.22$ V, $E^{\circ r} = -1.76$ V, 0.1 M TBAPF₆/DMF, vs. FcH/FcH⁺)²⁷ and [Pt(tpy)(C₆H₅C=C)](ClO₄) ($E^{\circ r} = -0.83$ V, $E^{\circ r} = -1.29$ V, 0.1 M TBAPF₆/DMF, vs. SCE).¹⁹ The first reduction process for those systems has previously been assigned as a terpyridyl-centered reduction,^{4,9,13,19,25-27} and a similar assignment is made for **1-4**. The positive shift of this couple from those of other metal terpyridine complexes is attributable to coupling of the empty $6p_z(Pt)$ orbital with the π^* orbital of tpy, stabilizing the reduced complex. Interestingly, there has been some disagreement surrounding the assignment of the second process. Both terpyridyl-ligand reduction^{9,28} and metal-centered reduction involving the d_{x2-y2}(Pt) level have been proposed.^{4,13,25}

Examination of the first reduction process for the series of complexes with tpy ligands (**1a-4a**) and the series with phtpy ligands (**1b-4b**) reveals that the potentials span a very narrow range (**1a-4a**: -0.91 to -0.93 V; **1b-4b**: -0.88 to -0.91 V), indicating that the process is only weakly dependent on substitution of the ancillary aryl ligand with electron donating methyl groups. Similarly, only small shifts are observed for the second reductions as the aryl ligand is substituted with methyl groups (**1a-4a**: -1.42 to -1.45 V; **1b-4b**: -1.37 to -1.41 V). These results suggest that the second reduction is not metal-centered, because the $d_{x^2-y^2}$ (Pt) level is expected to be much more sensitive to the electron-donating properties of the ancillary aryl ligands than the $\pi^*(tpy)$ levels. To

illustrate this point, consider that the metal-centered Ru(II/III) couple for *trans*- $Ru(tpy)(pyridine)_2Cl^+$ in acetonitrile shifts from 0.83 to 0.78 V vs. SCE when methyl substituents are place at the 4' position of the pyridyl groups.²⁹ The \sim 70 mV cathodic shift is consistent with a net destabilization of the $4d\pi(Ru)$ levels, as expected for the increased electron-donor character of the pyridyl ligand. In the case of the platinum(II) terpyridyl complexes discussed here, one would expect the effect to be more exaggerated since the $d_{x^2-y^2}(Pt)$ is formally σ -antibonding with respect to the aryl ligand. Therefore, given the similar aryl ligand substituent dependence of the first and second reduction potential, we tentatively assign the second reduction process as being terpyridyl-ligand centered. In keeping with this interpretation, substitution of terpyridine with a phenyl group at the 4' position results in the expected slight anodic shift of the first (20 to 30 mV) and second (40-50 mV) reduction potentials. A similar stabilization of the terpyridine π^* orbital has been noted for Pt(tpy)Cl⁺ (-1.24 V; DMF, 0.1 M TBAPF₆ vs. FcH/FcH⁺) substituted with a phenyl ring on the 4' position of the tpy ligand (-1.22 V; DMF, TBAPF₆ vs. FcH/FcH⁺).²⁷

Complexes 1-4 also exhibit a third irreversible reduction at potentials <-2 V. This reduction process appears more electrochemically reversible than the corresponding reduction for $Pt(tpy)Cl^+$ ($E_{pc} = -2.1 V$, 0.1 M TBAPF₆/DMF vs. Ag/AgCl), but less reversible than observed for $Pt(tpy)(py)^{2+}$ ($E^{\circ} = -1.90 V$, 0.1 M TBAPF₆/DMF vs. Ag/AgCl). Hill *et al.*¹³ have proposed that the third reduction of $Pt(tpy)Cl^+$ is coupled to loss of a Cl⁻ ligand. The improved reversibility of this process for 1-4 is consistent with the reduced lability of the phenyl ligand as compared to chloride.

The peak-to-peak separations (ΔE_p) for the first reductions of **1** and **2** (ΔE_p =**1a**, 72; **1b**, 91; **2a**, 61; **2b**, 77 mV) are larger than predicted for a Nernstian process, whereas the values for **3** and **4** are consistent with an electrochemically reversible process (ΔE_p = **3a**, 62; **3b**, 60; **4a**, 61; **4b**, 60 mV). In fact, ΔE_p values of many previously reported platinum(II) terpyridyl complexes are much larger than 59 mV: Pt(tpy)Cl⁺ (E^o' = -1.24 V, $\Delta E_p = 70$ mV, TBAPF₆/DMF vs. FcH/FcH⁺),^{27,30} Pt(tpy)(NH₃)²⁺ (E^o' = -0.74 V, $\Delta E_p =$ 80-90 mV, 0.1 M TBAPF₆/DMF vs. Ag/AgCl),¹³ and Pt(phtpy)Cl⁺ (E^o' = -1.22 V, $\Delta E_p =$ 80 mV, TBAPF₆/DMF vs. FcH/FcH⁺).^{27,30} In contrast, ΔE_p values for the second reductions of **1-4** are generally consistent with an electrochemically reversible process. A possible exception is **3a** ($\Delta E_p = 68$ mV).

Temperature dependent cyclic voltammetry. Cyclic voltammograms were recorded for 1.0 mM solutions of **1-4** at room temperature, 0°, and -40°C (Tables 6.3 and 6.4, Figures 6.1 through 6.8). The second reduction process for all complexes behaved as expected for a Nernstian process. At room temperature, the average ΔE_p value is 60(2) mV, and upon cooling to 0° and -40°C, the peak-to-peak separation approaches the Nernstian limits of 54 and 46 mV, respectively. However, the first reduction process behaves much differently, it does not appear Nernstian for all eight platinum-terpyridyl complexes. For **3a** and **4a**, the first reduction process also appears to be a Nernstian oneelectron process at room temperature, 0°, and -40°C, with ΔE_p values similar to those observed for the second reduction process. However, as Liu *et al.*⁴ observed for Pt(4'-OCH₂CH₂CH₃-tpy)Cl⁺, the first reduction appears as a broadened wave for several of the complexes. The ΔE_p values approach the predicted values only at room As the
Compound	Temp (°C)	E °' (V)	$\Delta E_{p} (mV)$
1 a(BF4)	23	-0.93	80
Iu (D14)	25	-1.45	60
	0	0.01	96
	0	-0.91 -1.42	86 57
$1b(BF_4)$	23	-0.92	133
		-1.41	38
	0	-0.90	126
		-1.39	55
	-40	-0.86	167
	40	-1.33	42
$2a(BF_4)$	23	-0.92	68
		-1.43	60
	0	-0.92	70
		-1.42	53
	-40	-0.91	85
	-40	-1.40	41
$2b(BF_4)$	23	-0.91	120
		-1.40	58
	0	-0.89	124
		-1.37	51
	-40	-0 02	169
	-10	-1.36	54

Table 6.3. Cyclic voltammetry data for salts of **1** and **2** at 23°, 0°, and -40°C a

^a Cyclic voltammograms were recorded in 0.1 M TBAPF₆/CH₃CN at 250 mV/s; potentials are referenced against Ag/CH₃CN/TBAPF₆. E^o' and Δ E_p were calculated from waves recorded between -0.5 and -1.8 V.

Compound	Temp (°C)	E °' (V)	$\Delta E_{p}\left(mV ight)$
3 9(BF. ⁻)	23	_0.99	63
Ja (D14)	23	-0.55	61
		1.52	01
	0	-0.98	58
		-1.50	58
	-40	-0.96	53
		-1.46	50
$2\mathbf{L}(\mathbf{D}\mathbf{F}^{-1})$	22	0.01	(2
$\mathbf{3D}(\mathbf{BF}_4)$	23	-0.91	62 62
		-1.42	02
	0	-0.90	57
	0	-1.40	56
	-40	-0.91	66
		-1.38	47
$4a(BF_4)$	23	-0.90	63
		-1.44	63
	0	0.01	(0
	0	-0.91	60 61
		-1.43	01
	-40	-0.93	53
	10	-1.42	53
$4\mathbf{b}(\mathrm{BF}_{4})$	23	-0.92	59
		-1.43	60
	0	-0.91	56
		-1.42	56
	40	0.01	(7
	-40	-0.91	0 / 47
		-1.38	4 /

Table 6.4. Cyclic voltammetry data for salts of 3 and 4 at 23°, 0°, and -40°C.^a

^a Cyclic voltammograms were recorded in 0.1 M TBAPF₆/CH₃CN at 250 mV/s; potentials are referenced against aqueous Ag/CH₃CN/TBAPF₆. E°' and ΔE_p were calculated from waves recorded between -0.5 and -1.8 V.



Figure 6.1. Cyclic Voltammograms of 1a recorded at room temperature and 0°C. Poor solubility of 1a(BF₄⁻) prevented measurements at -40°C.



Figure 6.2. Cyclic Voltammograms of 1b recorded at room temperature, 0°, and -40°C.



Figure 6.3. Cyclic Voltammograms of 2a recorded at room temperature, 0°, and -40°C.



Figure 6.4. Cyclic Voltammograms of 2b recorded at room temperature, 0°, and -40°C.



Figure 6.5. Cyclic Voltammograms of 3a recorded at room temperature, 0°, and -40°C.



Figure 6.6. Cyclic Voltammograms of 3b recorded at room temperature, 0°, and -40°C.



Figure 6.7. Cyclic Voltammograms of 4a recorded at room temperature, 0°, and -40°C.



Figure 6.8. Cyclic Voltammograms of 4b recorded at room temperature, 0°, and -40°C.

temperature and 0°C for **3b** (RT, 62 mV; 0°C, 57 mV) and **4b** (RT, 59 mV; 0°C, 56 mV). temperature is lowered to -40°C, ΔE_p increases to 66 and 67 mV for **3b** and **4b**, respectively.

This apparent deviation from ideal Nernstian behavior is even more dramatic for **1** and **2**. At room temperature ΔE_p ranges from 70 to 140 mV and is clearly much larger than predicted for an electrochemically reversible process. In contrast to observations for **3** and **4**, ΔE_p for the first reduction wave of **1** and **2** increases as the system is cooled. In fact, at -40°C the waves for **1b** and **2b** appear to split into overlapping waves, suggestive of multiple processes with slightly different redox potentials. The data for **1b** are consistent with the presence of three electrochemically active species having slightly different reduction potentials.

Temperature dependent differential pulse voltammetry. Differential pulse voltammograms of 1.0 mM solutions of **1-4** were recorded in an attempt to resolve the two processes observed in the cyclic voltammograms of **1b** and **2b**. Differential pulse voltammetry data for **1-4** are listed in Tables 6.5 and 6.6, and room temperature, 0° and -40°C differential pulse voltammograms of **1-4** are shown in Figures 6.9 through 6.18. The data are generally consistent with the cyclic voltammograms, showing two redox couples near E° = -0.9 V and E° = -1.4 V vs. Ag/AgCl. Only one peak was fully resolved for each of these complexes, even at -40°C. However, for several of the complexes, the first couple appears as a broaden peak and the data are consistent with two or more processes occurring at slightly different potentials.

The peak potentials (E_p) are in good agreement with E° values obtained from the cyclic voltammetry experiments. The second reduction for **1-4** is Nernstian and the peak

Cmpd	Temp (°C)	E _p (V)	$W_{1/2}\left(mV\right)^{b}$	<i>i</i> _p (x 10 ⁻⁷ A)	$i_{\mathrm{p1}/} i_{\mathrm{p2}}{}^{\mathrm{c}}$
$1a(BF_4)$	23	-0.91	110	5.53	1.06
		-1.41	125	5.23	
	0	-0.90	125	5.31	1.10
		-1.39	130	4.84	
	-40	-0.93	170	1.66	0.32
		-1.47	100	5.23	
$1b(BF_4)$	23	-0.89	160	2.03	0.63
		-1.39	100	3.24	
	0	-0.90	200	1.42	0.51
		-1.38	100	2.77	
	-40	-0.91	240	0.19	0.88
		-1.33	90	0.21	
$2a(BF_4)$	23	-0.91	130	1.85	0.86
(. ,		-1.42	115	2.15	
	0	-0.90	135	1.94	0.86
		-1.41	105	2.54	
	-40	-0.90	170	1.06	0.54
		-1.40	100	1.95	
2b (BF₄ ⁻)	23	-0.90	175	2.39	0.53
		-1.39	90	4.49	
	0	-0.90	205	1.79	0.46
	-	-1.36	85	3.91	
	-40	-0.90	225	0.37	0.52
		-1.35	95	0.71	

Table 6.5. Differential Pulse Voltammetry data for salts of 1 and 2 at 23°, 0°, and $-40^{\circ}C$.^a

^a Cyclic voltammograms were recorded in 0.1 M TBAPF₆/CH₃CN at 250 mV/s; potentials are referenced against aqueous Ag/CH₃CN/TBAPF₆. ^b W_{1/2} = width of peak at half height. ^c $i_{p1/}i_{p2}$ = ratio of the cathodic peak currents for the first and second reductions.

Cmpd	Temp (°C)	E _p (V)	$W_{1/2}\left(mV\right)^{b}$	$i_{\rm p} ({\rm x} 10^{-7} {\rm A})$	$i_{\mathrm{p1/}} i_{\mathrm{p2}}{}^{\mathrm{c}}$
$3a(BF_4)$	23	-0.98	100	3.83	0.98
		-1.51	95	3.90	
	0	-0.97	100	3.31	0.90
		-1.49	90	3.68	
	-40	-0.93	95	2.68	0.95
		-1.44	100	2.82	
3b (BF ₄ ⁻)	23	-0.89	100	4.76	0.95
		-1.40	90	4.99	
	0	-0.89	95	4.90	0.95
		-1.39	90	5.06	
	-40	-0.90	105	2.97	0.78
		-1.37	80	3.81	
$4a(BF_{4})$	23	-0.89	90	4.90	1.01
		-1.42	95	4.87	
	0	-0.89	95	4.31	0.91
		-1.42	90	4.73	
	-40	-0.90	95	3.00	0.89
		-1.40	90	3.37	
$4b(BF_4)$	23	-0.91	100	2.98	0.93
(.)		-1.43	100	3.19	
	0	-0.90	90	3.08	1.04
	-	-1.40	100	2.96	-
	-40	-0 90	115	2 89	0.87
		-1.38	90	3.31	

Table 6.6. Differential Pulse Voltammetry data for salts of **3** and **4** at 23°, 0°, and
 $-40^{\circ}C.^{a}$

^a Cyclic voltammograms were recorded in 0.1 M TBAPF₆/CH₃CN at 250 mV/s; potentials are referenced against aqueous Ag/CH₃CN/TBAPF₆. ^b W_{1/2} = width of peak at half height. ^c $i_{p1/}$ i_{p2} = ratio of the cathodic peak currents for the first and second reductions.



Figure 6.9. Differential Pulse Voltammograms of **1a** recorded at room temperature, 0°, and -40°C.



Figure 6.10. Differential Pulse Voltammograms of **1b** recorded at room temperature, 0°, and -40°C.



Figure 6.11. Differential Pulse Voltammograms of **2a** recorded at room temperature, 0°, and -40°C.



Figure 6.12. Differential Pulse Voltammograms of **2b** recorded at room temperature, 0°, and -40°C.



Figure 6.13. Differential Pulse Voltammograms of **3a** recorded at room temperature, 0°, and -40°C.



Figure 6.14. Differential Pulse Voltammograms of **3b** recorded at room temperature, 0°, and -40°C.



Figure 6.15. Differential Pulse Voltammograms of **4a** recorded at room temperature, 0°, and -40°C.



Figure 6.16. Differential Pulse Voltammograms of **4b** recorded at room temperature, 0°, and -40°C.

width at half height ($W_{\frac{1}{2}}$) approaches the theoretical limiting width of 90 mV for a oneelectron transfer process.³¹ For **3** and **4**, $W_{\frac{1}{2}}$ for the first reduction is generally 90-100 mV over all temperatures. Similarly, the ratio of peak current for the first reduction to that of the second reduction is typically 0.9-1.0, with the lone exception being **3b** (0.78) at -40°C. Therefore, these data are largely consistent with the first reduction involving addition of one electron to a discrete monomer.

In contrast, the first reduction appears as a broadened peak for 1 and 2. For 1a and 2a, $W_{\frac{1}{2}}$ of the first reduction increases from 110 and 130 mV, respectively, to 170 mV as the temperature is lowered from 23°C to -40°C. The ratio of the peak currents for the first and second reductions (i_{p1}/i_{p2}) decreases from 1.1 to 0.3 for **1a** and from 0.9 to 0.5 for 2a. The temperature dependence is even more pronounced for 1b and 2b. $W_{\mbox{\tiny 12}}$ increase from ~ 165 mV to over 220 mV as the temperature is decreased. The value of i_{p1}/i_{p2} remains ~0.5 with the lone exception of **1b** (0.9) at -40°C. These data are consistent with the presence of more than one electrochemically active species in solution, presumably monomers and dimers. Overlapping processes occurring at slightly different potentials will result in broaden peaks and increased W_{1/2} values. The peak current also is expected to be decreased. However interpretation of the i_{p1}/i_{p2} value is complicated by uncertainties surrounding the second reduction process (vide infra). In addition, precipitation at low temperatures is a concern. The solubilities of the cation and the one- and two-electron reduced complexes are likely to be different, possibly affecting the ratio of the peak currents.

The profiles of the reduction peaks in differential pulse voltammograms provide additional insight. For **3** and **4**, both reductions appear as a single symmetric peak.

However, the peaks for the first reduction of **1a**, **1b**, and **2b** become increasingly asymmetric as the temperature is lowered. Notably, at -40°C, the observed peaks exhibit distinct shoulders, as expected for overlapping peaks. In the case of **1b**, the profile is consistent with three overlapping peaks, suggesting the presence of three electrochemically active species in solution. It also is intriguing that both the first *and second* reductions of **1a** appear as overlapping peaks, as might be expected for the presences of dimers of the reduced complex. At present we do not fully understand why the other seven dimers do not exhibit splitting of the second reduction peak. Liu *et al.*,⁴ obtained similar results for Pt(4'-OCH₂CH₂CH₃-tpy)Cl⁺ and concluded that the second reduction must involve an orbital that is only weakly perturbed by dimerization. An alternative thermodynamic interpretation is that the dimer formed by the neutral complex is much more weakly bonded than that formed by the cationic complex. A third explanation might take into account relative rates of dimer formation and dissociation for the cationic and the neutral radical complexes.

Steric Effects on Aggregation. The accumulated data are consistent with the notion that methyl groups directed toward the axial sites of the metal center in **3** and **4** impede formation of dimers by interfering with stacking interactions. Thus, we conclude that protecting the metal center is a viable means of preventing stacking interactions in room temperature fluid solution samples of platinum(II) terpyridyl complexes. We suggest that blocking the axial sites of the Pt center with methyl groups specifically interferes with formation of aggregates supported by metal…metal interactions. Consequently, the first reduction process of **3a** and **4a**, as indicated by the cyclic and differential pulse voltammograms, appears as electrochemically reversible one-electron

processes. However, the extended aromatic system of the phtpy ligand in **3b** and **4b** may allow for weak ligand...ligand interactions, as indicated by broadening of the first reduction wave upon cooling to -40°C.

The first reduction process for complexes 1 and 2 has the appearance of being much less reversible than observed for **3** and **4**. For **1** and **2**, the data are consistent with significant aggregation in solution, even at room temperature. Notably, the broad first reduction wave in the cyclic voltammograms of 1 and 2 tends to further broaden with decreasing temperature. In the case of **1b** the wave appears to split into three overlapping waves as the temperature is lowered to -40°C. To our knowledge, this is the first report of the resolution of multiple waves for the first reduction process in cyclic voltammograms of platinum(II) terpyridyl complexes. These observations are corroborated by the differential pulse voltammetry measurements that show a broadening of the first reduction peak with decreasing temperature. In the case of **1a** and **2b**, distinct shoulders are evident as expected for the formation of dimers that are reduced at slightly different potentials than the monomers. In solutions of **1b**, it appears that two types of dimers are present. Interestingly, in an investigation of non-Beer's law behavior of Pt(tpy)Cl⁺ in 0.1 M LiCl/H₂O, Bailey et al.² found that the UV-visible absorption data also were consistent with the formation of two types of dimers. The authors proposed that one dimer is stabilized by metal---metal interactions and the other is stabilized by ligand...ligand interactions. A similar explanation may apply to **1b**.

Comparison of the electrochemical behavior of **2** and **3** suggests that switching the positions of the methyl groups on the ancillary aryl ring from the 3 and 5 positions to the 2 and 6 positions destabilizes the dimer that forms in solutions of **2**. Because these

groups are situated close to the axial sites of the metal center in **3**, we believe they primarily destabilize intermolecular metal…metal interactions. For this reason, we suggest that the most stable dimers formed by these complexes are supported by Pt…Pt interactions. However, we cannot entirely exclude the possibility that all of the dimers are supported by ligand…ligand interactions, since methyl groups at the 2 and 6 position also would be expected to interfere with this mode of association.

Future Directions. There remain at least several interesting questions surrounding this system. The preceding analysis rests heavily on earlier work by Hill et al.¹³ and Liu et al.⁴ dealing with the electrochemical properties of platinum(II) terpyridyl chloride complexes. The assignment of the first reduction couples should be confirmed by independent methods. For example, spectroelectrochemical measurements should allow for direct observation of bands associated with the terpyridyl radical. In addition, observation of non-Beer's law behavior for the cation and neutral complexes should allow for the determination of dimerization constants. Using variable sweep rates, it may be possible to corroborate these values by electrochemical methods, as well as estimate rates for dimer formation and dissociation. These results could help to explain the absence of splitting of the second reduction process. In addition, it is intriguing that the first reduction wave in cyclic voltammograms of 3b and 4b initially narrows with the decreasing temperature and then broadens between 0° and -40°C. This result may be evidence of a weakly stabilized dimer, perhaps supported by ligand...ligand interactions. It should be possible to follow the formation of the corresponding dimer by monitoring ΔE_p as a function of temperature. It also may be possible to prevent intermolecular association by substituting the tpy ligand with bulky substituents, such as *t*-butyl groups.

The success or failure of this endeavor should shed light on the relative significance of ligand...ligand and metal...metal interactions for solution dimerization.

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CHAPTER 7:

Spectroscopic Properties of Platinum(II) Terpyridyl Complexes with Aryl Ligands.

Introduction

Platinum(II) terpyridyl complexes often exhibit intermolecular metal…metal and/or ligand…ligand interactions in the solid state¹⁻¹¹ and fluid solution. For example, the UV-visible absorption spectra of $Pt(tpy)Cl^+$ in aqueous 0.1 M NaCl solution do not obey Beer's Law. With increasing concentration, Bailey and coworkers² observed the appearance of a new band near ~470 nm that is absent in the spectra of dilute solutions. From modeling of the absorption data, dimerization constants of $1.3(1) \times 10^3$ and $1.0(1) \times 10^3$ 10³ M⁻¹ were calculated for dimers supported by metal…metal and ligand…ligand interactions, respectively.² The aggregation of $Pt(tpy)Cl^+$ in frozen solution also is easily detected by emission spectroscopy.^{1-5,12-19} In dilute (<10 μ M) 77 K glassy solutions, highly structured luminescence is observed from a lowest π - π * excited state. Emission from a 0.15 mM sample exhibits two additional features, an unstructured band at 680 nm and a broader weakly structured band at 600 nm. The 680 nm feature was attributed to emission from a $d\sigma^*(Pt) \rightarrow \pi^*(tpy)$ excited state; the $d\sigma^*$ level is the antibonding combination resulting from the overlap of $5d_{z^2}$ orbitals of two closely interacting Pt centers. The 600 nm feature was attributed to excimeric emission from a dimer stabilized by terpyridine...terpyridine π - π interactions.² The preceding observations have inspired the present investigation aimed at understanding how steric bulk of platinum(II) terpyridyl complexes influences these intermolecular interactions.

In Chapter 5 we reported the synthesis and characterization of a series of platinum(II) terpyridyl complexes with ancillary aryl ligands having different steric properties (Scheme 7.1). For complexes **3** and **4**, the ancillary aryl ring is substituted with methyl groups directed above and below the platinum center. In **2**, the methyl groups are directed away from the platinum center. In **1**, the platinum center also is relatively exposed. Intermolecular metal…metal interactions, as well as ligand…ligand interactions to a lesser extent, should be hindered in **3** and **4**, as compared to **1** and **2**. In Chapter 6, we undertook an electrochemical investigation of this series of compounds. The results provided evidence that steric effects can be used to control aggregation of platinum(II) terpyridyl complexes in fluid solution. Comparison of the electrochemical



Scheme 7.1. Eight $Pt(R-tpy)(Ar)^+$ complexes (R=H or Ph; Ar = Ph, 3,5-dmph, 2,6-dmph, or mes).

behavior of 2 and 3 suggests that switching the positions of the methyl groups on the ancillary aryl ring from the 3 and 5 positions to the 2 and 6 positions destabilizes the dimer that forms in solutions of 2.

In this chapter we report the UV-visible absorption and emission spectra for this series of compounds. Emission measurements confirm that steric effects can be utilized to control intermolecular metal…metal and ligand…ligand stacking interactions in 77 K frozen solutions of these complexes.

Experimental. [Pt(tpy)(Ph)](BF₄) (**1a**(BF₄⁻)), [Pt(phtpy)(Ph)](BF₄) (**1b**(BF₄⁻)), [Pt(tpy)(3,5-dmph)](BF₄) (**2a**(BF₄⁻)), [Pt(phtpy)(3,5-dmph)](BF₄) (**2b**(BF₄⁻)), [Pt(tpy)(2,6-dmph)](BF₄) (**3a**(BF₄⁻)), [Pt(phtpy)(2,6-dmph)](BF₄) (**3b**(BF₄⁻)), [Pt(tpy)(mes)](BF₄) (**4a**(BF₄⁻)), and [Pt(phtpy)(mes)](BF₄) (**4b**(BF₄⁻)) were prepared as reported in Chapter 5. UV-visible absorption spectra were recorded using a HP8453 UVvisible spectrometer. Acetonitrile and methylene chloride were distilled from CaH₂. Ethanol was distilled from zinc metal and potassium hydroxide. Spectroscopic grade methanol and all other reagents were purchased from Acros (Pittsburg, PA).

Emission spectra were recorded with a SPEX Fluorolog-3 fluorimeter equipped with a double emission monochromator and a single excitation monochromator. 77 K glassy solutions were prepared by inserting a quartz EPR tube containing either a 4:1 EtOH:MeOH or a 2:1 MeOH:2-MeTHF solution of the complex into a quartz-tipped finger dewar. Emission spectra were corrected for instrumental response. 77 K glassy solutions were prepared by inserting a quartz EPR tube containing either a 4:1 EtOH:MeOH solution of the complex into a quartz-tipped finger dewar. Emission spectra were prepared by inserting a quartz EPR tube containing either a 4:1 EtOH:MeOH solution of the complex into a quartz-tipped finger dewar. Emission spectra were corrected for instrumental response. Emission samples for lifetime

measurements at 77 K were excited with 4-6 ns pulses from a Continuum Panther Optical Parametric Oscillator (420 nm) pumped with the third harmonic (355 nm) of a Continuum Surelite II Nd:YAG laser.

Results and Discussions

UV-Visible Absorption Spectroscopy. UV-visible absorption and 77 K emission data for complexes **1-4** are summarized in Table 7.1 and Figures 7.1 and 7.2. The eight complexes range in color from yellow to orange-red in the solid state, and dissolve to give yellow solutions. Platinum(II) terpyridyl complexes are known to stack in room temperature fluid solution and 77 K glassy solution through metal…metal and ligand…ligand interactions.^{2,3,12} These stacking interactions can be detected by changes in the UV-visible spectrum of the complexes as observed by Bailey and coworkers² for concentrated solutions of Pt(tpy)Cl⁺. In the present work, the aryl ligands are expected to interfere with room temperature stacking interaction.

The UV-visible absorption profiles of complexes **1-4** are similar to those of other platinum(II) terpyridyl complexes.^{1-3,10,12,14,17,19-22} The eight salts exhibits spin-allowed terpyridyl-center absorptions in the vicinity 240-290 nm (ε = 24000-40000 cm⁻¹M⁻¹) and 300-350 nm (ε = 6000-25000 cm⁻¹M⁻¹). These intense absorptions, which are relatively solvent insensitive, are similar to intense absorptions observed for Pt(tpy)Cl⁺ (DMF: 272 (36960), 284 (27710), 306 (12630), 318 (12800), 334 (17330), 350 nm (8860 cm⁻¹M⁻¹)),² Pt(4,4',4''-tri-*tert*-butyl-2,2';6',2''-terpyridine)Cl⁺ (CH₃CN: 256 (45100), 282 (33700), 306 (16400), 328 nm (20600), 343 nm (12300 cm⁻¹M⁻¹)),¹² Pt(tpy)(Me)⁺ (274 (15900), 314 nm (10100 cm⁻¹M⁻¹)),¹⁴ and Pt(phtpy)(Cl)⁺ (284 (36600), 334 nm (23500 cm⁻¹M⁻¹)).¹⁴

Compound	absorption λ_{max} , nm (ϵ , cm ⁻¹ M ⁻¹)
1a (BF ₄ ⁻)	231 (25900), 244sh (25100), 269 (25200), 278sh (24300), 315 (11800), 336 (9150), 400 (1750), 420 (1800), 475sh (270)
1b (BF ₄ ⁻)	245 (33500), 274 (40000), 284 (39700), 315 (24,500), 332sh (19500), 360sh (6000), 407 (4550), 425 (4300)
$2a(BF_4)$	236 (29300), 245sh (29200), 269 (27600), 278sh (26200), 316 (12700), 340 (9850), 400 (2000), 425 (2300), 480sh (550)
2b (BF ₄ ⁻)	234 (31500), 244sh (29400), 275 (34500), 285 (34300), 313 (20000), 335sh (14100), 403sh (3100), 430 (3750)
3a (BF ₄ ⁻)	247 (23100), 270 (26000), 278 (26000), 316 (11900), 332sh (7550), 345 (6150), 405 (1300), 430 (1150), 480sh (300)
3b (BF ₄ ⁻)	248 (31000), 275 (38300), 284 (36500), 315 (20800), 401 (2800), 433 (2200), 482sh (550)
4a (BF ₄ ⁻)	238 (30000), 247 (29300), 275 (35400), 281 (34500), 314 (19000), 403 (2700), 442 (1400), 492sh (600)
4b (BF ₄ ⁻)	247sh (26000), 267 (29200), 278 (28300), 316 (13500), 347 (6700), 403 (1550), 434 (1150), 490sh (400)

Table 7.1. Room-temperature UV-visible absorption data for 1-4 in acetonitrile.



Figure 7.1. Room-temperature UV-visible absorption spectra in acetonitrile for 1a (.....), 2a (____), 3a (____), and 4a (---). Right side of plots is scaled by a factor of 10.



Figure 7.2. Room-temperature UV-visible absorption spectra in acetonitrile for 1b
(.....), 2b (____), 3b (____), and 4b (---). Right side of plots is scaled by a factor of 10.

Two low-energy absorption bands are observed between 400 and 445 nm ($\varepsilon = 1100-4600 \text{ cm}^{-1}\text{M}^{-1}$). The solvent dependence of these bands (*e.g.*, **1a**. CH₃CN: 400, 420 nm; CH₂Cl₂: 408, 435 nm) and the magnitude of the molar absorbtivity (CH₃CN: (*e.g.*, **1a**, 400 (1750), 420 nm (1800 cm⁻¹M⁻¹)) are characteristic of spin-allowed 5d(Pt) $\rightarrow \pi^*(\text{tpy})$ metal-to-ligand charge transfer (¹MLCT) transitions. Similar assignments have been made for other platinum(II) terpyridyl complexes.^{1,2,12,17,23} However, due to the electron-donating properties of the aryl groups, these transition are shifted to lower energy than those observed for Pt(tpy)Cl⁺ (CH₃CN: 372 (1300), 398 nm (1200 cm⁻¹M⁻¹))¹ and Pt(phtpy)Cl⁺ (CH₃CN: 380 nm (shoulder), 402 nm (5200 M⁻¹cm⁻¹)).²³ Interestingly, there is little variation in the energies of these bands, though one would expect a stabilization of MLCT states as the ancillary ligand becomes more electron donating (ph < 3,5-dmph ≈ 2,6-dmph < mes).

For all complexes, except **1b** and **2b**, a weak shoulder (300-1000 cm⁻¹M⁻¹) is observed between 470 and 500 nm in the tail of the ¹MLCT absorption band. For **1b** and **2b**, this transition is likely buried in the tail of the ¹MLCT absorption band. It should be noted that previous emission studies of platinum(II) terpyridyl complexes suggest that the lowest predominantly spin-forbidden terpyridyl-centered π - π * transition lies near 21050 cm⁻¹ (475 nm). However, as the ancillary ligand becomes more electron donating (ph < 3,5-dmph \approx 2,6-dmph < mes), the energy of this shoulder distinctly decreases, **1a** (21050 cm⁻¹) > **2a** (20800 cm⁻¹) \approx **3a** (20800 cm⁻¹) > **4a** (20300 cm⁻¹). Therefore, we favor assignment to a lowest ³MLCT transition. This assignment is in agreement with that made by Lai and co-workers for Pt(4,4',4"-tri-*tert*-butyl-2,2':6',2"-terpyridine)Cl]⁺ (465 nm, 57 cm⁻¹M⁻¹),¹² though the weak intensity of that band is more consistent with a ³ π - π *
transition. The low-energy feature in the spectra of **1-4** is shifted 2000 to 4000 cm⁻¹ to the red of the ¹MLCT maximum, suggesting singlet-triplet splitting values comparable to that observed for Pt(phbpy)(4-aminopyridine)⁺ (2000 cm⁻¹) (phbpy = 6-phenyl-2,2'-bipyridine).²⁴ For comparison, typical singlet-triplet MLCT splittings for platinum(II) diimine complexes are 2000-3000 cm⁻¹.²⁵

Room-Temperature Fluid Solution Emission Spectroscopy. The roomtemperature fluid-solution emission spectra of **2a** and **3a** recorded in acetonitrile and **4a** and **4b** recorded in 4:1 EtOH:MeOH are shown in Figure 7.3. The data are summarized in Table 7.2. The broad emissions observed from **2a**, **3a**, **4a**, and **4b** are independent of concentration and exhibit maxima at 590, 615, 680, and 680 nm, respectively. The spectra are qualitatively similar to those reported for other platinum(II) terpyridyl complexes,^{1,1,2,17,19,20,26} including Pt(4,4',4"-trichloro-2,2';6',2"-terpyridine)Cl⁺ (620 nm, CH₃CN),¹⁷ Pt(4,4',4"-tri-*tert*-butyl-2,2';6',2"-terpyridine)(CH₂C(O)Me)⁺ (595 nm, CH₃CN),¹² and Pt(tpy)(OH)⁺ (621 nm, CH₃CN).²⁰ In all cases, the emissions from those complexes were assigned to a lowest ³MLCT excited state, and we make a similar assignment here. Though data were recorded in different solvents, it is noteworthy that the emission maxima appear to shift to lower energy as the ancillary aryl ligand becomes more electron donating, as expected for a MLCT excited state. The excited-state lifetimes of **2a** and **3a** in CH₂Cl₂ are short (τ <10 ns).

The room-temperature fluid solution emission spectra of 0.1 and 1.0 mM 4:1 EtOH:MeOH solutions of **1a** in are shown in Figure 7.4. The 0.1 mM solution exhibits a structured emission with maxima at 455 and 500 nm. A weaker emission is observed at 675 nm and it gains relative intensity as the concentration is increased (1.0 mM). As

compound -	$\lambda_{max} (nm)$		
	Room Temperature	77 K ^c	
1a (BF ₄ ⁻)		473, 509, 542, 587	
1b (BF ₄ ⁻)		505, 535	
2a (BF ₄ ⁻)	590 ^a	473sh, 510, 539	
2b (BF ₄ ⁻)		511, 535	
3a (BF ₄ ⁻)	615 ^a	473sh, 510, 540	
3b (BF ₄)		505, 540, 585	
4a (BF ₄ ⁻)	680 ^b	525	
4b (BF ₄ ⁻)	680 ^b	538	

 Table 7.2.
 Room-Temperature and 77 K Emission Data for 1-4.

^a Recorded in Acetonitrile. ^b Recorded in 4:1 Ethanol:Methanol. ^c 0.02 mM. in 4:1 EtOH:MeOH.



Figure 7.3. Room-temperature emission spectra of 2a (---), 3a (······) in acetonitrile and 4a (----), 4b (----) in 4:1 ethanol:methanol. Intensities have been arbitrarily scaled.



Figure 7.4. Room-temperature emission spectra of 1a in 4:1 ethanol:methanol,
0.10 mM (---) and 1.0 mM (---). Intensities have been arbitrarily scaled.

suggested for other platinum(II) terpyridyl complexes,^{1-5,12-19} the 675 nm emission is attributed to a lowest $d\sigma^*(Pt) \rightarrow \pi^*(tpy)$ excited state of a dimer supported by metal···metal interactions. A weak shoulder is observed at ~530 nm in the UV-visible spectrum of 1.0 mM solutions of **1a** (Figure 7.5a). This shoulder is attributed to a dimeric species. As observed for Pt(tpy)Cl⁺,² the band is not expected to follow Beer's law, and this possibility deserves further investigation. A similar feature (515 nm, λ_{em} =650 nm) is observed in the excitation spectrum of 1.0 mM solutions of **1a** (Figure 7.5b).



Figure 7.5. Room-temperature UV-visible (A) and Excitation spectra (B) of 1.0 mM $[Pt(tpy)(Ph)](BF_4) (\lambda_{em}=650 \text{ nm}) \text{ in } 4:1 \text{ EtOH:MeOH. For B, the short}$ wavelength data is not reliable due to the inner filter effect.

As expected for a charge-transfer transition, the emission from 2a and 3a are solvent sensitive. The emission maximum of 2a shifts from 600 nm in CH₂Cl₂ to 610 nm in CH₃CN, and a similar shift is observed for 3a (CH₂Cl₂: 620 nm; CH₃CN: 635 nm). Though the absolute emission quantum yields were not determined, the samples were excited at wavelengths where the absorbances were approximately equal (~0.44), allowing for determination of relative quantum yields. The ratio of the relative quantum yields was calculated using the integrated emission intensities (13500 to 19000 cm⁻¹) and corrected for differences in absorbances using equation $1:^{27}$

$$\frac{\Phi_1}{\Phi_2} = \frac{(1 - 10^{A_2})\eta_1^2 I_1}{(1 - 10^{A_1})\eta_2^2 I_2}$$
(1)

where A = absorbance of sample at the excitation wavelength, I = path length, η = refractive index of solvent, and I = integrated emission intensity.

While **2a** and **3a** are emissive in acetonitrile and methylene chloride, the emissions are much more intense in methylene chloride (Figures 7.6 and 7.7). The quantum yield of **2a** in CH₂Cl₂ (λ_{ex} =435 nm, λ_{max} =600 nm, *A*=0.43, *I*=7.76 x 10⁶) is 3.8 times larger than in CH₃CN (λ_{ex} =425 nm, λ_{max} =610 nm, *A*=0.45, *I*=2.16 x 10⁶). Similarly, the quantum yield of **3a** in CH₂Cl₂ (λ_{ex} =425 nm, λ_{max} =620 nm, *A*=0.44, *I*=6.42 x 10⁷) is 3.1 times larger than it is in CH₃CN (λ_{ex} =425 nm, λ_{max} =635 nm, *A*=0.44, *I*=2.16 x 10⁷). These data support Tears and coworkers²⁸ conclusion that quenching of the MLCT emission from platinum(II) terpyridyl chloride complexes by Lewis bases is relatively efficient (*e.g.*, Pt(4'-CN-tpy)Cl⁺ in CH₃CN, *k*_q=2.0 x10⁸ s⁻¹).

The emission spectra of **2a** and **3a** in methylene chloride and in acetonitrile are shown in Figures 7.8 and 7.9, respectively. The quantum yield of **3a** (λ_{ex} =425 nm, λ_{max} =620 nm, *A*=0.44, *I*=6.42 x 10⁷) in methylene chloride is 8.2 times larger than that of **2a** (λ_{ex} =435 nm, λ_{max} =600 nm, *A*=0.43, *I*=7.76 x 10⁶) in methylene chloride. The difference in quantum yield is slightly greater in acetonitrile, where the quantum yield of **3a** (λ_{ex} =425 nm, λ_{max} =635 nm, *A*=0.44, *I*=2.16 x 10⁷) is 9.6 times larger than that of **2a**



Figure 7.6. Room-temperature emission spectra of **2a** in methylene chloride (——, λ_{ex} =425 nm, absorbance=0.43) and acetonitrile (— —, λ_{ex} =425 nm, absorbance=0.45). The data were truncated at 540 nm because of light scatter.



Figure 7.7. Room-temperature emission spectra of **3a** in methylene chloride (——, λ_{ex} =425 nm, absorbance=0.44) and acetonitrile (— —, λ_{ex} =425 nm, absorbance=0.44).



Figure 7.8. Room-temperature emission spectra of **2a** (- -, λ_{ex} =435 nm, absorbance=0.43) and **3a** (----, λ_{ex} =425 nm, absorbance=0.44) in methylene chloride.



Figure 7.9. Room-temperature emission spectra of **2a** (— —, λ_{ex} =425 nm, absorbance=0.45) and **3a** (—, λ_{ex} =425 nm, absorbance=0.44) in acetonitrile.

 $(\lambda_{ex}=425 \text{ nm}, \lambda_{max}=610 \text{ nm}, A=0.45, I=2.16 \text{ x } 10^6)$. The observation that **3a** ($\lambda_{max}=635$ nm) has a larger quantum yield than **2a** ($\lambda_{max}=610 \text{ nm}$) is in contradiction to expectations based on the energy gap law.²⁹ However, these results are qualitatively consistent with the suggestion of Crites and coworkes²² that the short excited-state lifetime (<10 ns) and consequently low quantum yield (0.0004) observed for Pt(tpy)Cl⁺ in CH₂Cl₂ ($\lambda_{em}=500$, 535, and 590 nm) is due to quenching of the ³MLCT excited state by a low-lying ligand field (³LF) excited state ($k_{nr}=4 \text{ x } 10^{-12} \text{ s}^{-1}$). As the ³MLCT state shifts to lower energy as observed for Pt(4'-NMe₂-tpy)Cl⁺ ($\lambda_{em}=535$, 570, and 635sh), k_{nr} decreases ($k_{nr}=1.5 \text{ x } 10^{-7} \text{ s}^{-1}$) and the lifetime (1.92 µs) and quantum yield (0.08) increase.³⁰ An alternative explanation is that the methyl groups directed over the axial sites of the platinum center prevents quenching of the ³MLCT excited state by solvent.

77 K Glassy Solution Emission Spectroscopy. The 77 K emission spectra of dilute solutions (0.02 mM) of **1a-4a** in 4:1 EtOH:MeOH are shown in Figures 7.10, and data are summarized in Table 7.2. Samples of **1a** exhibit an intense and structured green emission (473, 509, 542, and 587 nm) with vibronic spacings of 1100-1500 cm⁻¹. The emission profile appears qualitatively similar to ${}^{3}\pi$ - π * ligand-centered emissions previously reported for platinum(II) terpyridyl complexes, 1,10,12,14,17 though the emission is somewhat broadened and more intense than expected from 525 to 600 nm. A careful investigation of this and the other complexes indicates that the emission spectra are concentration dependent. For example, as the concentration of **1a** is increased, two distinctly new features are observed maximizing at 545 and 700 nm (Figure 7.11). Initially, the 545 nm band gains intensity at the expense of the structured emission near 510 nm. At higher concentrations, the 700 nm band gains intensity relative to the 545 nm

emission. At the highest concentration investigated (1.0 mM), the 700 nm band dominates the spectrum. In analogy to the behavior observed for Pt(tpy)Cl⁺, the 545 nm emission is attributed to excimeric emission from a dimer stabilized by terpyridine…terpyridine π - π interactions. The 700 nm emission is attributed to emission from a d $\sigma^*(Pt) \rightarrow \pi^*(tpy)$ excited state in which the dimers are stabilized by metal…metal interactions. In the excitation spectrum (λ_{max} =678 nm) of a 1.0 mM sample of **1a** (Figure 7.11 inset), a band is observed at ~540 nm attributed to the d $\sigma^*(Pt) \rightarrow \pi^*(tpy)$ state. Similar behavior has been observed for more than several platinum(II) terpyridyl complexes.^{1,2,14,16,17,19,31} For example, Pt(phtpy)Cl⁺ in 77 K butyronitrile glassy solution exhibits a structured π - π^* emission (505, 540, and 580 nm). As the concentration is increased, two broad, unstructured bands of higher intensity are centered at 622 and 676 nm.¹⁶ Bailey and coworkers made similar assignments for Pt(tpy)Cl⁺.²

Emissions from 0.02 mM glassy solutions of **2a** and **3a** are qualitatively different than that observed for **1a** (Figures 7.12 and 7.13). The profiles of **2a** and **3a** are virtually identical; both are broad and weakly structured with maxima at 511 and 536 nm as well as a shoulder at 475 nm. The emission maxima occur at approximately the same energy as the maximum observed for **1a**, and also are tentatively assigned as originating from a ${}^{3}\pi$ - π * lowest excited state. The reason for the broadening is not certain; one possibility is that significant aggregation occurs at low concentrations. Due to low solubility, the most concentrated sample of **2a** examined was 0.5 mM (Figure 7.10), and the resulting emission is similar to those observed for 1.0 and 0.5 mM samples of **1a**. Intense, broad bands occur at 540 and 680 nm. The 540 nm band is attributed to excimer emission, and the 680 nm feature is attributed to emission from a d σ *(Pt) $\rightarrow \pi$ *(tpy) excited state. The

excitation spectra (λ_{max} =475 nm) of a 0.02 mM sample of **2a** are in good agreement with the room-temperature absorption spectra. However, when the emission is monitored at 510 or 575 nm, the excitation bands broaden and shift to lower energy (Figure 7.12 inset). The excitation spectrum (λ_{max} =530 nm) of a 1.0 mM sample of **2a** is broad, and the band shifts to lower energy when the emission is monitored at 670 nm. The emission and excitation data suggest the presence of more than one emitting species in 77 K glassy solution, even at low concentrations (0.02 mM). One possibility is that considerable stacking occurs even in 0.02 mM 77 K glassy solutions of **2a** and **3a**. On the other hand, broadened emissions are consistent with significant ³MLCT character. One possibility is that the emission originates from thermally equilibrated ³ π - π * and ³MLCT states. Alternatively, the lowest emissive state may be an admixture of MLCT and π - π * character.

Emissions from 0.02 mM glassy solutions of **4a** are broad and structureless with a maximum at 535 nm (Figure 7.14). The origin of this emission (490 nm) is shifted ~1100 cm⁻¹ from the origin of the structured π - π * emission observed for **1a**. Also, the emission maximum of **4a** is shifted by ~2000 cm⁻¹ to the red of the maximum observed for **1a**. These data are inconsistent with a lowest π - π * excited state as its energy is expected to be insensitive to substitution of the ancillary phenyl ligand, as observed for **1a**-**3a**. Because of the lack of structure and the shift of the emission origin, the emission is tentatively assigned to a ³MLCT lowest excited state. The mesityl groups appear to prevent stacking interactions at concentrations \leq 0.5 mM. However, the emission maximum (555 nm) of a 1.0 mM sample of **4a** is shifted to longer wavelengths than observed for more dilute solutions (Figure 7.14), suggesting the formation of dimers,

presumably stabilized by ligand...ligand interactions. The excitation spectra of 0.02 and 1.0 mM glassy solution samples of **4a** are in good agreement with the room-temperature absorption spectra. The emission decay of 0.05 mM **4a** is adequately modeled with a single exponential function (τ = 6.1 µsec).

The 77 K emission spectra of dilute solutions (0.02 mM) of salts of **1b-4b** in 4:1 EtOH:MeOH are shown in Figure 7.15, and the data are summarized in Table 7.2. The spectra of 1b, 2b and 3b are very similar. Complex 1b exhibits an intense and structured green emission (505, 535, and 585 nm) with vibrational spacings of 1100-1600 cm⁻¹. The origin (~480 nm) and maxima of the emissions are independent of substituents on the ancillary aryl ligand, and the emissive state is tentatively assigned to a lowest spinforbidden π - π * excited state. Emissions from **1b-3b** are concentration dependent, and emission spectra of 1b, 2b and 3b at various concentrations are shown in Figures 7.16, 7.17 and 7.18, respectively. Emission from 1.0 mM glassy solutions of **1b** originates at ~490 nm and exhibits maxima at 530, 570, and 615 nm. Emission from 0.02 mM glassy solutions of **3b** originates at ~480 nm and exhibits maxima at 508, 538 and 585 nm. For concentrated solutions of **3b** (1.0 mM), the emission maxima red shifts slightly and gains intensity, presumably due to ligand...ligand interactions. Complex 4b exhibits an intense green emission (0.02 mM, 537 nm, Figure 7.19) similar to the emission observed for 4a and is similarly assigned as originating from a ³MLCT excited state. However, emission from 77 K glassy solutions of **4b** is concentration dependent. At concentrations >0.02mM the emission origin shifts to slightly lower energy, presumably due to ligand…ligand interactions. The excitation spectra of 0.02 and 1.0 mM samples of 4b (λ_{em} =540 nm) are in good agreement with the room-temperature absorption spectra. The emission decay of

0.05 mM **4b** is adequately modeled with a single exponential function (τ = 6.6 µsec).

Conclusions and Future Directions. In this chapter, we investigated the spectroscopic properties of a series of platinum(II) terpyridyl complexes with an ancillary aryl ligand. In fluid solution, the complexes exhibit characteristic ³MLCT emission. Though the emissions are very short-lived, the emission intensities are consistent with an increase in emission quantum yield when methyl groups are situated at the 2 and 6 positions of the aryl ligand. This result may be a consequence of protecting the metal center from solvent. However, the data also are consistent with the presence of a low-lying ³LF state. A more detailed investigation may resolve the issue. It is expected that **2b** and **3b** will exhibit weak fluid solution emission, and attempts should be made to collect those data. Also, the fluid solution emission spectra of all complexes should be recorded in the same solvent for purposes of comparison. It would be interesting to determine the relative quantum yields of the other complexes with respect to **2a** and **3a**.

In 77 K glassy solution, complexes **1a** and **1b** exhibit emission from a lowest ${}^{3}\pi$ - π * excited state. Substitution of the phenyl ligand with three methyl groups results in a complex (**4**) with a lowest 3 MLCT excited state. The emission spectra of these eight complexes are concentration dependent. At 1.0 mM, the 77 K emission spectrum of **1** exhibits features characteristic of dimers stabilized through ligand…ligand and metal…metal stacking interactions. When the 2 and 6 positions of the ancillary aryl ligand are substituted with methyl groups, emissions from metal…metal aggregates are not observed. However, emissions from ligand…ligand aggregates are evident, albeit at higher concentrations. In a future investigation, the lifetimes of **1-3** should be recorded. Stacking interactions are prevalent in samples of these complexes, and single-exponential

decays are not expected; preliminary observations confirm this hypothesis. However, it may be possible to fit emission decay data of the selectively excited metal…metal aggregates using a single exponential function.

It is intriguing that the origin of the ${}^{3}MLCT$ emission of 4a at 77 K (20400 cm⁻¹) is only shifted by ~1100 cm⁻¹ to the red of the origin of the ${}^{3}\pi$ - π * emission observed for **1a** (21500 cm⁻¹). Connick and coworkers also observed distinct crossover between ${}^{3}\pi$ - π * and ³MLCT states of Pt(2,2'-bipyridine)(pyrazolyl)₂ over a very narrow energy region.²⁵ Qualitatively the data are very similar to those observed for 1a and 4a. A structured highenergy emission profile characteristic of a ${}^{3}\pi$ - π * lowest excited state is observed for one complex, and a broad emission characteristic of a ³MLCT lowest excited state shifted to slightly lower energy is observed for the other complex. It is intriguing that substitution of an ancillary phenyl ring with zero (1a), two (2a and 3a) or three (4a) electron donating methyl groups results in emissions that originate at similar energies, but have different profiles. Depending on the complex, the emissions originate from a predominately ${}^{3}\pi$ - π * state (1a), a predominately ³MLCT state (4a) and possibly a mixture of the two states (2a) and **3a**). The emission spectra of **2a** and **3a** should be investigated at even lower concentrations to determine if further concentration dependence can be observed. Nevertheless, the results clearly suggest that a sharp crossover of the lowest ${}^{3}\pi$ - π * and ³MLCT states occurs over a very narrow energy regime, suggesting only weak mixing of these states. This result seems to contradict earlier assumptions of strong mixing.^{21,32}



Figure 7.10. 77 K emission spectra of 0.02 mM samples of 1a (----), 2a (----), 3a (.....) and 4a (----) in 4:1 ethanol:methanol glassy solution. Intensities have been arbitrarily scaled.



Figure 7.11. 77 K emission spectra of **1a** in 4:1 ethanol:methanol glassy solution, 0.02 (----), 0.05 (----), 0.1 (----), 0.5 (----) and 1.0 mM (-----). Intensities have been arbitrarily scaled. Inset: Excitation spectra of a 1.0 mM sample of **1a** ($\lambda_{max} = 678$ nm).



Figure 7.12. 77 K emission spectra of 2a in 4:1 ethanol:methanol glassy solution, 0.02 (----), 0.067 (-----), 0.1 (-----) anc --.5 (----). Intensities have been arbitrarily scaled. Inset: Excitation spectra of a 0.02 mM sample of 2a, monitoring the emission at 475 (-----), : 0 (-----), and 575 nm (-----).



Figure 7.13. 77 K emission spectra of 3a in 4:1 ethanol:methanol glassy solution, 0.02 (----), 0.05 (----), 0.1 (----), 0.5 (----) and 1.0 mM (.....). Intensities have been arbitrarily scaled.



Figure 7.14. 77 K emission spectra of 4a in 4:1 ethanol:methanol glassy solution, 0.02 (----), 0.05 (----), 0.1 (----), 0.5 (----) and 1.0 mM (.....). Intensities have been arbitrarily scaled.



Figure 7.15. 77 K emission spectra of 0.02 mM samples of 1b (----), 2b (----), 3b
(······) and 4b (----) in 4:1 ethanol:methanol glassy solution. Intensities have been arbitrarily scaled.



Figure 7.16. 77 K emission spectra of 1b in 4:1 ethanol:methanol glassy solution, 0.02 (----), 0.05 (----), 0.1 (----), 0.5 (----) and 1.0 mM (.....). Intensities have been arbitrarily scaled.



 Figure 7.17.
 77 K emission spectra of 2b in 4:1 ethanol:methanol glassy solution, 0.005

 (---), 0.02 (----), 0.05 (-----), 0.1 (----), and 0.287 (----).
 Intensities have been arbitrarily scaled.



Wavelength

Figure 7.18. 77 K emission spectra of **3b** in 4:1 ethanol:methanol glassy solution, 0.005

(-----), 0.05 (-----), 0.02 (-----), 0.1 (------), 0.5 (-----) and 1.0 mM

 $(\cdots \cdots)$. Intensities have been arbitrarily scaled.



 Figure 7.19.
 77 K emission spectra of 4b in 4:1 ethanol:methanol glassy solution, 0.02

 (----), 0.05 (----), 0.1 (----), 0.5 (----) and 1.0 mM (.....).

Intensities have been arbitrarily scaled.

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CHAPTER 8:

Synthesis and Characterization of Two-Electron Platinum Reagents.[†]

Introduction. Late transition metal compounds typically undergo two-electron changes in oxidation state by inner-sphere mechanisms (*e.g.*, oxidative addition and reductive elimination reactions). This behavior suggests that we can design cooperative two-electron reagents, shuttles or reservoirs that reversibly transfer two electrons at the same potential in multi-redox catalytic reactions or molecular devices. In the case of platinum, an obvious practical problem is that the interconversion between square planar Pt(II) and octahedral Pt(IV) by outer-sphere electron transfer is slow and characterized by irreversible electrochemistry because of the accompanying large molecular reorganization.^{4,5} However, high concentrations of coordinating anions can facilitate interconversion, and cyclic voltammograms of the complexes can exhibit apparent two-electron waves, albeit with large peak-to-peak separations ($\Delta E_p = E_{pa} - E_{pc}$).⁵⁻⁷ Our general



[†] Chapter 8 is a compilation of several manuscripts,¹⁻³ as well as some unpublished data.

approach is to design complexes with meridional (*mer*) coordinating ligands (pip₂NCN⁻ and tpy) that are capable of stabilizing both four-coordinate Pt(II) and six-coordinate Pt(IV) geometries (Scheme 8.1).



Scheme 8.1. Schematic representation of a reversible two-electron platinum reagent.

Though several previously investigated systems are capable of supporting both oxidation states, the electronic and steric properties of the ligands in these complexes result in CVs characterized by one-electron waves corresponding to generation of Pt(III).⁸⁻¹⁵ In this chapter we report the first examples of platinum complexes that meet our criteria and provide proof-of-concept by undergoing a nearly electrochemically reversible two-electron oxidation process.

Experimental. Acetonitrile and methylene chloride were distilled over CaH₂. All other reagents were purchased from Acros and used as received. Pt(pip₂NCN)Cl (Chapters 2 & 3)^{1,16} [Pt(tpy)(2,6-dmph)](BF₄) (Chapter 5, dmph=dimethylphenyl) and phtpy (Chapter 5)^{17,18} were prepared as previously described. Tetrabutylammonium hexafluorophosphate (TBAPF₆) was recrystallized twice from boiling methanol and dried under vacuum prior to use.

¹H NMR spectra were recorded at room temperature using a Bruker AC 250 MHz spectrometer. Deuterated chloroform (0.03 % tetramethylsilane (TMS)) and acetonitrile were purchased from Cambridge Isotope Laboratories. Mass spectra were recorded using a Micromass Q-TOF hybrid quadrapole time of flight mass spectrometer with electrospray ionization. Elemental analyses were performed by Atlantic Microlabs (Norcross, GA). Cyclic voltammetery was carried out using a standard three-electrode cell and a CV50w potentiostat from Bioanalytical Systems. Scans were collected in acetonitrile solution containing 0.1 M TBAPF₆. All scans were recorded using a platinum wire auxiliary electrode, a Ag/AgCl reference electrode (3.0 M NaCl) and a 0.79 mm² gold working electrode. Between scans, the working electrode was polished with 0.05 µm alumina, rinsed with distilled water and wiped dry using a Kimwipe. Reported potentials are referenced against Ag/AgCl (3.0 M NaCl). Peak currents (i_p) were estimated with respect to the extrapolated baseline current as described elsewhere.¹⁹ 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° . Passed charge (Q) during the sweep was estimated by integrating the current from E°'+150 mV to E°'-150 mV. Calculated averages are reported as average value $\pm 2\sigma$. Under these conditions, the ferrocene/ferrocenium (FcH/FcH^{+}) couple occurs at 0.45 V.

 $[Pt(tpy)(pip_2NCN)](BF_4)$ (1(BF₄)). A mixture of silver tetrafluoroborate (0.077 g, 0.40 mmol) and Pt(pip_2NCN)Cl (0.20 g, 0.40 mmol) in 35 ml of acetone was allowed to stir for 30 minutes at room temperature. The resulting precipitate was removed by vacuum filtration through celite. After addition of tpy (0.093 g, 0.40 mmol), the filtrate was allowed to stir for 18 hours, and the solvent was removed by rotary-evaporation.

The red solid was dissolved in CH₂Cl₂ and ether was added to induce precipitation. The product was washed with ether and dried. Yield 0.22 g, 70%. Anal. Calcd. for $[C_{33}H_{38}N_5Pt]](BF_4) \cdot \frac{1}{2}CH_2Cl_2$: C, 48.53; H, 4.74; N, 8.45. Found: C, 48.55; H, 4.72; N, 8.32. ¹H NMR (CDCl₃, δ): 1.06 (8H, m, CH₂), 1.21 (4H, m, CH₂), 2.27 (8H, m, CH₂), 3.65 (4H, s, CH₂), 7.15 (3H, m, CH), 7.37 (2H, t, CH), 8.13 (2H, d with Pt satellites, J_{Pt-H}=50 Hz, CH), 8.28 (2H, t, CH), 8.44-8.69 (5H, m, CH). Variable temperature ¹H NMR studies show no evidence of fluxional behavior from 232 K to 298 K.

 $[Pt(tpy)(pip_2NCNH_2)](PF_6)_3$ (1H₂(PF₆)₃). A mixture of silver tetrafluoroborate (0.077 g, 0.40 mmol) and Pt(pip₂NCN)Cl (0.20 g, 0.40 mmol) in 35 ml of acetone was allowed to stir for 30 minutes at room temperature. The resulting precipitate was removed by vacuum filtration through celite. After addition of tpy (0.093 g, 0.40 mmol), the filtrate was allowed to stir for 18 hours. HNO₃ (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 NH₄PF₆ was added to precipitate the product. The yellow solid was collected by vacuum filtration, washed with ether and dried under vacuum. The product was recrystallized by dissolving in CH₃CN followed by precipitation with diethyl ether. Yield 0.29 g, 63%. Anal. Calcd. for $[C_{33}H_{40}N_5Pt](PF_6)_3$: C, 34.87; H, 3.55; N, 6.16. Found: C, 35.26; H, 3.44; N, 6.35. MS (ESI): m/z = 991.179 ((Pt(tpy)(pip_2NCNH₂) • $2PF_6$)⁺), m/z = 845.243 ((Pt(tpy)(pip_2NCNH) • PF_6)⁺), m/z = 466.181 (Pt(pip_2NCN)⁺), m/z= 350 (Pt(tpy)(pip_2NCNH)²⁺). ¹H NMR (CD₃CN, δ): 1.50 (12H, m, CH₂), 2.80 (4H, m, CH₂), 3.27 (4H, m, CH₂), 4.63 (4H, d, CH₂), 6.88 (2H, broad, NH), 7.47-7.61 (5H, m, CH), 7.93 (2H, d with Pt satellites, J_{Pt-H}=48 Hz, CH), 8.30-8.56 (7H, m, CH).

[Pt(phtpy)(pip₂NCN)](BF₄) (2(BF₄⁻)). Prepared by the same procedure as **1**(BF₄⁻), substituting the appropriate starting materials. Silver tetrafluoroborate (0.077 g, 0.40 mmol), Pt(pip₂NCN)Cl (0.20 g, 0.40 mmol), and phtpy (0.123 g, 0.40 mmol). The product was recrystallized by slow vapor diffusion of Et₂O into a CH₂Cl₂ solution of **2**(BF₄⁻). Yield 0.22 g, 70%. Anal. Calcd. for **2**(BF₄⁻): C, 54.30; H, 4.11; N, 8.12. Found: C, 54.22; H, 4.96; N, 8.00. ¹H NMR (CDCl₃, δ): 1.20 (12H, m, CH₂), 2.33 (8H, m, CH₂), 3.80 (4H, s, CH₂), 7.04-7.28 (6H, m, CH), 7.41 (2H, t, CH), 7.91 (2H, m, CH), 8.13 (2H, d with Pt satellites, J_{Pt-H}=54 Hz, CH), 8.30 (2H, t, CH), 8.52 (2H, s, CH), 8.72 (2H, d, CH). The CF₃SO₃⁻ salt (**2(CF₃SO₃⁻)**) was prepared by the same procedure as **2**(BF₄⁻), substituting silver triflate for silver tetrafluoroborate. MS (ESI): *m*/*z* = 925.260 ((Pt(phtpy)(pip₂NCNH) • CF₃SO₃)⁺), *m*/*z* = 775.307 (Pt(phtpy)(pip₂NCN)⁺), *m*/*z* = 466.181 (Pt(pip₂NCN)⁺).

[Pt(phtpy)(pip₂NCNH₂)](PF₆)₃ (2H₂(PF₆⁻)₃). Prepared by the same procedure as 1H₂(PF₆⁻)₃, substituting the appropriate starting materials. Silver tetrafluoroborate (0.070 g, 0.36 mmol), Pt(pip₂NCN)Cl (0.18 g, 0.36 mmol), and phtpy (0.111 g, 0.36 mmol). Yield 0.29 g, 63%. Anal. Calcd. for 2H₂(PF₆⁻)₃ • 3/2CH₃CN: C, 38.96; H, 3.72; N, 6.25. Found: C, 39.17; H, 3.75; N, 6.11. ¹H NMR (CD₃CN, δ): 1.45-1.61 (12H, m, CH₂), 2.82 (4H, m, CH₂), 3.29 (4H, m, CH₂), 4.66 (4H, d, CH₂), 6.96 (2H, broad, NH), 7.51-7.64 (5H, m, CH), 7.95 (2H, d with Pt satellites, J_{Pt-H}=50 Hz, CH), 8.05 (2H, m, CH), 8.34 (2H, dd, CH), 8.51 (2H, d, CH), 8.68 (2H, s, CH).

X-ray crystallography. Yellow plates of $1H_2(Cl^-)_3 \cdot 4H_2O$ were grown by slow evaporation of an acetone solution of 1 containing excess HCl(aq). Single crystals of $2(BF_4^-)$ were obtained as red blocks by slow vapor diffusion of Et₂O into an acetone

solution. For X-ray examination and data collection, suitable crystals of $1H_2(Cl^{-})_3$. 4H₂O were mounted on the tip of a glass fiber with epoxy resin and suitable crystals of $2(BF_4)$ were mounted on a cryo-loop with paratone-N. Intensity data were collected using a standard Siemens SMART 1K CCD diffractometer for 1H₂(Cl⁻)₃ • 4H₂O and a SMART6000 CCD diffractometer for $2(BF_4)$. Graphite-monochromated Mo Ka radiation, $\lambda = 0.71073$ Å, was used for the X-ray source. The data frames were processed using the program SAINT.²⁰ Intensities were corrected for Lorentz, polarization and decay effects. Absorption and beam corrections based on the multi-scan technique were applied using SADABS.²¹ The structures were solved by a combination of the Patterson method in SHELXTL²² and the difference Fourier technique, and the models refined by full-matrix least squares on F² for data out to 0.8 Å resolution. Non-hydrogen atoms were refined with anisotropic displacement parameters. Weights were assigned as $w^{-1} = [\sigma^2(F_0^2) + (0.0658P)^2 + 21.0649P]$ where P=0.33333F_0^2 + 0.66667F_c^2. The H atoms bonded to nitrogen for $1H_2(Cl^{-})_3 \cdot 4H_2O$ were located directly, whereas the remaining H atoms for $1H_2(Cl^-)_3 \cdot 4H_2O$ and all H atoms for $2(BF_4^-)$ were either located directly or calculated based on geometric criteria and treated with a riding model. Hydrogen atom isotropic displacement parameters were assigned as a times U_{eq} of the adjacent atom where a=1.5 for -OH, and 1.2 for all others. One of the chloride ions in $1H_2(Cl^-)_3 \cdot 4H_2O$ is disordered (occupancy set at 0.5), and the molecule crystallizes with 4 waters, one of which is disordered (occupancy set at 0.5). Crystallographic data are summarized in Table 8.1.

Formula	$(\mathbf{1H}_2(\mathrm{Cl}^-)_3 \bullet 4\mathrm{H}_2\mathrm{O})$	$(2(BF_{4}))$
Fw, g/mol	880.20	862.68
Space group	$P2_1/c$	$P2_1/n$
<i>a</i> , Å	23.5863(17)	17.0146(6)
b, Å	15.7557(11)	18.9722(7)
c, Å	10.2636(7)	22.7738(8)
<i>α</i> , °	90	90
<i>β</i> , °	91.5510(10)	102.354(1)
γ, °	90	90
V, Å ³	3812.7(5)	7181.3(4)
Ζ	4	8
<i>T</i> , K	298(2)	150(2)
reflns collected	37844	99199
Ind reflns	7793	17868
R _{int}	0.0404	0.0936
GOF on F^2	1.125	1.020
$R_1/wR_2 [I \ge 2\sigma(I)]^a$	0.0527/0.1405	0.0382/0.0787
R_1/wR_2 (all data) ^a	0.0644/0.1460	0.0779/ 0.0969

Table 8.1. Crystallographic Data for $1H_2(Cl^-)_3 \cdot 4H_2O$ and $2(BF_4^-)$.

^a $R_1 \Sigma ||F_o| - |F_c|| \Sigma |F_o|, wR_2 = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2]^{\frac{1}{2}}.$
Results and Discussion.

Synthesis and Characterization. The synthesis of 1-2 is shown in Scheme 8.2. The chloride ion was displaced by first stirring an acetone solution (40 ml) of Pt(pip₂NCN)Cl with a silver salt (e.g., AgBF₄). After removal of the resultant silver chloride by filtration, one equivalent of tpy or phtpy was added to the filtrate. After ~ 10 minutes, the solution turned deep red and was stirred overnight. During the course of this reaction, the terpyridyl ligand displaces the piperidyl groups of the pip₂NCN⁻ ligand, as confirmed by ¹H NMR and X-ray crystallographic studies of the product (*vide infra*). The solvent was removed by rotory-evaporation and the red oil was dissolved in CH₂Cl₂. Diethyl ether was added to induce precipitation of the red product. Complexes 1 and 2 were recrystallized by slow vapor diffusion of diethyl ether into a methylene chloride solution. The triflate salts of 1 and 2 were prepared by substituting $AgBF_4$ with AgCF₃SO₃. The most challenging part of the synthesis is obtaining analytically pure samples. Vapor diffusion, as described above, gave the most consistent results, though some of the highest grade samples were isolated as crystals from the filtrate during product collection. Powder samples tend to have a red-brown color while crystalline samples have a very deep red color. Obtaining analytical samples of $1H_2$ and $2H_2$ is much easier. A solution of 1 M HNO₃ was added dropwise to the deep red acetone solution from the initial preparation of 1 and 2 until the solutions turned bright yellow. The yellow solution was allowed to stir for 30 minutes, and H₂O (20 ml) was added. The volume was reduced to ~ 20 ml by rotary evaporation. The yellow solution was filtered, and a concentrated aqueous solution of NH₄PF₆ was added to precipitate a yellow powder. The product was recrystallized by dissolving in CH₃CN and inducing

precipitation with Et_2O . Complexes 1-2 were fully characterized by elemental analysis, ¹H NMR spectroscopy and mass spectrometry.

The ¹H NMR spectra of **1** and **2** were recorded in CDCl₃ (Figures 8.1 and 8.3) and the ¹H NMR spectra of **1H**₂ and **2H**₂ were recorded in CD₃CN (Figures 8.2 and 8.4). A general labeling scheme for non-equivalent protons (A-O) is shown in Scheme 8.2 for



(i) AgBF₄, tpy; (ii) HNO₃, NH₄PF₆; (iii) AgBF₄, phtpy; (iv) HNO₃, NH₄PF₆

Scheme 8.2. Syntheses of 1-2.

complex 2. Resonances were fully assigned by comparison with similar complexes (Chapters 2-5) and the presence of ¹⁹⁵Pt satellites associated with resonance G (Scheme 8.2). Resonances A and B overlap and appear as multiplets between 7.1 and 7.6 ppm. For **1**, **1H**₂, **2**, and **2H**₂, resonance G is coupled to the platinum with coupling constants ($J_{\text{H-Pt}}$) of 50, 48, 54, and 50 Hz, respectively, comfirming that the tpy ligand is tridentate in solution. For **2** and **2H**₂, resonance K is a singlet at 8.52 and 8.68 ppm, respectively. The resonances for the pip₂NCN⁻ benzylic protons appear as singlets without ¹⁹⁵Pt satellites for **1** (3.65 ppm) and **2** (3.80 ppm), and as doublets with small coupling constants of ~4 Hz for **1H**₂ (4.63 ppm) and **2H**₂ (4.66 ppm). Thus the ¹H NMR spectra provide no indication of direct interaction between the piperidyl groups and the plaitinum center. Because the piperidyl aliphatic protons D, E, and F are necessarily diastereotopic in the protonated complexes, **1H**₂ and **2H**₂, these resonances appear as complex multiplets, as previously noted for complexes with tridentate pip₂NCN⁻ (Chapters 2-4).^{1,16}

Crystal Structures. The structures of $1H_2(C\Gamma)_3 \cdot 4H_2O$ and $2(BF_4)$ were confirmed by single-crystal X-ray diffraction. ORTEP diagrams are shown in Figures 8.5 and 8.6, and relevant data are summarized in Tables 8.1 and 8.2. One of the chloride ions in crystals of $1H_2(C\Gamma)_3 \cdot 4H_2O$ is disordered (occupancy set at 0.5), and the molecule crystallizes with 4 water molecules, one of which is disordered (occupancy set at 0.5). The BF₄⁻ salt of **2** crystallizes with two cation molecules in the asymmetric unit. The complexes adopt distorted square planar structures that are qualitatively similar to those of other platinum(II) terpyridine complexes.²³⁻³⁴

The Pt-C(phenyl) distances for $1H_2$ (2.031(8) Å) and 2 (2.041(5),2.047(5) Å) are similar to the Pt-C(phenyl) distances reported for Pt(phtpy)(Ph)⁺ (2.025(2) Å),



Figure 8.1. ¹H NMR spectrum of **1**(BF₄⁻) in CDCl₃. Solvent and TMS resonances are labeled with *.



Figure 8.2. ¹H NMR spectrum of $1H_2(PF_6)_3$ in CD₃CN. Solvent resonances are labeled with *.



Figure 8.3. ¹H NMR spectrum of **2**(BF₄⁻) in CDCl₃. Solvent and TMS resonances are labeled with *.



Figure 8.4. ¹H NMR spectrum of $2H_2(PF_6)_3$ in CD₃CN. Solvent resonances are labeled with *.

	$\mathbf{1H}_{2}(\mathrm{Cl}^{-})_{3}\bullet 4\mathrm{H}_{2}\mathrm{O}$	2 (BF ₄ ⁻)
Pt-C(16)	2.031(8)	2.041(5)/2.047(5)
Pt-N(1)	2.030(6)	2.027(4)/2.035(4)
Pt-N(2)	2.010(7)	2.032(4)/2.029(4)
Pt-N(3)	2.005(6)	1.980(4)/1.972(4)
N(1)-C(5)	1.368(9)	1.378(6)/1.380(6)
N(2)-C(11)	1.382(10)	1.378(6)/1.379(6)
N(3)-C(6)	1.316(10)	1.344(6)/1.341(6)
N(3)-C(10)	1.337(10)	1.350(6)/1.349(6)
C(5)-C(6)	1.485(11)	1.485(7)/1.472(7)
C(10)-C(11)	1.470(12)	1.493(7)/1.487(7)
C(16)-Pt-N(1)	100.9(3)	98.21(18)/102.22(19)
C(16)-Pt-N(2)	98.8(3)	101.61(18)/97.72(19)
C(16)-Pt-N(3)	176.0(3)	176.52(19)/176.4(2)
N(1)-Pt-N(2)	160.2(3)	160.17(16)/160.06(16)
N(2)-Pt-N(3)	80.7(3)	79.78(16)/ 80.29(17)
N(1)-Pt-N(3)	79.5(3)	80.43(16)/79.84(16)
C(5)-N(1)-Pt	113.5(5)	113.5(3)/113.0(3)
C(11)-N(2)-Pt	113.8(5)	114.5(3)/113.1(3)
C(6)-C(5)-N(1)	116.1(7)	115.4(4)/116.0(4)
C(10)-C(11)-N(2)	114.9(7)	114.7(4)/116.1(4)
C(6)-N(3)-Pt	118.8(5)	118.3(3)/119.4(3)
C(10)-N(3)-Pt	116.2(5)	119.0(3)/119.1(3)

Table 8.2. Selected Distances (Å) and Angles (°) for $1H_2(Cl^-)_3 \cdot 4H_2O$ and $2(BF_4^-)$.

(1.980(4),1.972(4) Å)) are consistent with the strong trans directing properties of a phenyl anion, as also observed for Pt(phtpy)(Ph)⁺ (1.9929(16) Å), Pt(tpy)(3,5-dmph)⁺ (1.992(3) Å), Pt(tpy)(mes)⁺ (1.987(4) Å), and Pt(phtpy)(mes)⁺ (1.998(4) Å) (Chapter 5),³⁵ but are significantly longer than the Pt-N(tpy) distances observed when N(tpy) is trans to a weak trans directing group such as in [Pt(4'-*o*-tolyl-tpy)Cl](BF₄) (1.935(9) Å),²⁵ [Pt(tpy)(1-methylimidazole)](ClO₄) (1.943(7) Å),²³ and [Pt(4,4',4"-tri-*tert*-butyl-tpy)Cl](ClO₄) (1.935(6) Å).³³

As previously noted,²³⁻²⁵ the restricted bite angle of the tridentate terpyridine ligand precludes the 90° and 180° ligand-metal-ligand bond angles of an idealized square planar complex. The N1-Pt-N3 and N2-Pt-N3 bond angles ($1H_2$: 79.5(3), 80.7(3)°; **2**: 80.43(16), 79.8(16), 79.78(16), 80.29(17)°) are characteristically smaller than 90°. The strong trans directing phenyl groups might be expected to aggravate the situation, because the long Pt-N2 bond distances necessitate even smaller N1-Pt-N2 bond angles ($1H_2$, 160.2(3)°; **2**, 160.17(16)/160.06(16)°). These angles are comparable to those observed for [Pt(tpy)(CH₃)](B(C₆H₅)₄) (160.6(3), 160.8(2)°),²⁹ Pt(phtpy)(Ph)⁺ (159.54(7)°), Pt(tpy)(3,5-dmph)⁺ (160.25(14)°), Pt(tpy)(mes)⁺ (159.41(18)°), and Pt(phtpy)(mes)⁺ (160.23(19)°) (Chapter 5),³⁵ but are smaller than those observed for compounds with weaker trans directing groups, including [Pt(4'-o-tolyl-tpy)Cl](BF₄) (162.3(4))²⁵ and [Pt(4,4',4"-tri-*t*-butyl-tpy)Cl](ClO₄) (161.8(3)).³³

The dihedral angles formed by the Pt coordination plane, defined by Pt and the four atoms bonded to the Pt center, and the plane of the phenyl ring are 77.0(2) (**1H**₂) and 85.5(1)/89.1(1) (**2**). These angles are slightly larger than those observed for Pt(phtpy)(Ph)⁺ (51.40(6) °), Pt(tpy)(3,5-dmph)⁺ (54.7(1) °), Pt(tpy)(mes)⁺ (74.6(1)°), and



Figure 8.5. ORTEP diagram of $1H_2(Cl^{-})_3 \cdot 4H_2O$. Anion and H-atoms (with the exception of those bonded to the N(piperidyl) are omitted for clarity.



Figure 8.6. ORTEP diagram of 2(BF₄⁻). Anion and H-atoms are omitted for clarity.

Pt(phtpy)(mes)⁺ (69.5(2)°) (Chapter 5).³⁵ The angle for **2** is even larger than that of **1H**₂, possibly due to agostic interactions between the Pt center and one piperidyl nitrogen in each of the two molecules in the asymmetric unit cell (Pt1A····N4A, 3.512(5) Å, Pt1B···N5B, 3.195(5) Å).

Electrochemical properties. A series of electrochemical experiments was undertaken to characterize the redox properties of 1 and 2. The cyclic voltammogram of $1(BF_4)$ in acetonitrile solution (0.1 M TBAPF₆, 0.25 V/s) exhibits two reversible one-electron reduction waves at E^o=-0.98 V (i_{pc}/i_{pa} =0.80) and E^o=-1.50 V (i_{pc}/i_{pa} =0.52), with peak-to-peak separations (ΔE_p) of 65 and 61 mV, respectively (Figure 8.7A). As expected for a Nernstian one-electron process, the average ΔE_p of the first reduction process (E°=-0.98 V) is 59±6 mV for fourteen measurements with scan rates from 0.02 to 2.5 V/s. The complex also undergoes a nearly reversible two-electron oxidation process at E^o=0.40 V (i_{pc}/i_{pa} =1.08, ΔE_p =74 mV, 0.25 V/s).³⁶ At 0.25 V/s, the ratio of the peak anodic current of the oxidation process ($i_{pa}=8.14 \ \mu A$) to the peak cathodic current of the first reduction wave (i_{pc} =3.82 µA) is 2.1. Though somewhat less than 2.8 (=2^{3/2}), which is predicted for a Nernstian two-electron process, the ratio clearly exceeds the expected value (1.0) for a one-electron step. Similarly, the ratio of charge passed during oxidation (Q_a) to the charge passed during the first reduction (Q_c) is 1.7. Similar results were obtained for $[Pt(phtpy)(pip_2NCN)][PF_6]$ (2(PF₆)), which undergoes two reversible oneelectron reductions at E^o'=-0.98 V (ΔE_p =68 mV, i_{pc}/i_{pa} =0.94) and E^o'=-1.49 V (ΔE_p =67, $i_{\rm pc}/i_{\rm pa}$ =1.38) and a nearly reversible two-electron oxidation at E°=0.40 V (ΔE_p =78 mV, i_{pc}/i_{pa} =1.23, 0.25 V/s) (Figure 8.7B).



Figure 8.7. Cyclic voltammograms of A) **1** and B) **2** in acetonitrile (0.1 M TBAPF₆, 0.25 V/s).



Scheme 8.3. Pt(pip₂NCN)Cl and Pt(tpy)(2,6-dmph)⁺

Assignment of the observed redox processes can be inferred from comparison to the electrochemical behavior of a series of related compounds, including those shown in Scheme 8.3. Under identical conditions, neither free tpy, pip₂NCNBr nor Pt(pip₂NCN)Cl is reduced at potentials >-2.10 V, suggesting that the one-electron reduction processes for **1** and **1H**₂ are associated with the Pt(tpy) unit. Gray and coworkers³¹ have observed that Pt(tpy)Cl⁺ undergoes reversible one-electron reductions in DMF (0.1 M TBAPF₆) at E^{o1} =-0.74 and E^{o1} =-1.30 V, whereas Zn(tpy)Cl₂ undergoes reversible one-electron reduction at E^{o1} =-1.36 V. The anodic shift of the ligand-centered couples in platinum(II) complexes is attributed to stabilization of the reduced tpy ligand as a result of coupling between the empty $6p_2$ (Pt) and the π^* (tpy) orbital.³¹ As observed for **1** and **1H**₂, [Pt(tpy)(2,6-dmph)](BF₄) in acetonitrile solution also undergoes two reversible oneelectron reductions (E^{o1} =-0.96 V, ΔE_p =60 mV, i_{pc}/i_{pa} =0.91; E^{o1} =-1.49 V, ΔE_p =64 mV, i_{pc}/i_{pa} =0.90) (Figure 8.8). The small anodic shifts (10 and 20 mV, respectively) of these processes with respect to those observed for **1** are attributed to the influence of the



Figure 8.8. Cyclic voltammogram of [Pt(tpy)(2,6-dmph)](BF₄) in acetonitrile (0.1 M TBAPF₆, 0.25 V/s).

irreversibly reduced near -1.2 V, and the tpy anion is expected to react rapidly with protic acid.

The reversible two-electron oxidation waves observed for **1** and **2** are absent in cyclic voltammograms of related compounds. Neither $Pt(tpy)(dmph)^+$, pip_2NCNBr nor $pip_2NCNBrH_2^{2+}$ is oxidized at potentials <1.2 V,³⁷ and $Pt(pip_2NCN)Cl$ undergoes irreversible metal-centered oxidation near 0.8 V.¹⁶ Taken together, these data indicate that both the pip_2NCN^- and terpyridyl ligands play important roles in the unusual redox chemistry of **1** and **2**. The availability of the amine lone electron pairs is critical to facilitating reversible two-electron oxidation and stabilizing the resulting Pt(IV) center. For example, protonation of the piperidyl groups, as in compounds **1H**₂ and **2H**₂ results in irreversible oxidation near 0.4 V accompanied by electrode fouling (Figure 8.9a). This



Figure 8.9. Cyclic voltammograms of 1H₂ in acetonitrile (0.1 M TBAPF₆, 0.25 V/s):
(A) 2.5 cycles between 0 and 1000 mV, (B) one cycle between -400 and -1500 mV.

process most likely involves the platinum center as observed for **1**, but protonation slows the overall kinetics and also causes increased surface adsorption.

In order to further characterize the electrochemical behavior of these systems, cyclic voltammograms of 1 were recorded for the first reduction process (-1.2 to -1.7 V) and the oxidation process (0.2 to 0.6 V) over a range of scan rates from 0.005 to 25.6 V/s. ΔE_p of the first reduction (E°=-0.98 V) is essentially invariant (59±6 mV) for scan rates ranging from 0.02 to 2.5 V/s. Outside this range (0.01-0.015 and 5.1-25.6 V/s), the process is less reversible. As the scan rate increases from 5.1 to 25.6 V/s, ΔE_p increases from 66 to 88 mV, as expected from uncompensated resistance effects and the onset of slow electron-transfer kinetics relative to the scan rate. Below 0.01 V/s, the anodic and cathodic peak maxima were not resolved. Over the range of scan rates for which the electron transfer is under diffusion control (0.02 to 2.5 V/s), the average ratio of cathodic charge (Q_c) to the anodic charge (Q_a) is 3.8±1.7 for fourteen measurements. For faster scan rates, Q_c/Q_a lies near 3.0, as predicted for a chemically reversible process (e.g., $Q_c/Q_a=2.9$, 2.5 V/s). With decreasing scan rate, the ratio increases (e.g., $Q_c/Q_a=5.7$, 0.02 V/s), as expected for the onset of decomposition of the reduced complex on these slow timescales. The variation and deviation of Q_c/Q_a with respect to the predicted ratio of 3.0 is partially a result of uncertainty in background current corrections. The cathodic peak current (i_{pc}) exhibits an approximately linear dependence on the square root of the scan rate $(v^{\frac{1}{2}})$, as predicted by the Randles-Ševčik equation for Nernstian conditions:³⁸⁻⁴⁰

$$i_{\rm p} = 2.69 \times 10^5 n^{3/2} \rm{AD}^{\frac{1}{2}} \rm{Cv}^{\frac{1}{2}}$$
(1)



Figure 8.10. Dependence of cyclic voltammogram of 0.1 mM [Pt(tpy)(pip₂NCN)][BF₄] (1(BF₄⁻)) in acetonitrile on scan rate (0.1 M TBAPF₆). Scans are scaled by factors of 1 (2.0), 1.33 (1.0), 2 (0.25), 3 (0.05), and 4 (0.01 V/s), respectively.

where *n*=electron stoichiometry, A=electrode area, D=diffusion coefficient, and C=concentration (Figure 8.11). The slope of the linear fit over the range for which the reduction is electrochemically reversible (0.02 to 2.5 V/s) is 91.6 μ A(s/mV)^½.

For the two-electron oxidation process, adsorption probably causes the slight anodic shift of E_{pa} and cathodic shift of E_{pc} during consecutive cycles. As a consequence, ΔE_p increases by 2-4 mV for scan rates ≤ 1 V/s. For faster scan rates or using other electrode materials (glassy carbon or platinum) larger increases are observed during consecutive cycles, indicating further that the electron transfer is not purely outer-sphere and the process is complicated by the kinetics of adsorption and desorption.

At a gold electrode, ΔE_p for the first cycle increases continuously from 43 to 224 mV as the scan rate is increased from 0.01 to 20.5 V/s (Figure 8.10). In contrast to studies of Ru(η^6 -C₆Me₆)₂²⁺ by Geiger and coworkers,⁴¹ it was not possible to isolate individual one-electron steps comprising the overall two-electron reaction at fast scan rates, and the oxidation remains characterized by a single anodic and a single cathodic wave at even the fastest sweep rates. With decreasing scan rate, ΔE_p and E_p - $E_{p/2}$ (30 mV, 0.01 V/s) approach the two-electron Nernstian limits of 29.5 and 28.25 mV, respectively.^{42,43} Thus, over the range of scan rates for which the peak-to-peak separation of the first reduction process is essentially invariant, ΔE_p for the oxidation process ranges from 43 to 150 mV. This behavior is consistent with a large structural reorganization resulting in slow reaction kinetics. At the slowest scan rates, the value approaches the two-electron Nernstian limit of 29.5,^{42,43} however the process has slightly less than ideal behavior (*e.g.*, ΔE_p =43 mV, i_{pc}/i_{pa} =1.27, 0.01 V/s), indicating that the oxidized product is not long-lived at room temperature. This instability is not surprising as we know of no

Pt(IV) terpyridyl complexes in which the tpy ligand is tridentate.^{44,45} At 273 K, the chemical reversibility approaches ideal behavior, but the process is less electrochemically reversible as indicated by an increase in ΔE_p (*e.g.*, ΔE_p =91 mV, i_{pc}/i_{pa} =1.00, 0.01 V/s). While the lifetime of the oxidized product is improved at low temperature, the rate of electron transfer at the electrode is decreased, and the overall redox process is under increased kinetic control.

In order to verify the electron stoichiometry of the oxidation process for **1**, the anodic peak current (i_{pa}) is plotted against $v^{\frac{1}{2}}$ in Figure 8.11. Though the process clearly exhibits non-Nernstian behavior as discussed earlier, the data are remarkably linear over the entire range of scan rates (0.01 to 25.6 V/s) as predicted by equation (1). The ratio of the slope of the best fit line to that obtained for the first reduction process can be used to derive an estimate of (n_{ox}/n_{red}) (=1.70) that is consistent with the notion that oxidation of **1** involves transfer of two electrons per Pt center.

Discussion. Compounds 1 and $1H_2$ afford the opportunity to investigate the fundamental parameters that govern cooperative multi-redox processes that are critical to chemical and biochemical catalysis. At present, it is not possible to unambiguously identify the mechanism of two-electron transfer. Nevertheless, the observed kinetic control of the oxidation reaction and the structural rearrangement anticipated for the interconversion of Pt(II) and Pt(IV) suggest that the electron transfers are not concerted.

Though the exact structure of the Pt(III) complex formed by removal of an electron from the d_{z^2} level is uncertain, the resulting d^7 metal center in the presence of nucleophiles is expected to adopt a distorted five or six-coordinate structure.^{13,15,46-50} For either case, the remaining unpaired electron may lie at higher energy than the d_{z^2} level in



Figure 8.11. Dependence of anodic peak current (*i*_{pa}) for 0.4 V oxidation process (■) and cathodic peak current (*i*_{pc}) for 0.98 V reduction process (●) on the square root of the scan rate (v^{1/2}) for 1(BF₄⁻) in acetonitrile (0.1 M TBAPF₆). Scans recorded from 0.2 to 0.6 V and from 1.2 to 1.7 V. Lines represent linear fits of all oxidation data and reversible reduction data (0.022.5 V/s).

the Pt(II) complex, allowing for oxidation at low potential and formation of a transiently stable six-coordinate Pt(IV) product. Thus, ligation accompanying the first electron transfer effectively drives the second charge-transfer step. Accordingly, the observation that ΔE_p and E_{pa} - $E_{pa/2}$ exceed the Nernstian two-electron values at slow scan rates is consistent with stepwise electron-transfer in which the second electron-transfer step is slightly more favorable than the first (*i.e.*, $E_2^{\text{ot}}>E_1^{\text{ot}}$).⁴² It also is noteworthy that the anodic shift of E_{pa} with increasing scan rate is smaller than the cathodic shift of E_{pc} . As a consequence, E^{ot} shifts from 0.40 V at 0.005 V/s to 0.44 V at 20.5 V/s for **1**. This behavior is consistent with formation of an organized structure, such as a five or sixcoordinate complex, prior to or during anodic electron transfer. The conversion of Pt(IV) to Pt(II) and axial bond cleavage during the reverse (cathodic) process is likely to require less pre-organization, making E_{pc} less sensitive to scan rate.

The facile Pt(II)/Pt(IV) interconversion observed for **1** and **1H**₂ contrasts sharply with well-studied platinum couples,^{5,6,8-15,49,51} the majority of which undergo electrochemically and chemically irreversible oxidation because of accompanying changes in coordination sphere. One exception occurs when the electrochemistry of certain complexes is carried out in the presence of high concentrations of halide ions. In that case the cyclic voltammogram can exhibit a two-electron wave with large ΔE_p .^{5,6} For example, square planar Pt([14]aneS₄)²⁺ ([14]aneS₄=1,4,7,11tetrathiacyclotetradecane) in a 0.1 M LiCl 4:1 CH₃CN:H₂O solution undergoes twoelectron oxidation at 0.8 V (ΔE_p =127 mV, 0.01 V/s).⁶ Interestingly, there have been several reports of platinum(II) complexes with one or two pendant groups available to bind to the platinum(IV) center upon oxidation. However, complexes such as Pt([9]aneS₃)₂²⁺ ([9]aneS₃=1,4,7-trithiacyclononane) exhibit one-electron waves corresponding to generation of a five- or six-coordinate Pt(III) species.^{8-10,14,49} In some cases, it is possible to resolve the second one-electron Pt(III)/Pt(IV) step at higher potentials. A case-by-case analysis of these previously investigated systems suggest that the ligands may not be well-suited for stabilization of six-coordinate Pt(IV), and consequently the Pt(III) one-electron product tends to be more stable than the Pt(IV) twoelectron product. Broadly speaking, ligand donor properties, steric effects and ligand conformational flexibility must determine the relatively stabilities of Pt(II) and Pt(IV) and the case of interconversion between these oxidation states.

The facile Pt(II)/Pt(IV) interconversion observed for **1** may be in part related to the relative instability of a Pt(III) center bonded to ligands that favor small bite angles and meridional coordination geometries. The special role of the pip₂NCN⁻ ligand in facilitating electron transfer is further suggested by the comparison with the electrochemistry of $W_2(CO)_8(\mu$ -SBz)₂²⁻ (HSBz=benzyl mercaptan) reported by Schultz.^{52,53} The dimer undergoes nearly reversible two-electron oxidation at -0.87 V vs. Ag/0.01 M AgNO₃ (Δ E_p=42 mV, 0.2 V/s), accompanied by metal-metal bond formation and modest structural rearrangement (~1 Å decrease in W-W distance and ~25° change in W-S-W and S-W-S bond angles).^{52,53} Though the variation of Δ E_p with scan rate (104 mV, 20V/s) is somewhat less pronounced than observed for **1**, the value of Δ E_p (37 mV, 0.005 V/s) is similar to that observed at slow scan rates. It is conceivable that weakly favorable interactions between the pip₂NCN⁻ amine groups and the Pt(II) center in solution (as observed in solid state structure of **2**) effectively preorganize **1** and **2** for electron transfer. This possibility is examined in more detail in Chapter 9.

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CHAPTER 9:

An investigation into the Mechanism of Two-Electron Transfer Reactions.

Introduction. In Chapter 8, we described a successful strategy for designing reversible outer-sphere two-electron transfer reagents.¹⁻³ The central premise is that the two potentially *mer*-coordinating ligands bonded to a platinum center are capable of stabilizing both the Pt(II) and Pt(IV) oxidation states. In the d⁶ octahedral Pt(IV) case, both ligands are expected to be tridentate occupying all six binding sites around the metal center. In the d⁸ square planar Pt(II) case, one ligand will remain tridentate, while the other coordinates in a monodentate fashion through the central binding site (Figure 9.1). To test this strategy, we prepared two complexes, Pt(tpy)(pip₂NCN)⁺ and Pt(phtpy)(pip₂NCN)⁺ (Figure 9.2), and demonstrated that each undergoes a nearly reversible two-electron platinum-centered oxidation near ~0.40 V vs. Ag/AgCl (3.0 M NaCl). These are the first examples of outer-sphere reversible two-electron platinum reagents.



Figure 9.1. Schematic representation of a reversible two-electron platinum reagent.

The results of an electrochemical study these compounds suggested that the amine lone electron pairs are critical to facilitating reversible two-electron oxidation and stabilizing the resulting Pt(IV) center. Specifically, we found that the reversible twoelectron behavior disappeared when the complexes were protonated. However, these circumstantial data provide no indication of whether both piperidyl groups are necessary for two-electron transfer. It also is unclear whether these groups influence the redox chemistry by inductive effects, through-space interactions with the metal center as suggested above, or some other mechanism.



Figure 9.2. Two-electron platinum reagents: $Pt(tpy)(pip_2NCN)^+$ and $Pt(phtpy)(pip_2NCN)^+$.

It also was noted that the redox chemistry of Pt(tpy)(pip₂NCN)⁺ and Pt(phtpy)(pip₂NCN)⁺ is remarkably reversible. Comparison with other two-electron systems suggests the platinum complexes undergo relatively little intramolecular reorganization during oxidation. This conclusion seems to contradict the notion that the pendant piperidyl groups freely rotate above and below the coordination plane. For these reasons, we have hypothesized that there exists a weak interaction between the metal center and one or both piperidyl groups. This preorganized structure is believed to be the electrochemically active species.

In this chapter, we investigate a series of model complexes (Figure 9.3) in an effort to better understand the parameters that govern the cooperative two-electron oxidation observed for $Pt(tpy)(pip_2NCN)^+$. The electrochemistry of these complexes verifies that two piperidyl groups positioned over the axial sites of the platinum(II) center are required for reversible two-electron oxidation to occur. UV-visible spectroscopic data are consistent with the formation of a preorganized structure.





Pt(tpy)(3,5-pip₂NCN)⁺

Pt(tpy)(pipNC)⁺



Pt(phbpy)(pip₂NCN)

Figure 9.3. Models for two-electron platinum reagents: $Pt(tpy)(pipNC)^+$, $Pt(tpy)(3,5-pip_2NCN)^+$, and $Pt(phbpy)(pip_2NCN)$.

Experimental. K₂PtCl₄ was obtained from Pressure Chemical (Pittsburg, PA). Acetonitrile, methylene chloride, benzene, and toluene were distilled over CaH₂. Tetrahydrofuran (THF) was distilled from Na(s)/benzophenone. Ethanol was distilled from zinc metal/potassium hydroxide. Spectroscopic grade methanol was purchased from Acros. All other reagents were purchased from Acros (Pittsburg, PA) or Aldrich Chemical Companies (Milwaukee, WI). Synthetic procedures for [Pt(tpy)(pip₂NCN)](BF₄), [Pt(tpy)(pip₂NCNH₂)](PF₆)₃, [Pt(phtpy)(pip₂NCN)](BF₄), and [Pt(phtpy)(pip₂NCNH₂)](PF₆)₂ were reported in Chapter 8. Pt(COD)Cl₂ was prepared as reported in Chapter 2.⁴ 4-phenyl-2,2':6',2"-terpyridine (phtpy) was prepared following

the method of Constable and coworkers as reported in Chapter 5.^{5,6}

Tetrabutylammonium hexafluorophosphate (TBAPF₆) was recrystallized twice from boiling methanol and dried under vacuum prior to use. Argon was pre-dried using activated sieves and trace oxygen was removed with activated R3-11 catalyst from Schweizerhall (New Jersey).

¹H NMR spectra were recorded at room temperature, unless otherwise noted, using a Bruker AC 250 MHz spectrometer. Deuterated chloroform (0.03 % tetramethylsilane (TMS)) and acetonitrile were purchased from Cambridge Isotope Laboratories (Andover, MA). UV-visible absorption spectra were recorded using a HP8453 UV-visible spectrometer. Mass spectra were recorded using a Micromass Q-TOF hybrid quadropole time of flight mass spectrometer with electrospray ionization. Elemental analyses were performed by Atlantic Microlabs (Norcross, GA). Cyclic voltammetry was carried out using a standard three-electrode cell and a CV50w potentiostat from Bioanalytical Systems. Scans were collected in methylene chloride

solution containing 0.1 M TBAPF₆. All scans were recorded using a platinum wire auxiliary electrode, a Ag/AgCl reference electrode (3.0 M NaCl) and a 0.79 mm² gold working electrode. Between scans, the working electrode was polished with 0.05 μ m alumina, rinsed with distilled water and wiped dry using a Kimwipe. Reported potentials are referenced against Ag/AgCl (3.0 M NaCl). Peak currents (*i*_p) were estimated with respect to the extrapolated baseline current as described elsewhere.⁷ 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°'. Under these conditions, the ferrocene/ferrocenium (FcH/FcH⁺) couple occurs at 0.45 V. Emission spectra were recorded with a SPEX Fluorolog-3 fluorimeter equipped with a double emission monochromator and a single excitation monochromator.

2-(CH₂(C₅H₁₀N))C₆H₃Br (pipNCBr). This compound was synthesized by a modification of the procedure originally reported by Mehta and coworkers.⁸ A mixture of 2-bromobenzyl bromide (10.6 mL, 0.042 mol) and piperidine (45 mL, 0.42 mol) in 350 mL of benzene was refluxed for 24 hours. The white solid ([C₅H₁₀NH₂]Br) was filtered off and discarded. The solvent was removed by rotary-evaporation leaving a yellow-orange oil. The oil was dissolved in CH₂Cl₂, and hexanes were added to precipitate residual [C₅H₁₀NH₂]Br, which was removed by vacuum filtration. The filtrate was rotary-evaporated to dryness, and the resulting oil was used in the following syntheses without further purification. Yield: 10.8g, 99%, MS (GCMS): m/z = 254.

 $Pt(pipNC)_2$. Under an Ar(g) atmosphere, *N*-butyllithium (3.42 mL of 1.6 M solution in hexanes; 5.5 mmol) was added to a stirred solution of pipNCBr (1.52 g, 6.0 mmol) in 20 mL of THF at -70°C. After 30 minutes, the solution of lithiated ligand was cannula transferred to a mixture of $Pt(COD)Cl_2$ (0.93 g, 2.5 mmol) in 75 mL THF at -

70°C. The mixture was stirred for 1 hour at -70° C, warmed to room temperature, and then stirred for an additional 12 hours. The filtrate was rotary-evaporated to dryness. Water (50 mL) was added to the solid and the product was extracted with CH_2Cl_2 (3 x 50 mL). The organic layers were dried over MgSO₄ and rotary-evaporated to dryness. After addition of hexanes to the residue, the mixture was sonicated, and the white solid was collected. Yield: 0.82 g, 61%. Anal. Calcd. for $C_{24}H_{32}N_2Pt$: C, 53.03 H, 5.93; N, 5.12. Found: C, 53.17; H, 5.85; N, 5.12. ¹H NMR (CDCl₃, δ): 1.35-1.6 (4H, m, CH₂), 1.85-2.0 (8H, m, CH₂), 3.21 (4H, m, CH₂), 3.36 (4H, m, CH₂), 4.23 (4H, s with Pt satellites, J_{H-Pt}=21 Hz, benzylic CH₂), 6.9-7.0 (5H, m, CH), 7.31 (2H, t, CH), 7.41 (1H, d with Pt satellites, J_{H-Pt}=50 Hz, CH).

2-(CH₂(C₅H₁₀N))C₆H₄ (pipNCH). A mixture of benzyl bromide (10 mL, 0.082 mol) and piperidine (41 mL, 0.41 mol) in 500 mL of benzene was refluxed for 24 hours. The white solid ([C₅H₁₀NH₂]Br) was filtered off and discarded. The filtrate was reduced in volume by rotary evaporation. The yellow oil was dissolved in CH₂Cl₂ and hexanes were added to precipitate residual [C₅H₁₀NH₂]Br, which was removed by vacuum filtration. The filtrate was rotary-evaporated, and the resulting oil was used in the following syntheses without further purification. ¹H NMR (CDCl₃, δ): 1.35-1.61 (2H, m, CH₂), 2.38 (4H, m, CH₂), 3.71 (2H, s, CH₂), 7.09-7.17 (2H, m, CH), 7.22-7.38 (2H, m, CH).

Pt(pipNC)(DMSO)Cl. Sodium acetate (0.32 g, 2.4 mmol), pipNCH (0.415 g, 2.4 mmol) and Pt(DMSO)Cl₂ (1.0 g, 2.4 mmol) were dissolved in 75 mL of methanol. The solution was stirred for four days at room temperature. The solution was rotary-evaporated to dryness. The residue was treated with water (25 mL) and extracted with

CH₂Cl₂ (3 x 50 mL). The combined CH₂Cl₂ layers were dried over MgSO₄, filtered and rotary-evaporated to dryness. The residue was purified by column chromatography (Silica: 10" length, 1.25" diameter, 19:1 CHCl₃:acetone). The product was further purified by vapor diffusion of diethyl ether into a methylene chloride solution. Yield: 0.44 g, 39%. Anal. Calcd. for (C₁₂H₁₆N)(C₂H₆SO)PtCl: C, 34.82; H, 4.59; N, 2.90. Found: C, 34.57; H, 4.52; N, 2.92. ¹H NMR (CDCl₃, δ): 1.42-1.92 (6H, m, CH₂), 3.13 (2H, m, CH₂), 3.55 (6H, s with Pt satellites, J_{H-Pt}=25 Hz, CH₃), 3.92 (2H, m, CH₂), 4.28 (2H, s with Pt satellites, J_{H-Pt}=45 Hz, CH₂), 6.99-7.13 (3H, m, CH), 7.92 (2H, d with Pt satellites, J_{H-Pt}=47 Hz, CH).

[Pt(tpy)(pipNC)](BF₄). Pt(pipNC)(DMSO)Cl (0.100 g, 0.021 mmol) and AgBF₄ (0.04 g, 0.021 mmol) were dissolved in 30 mL of acetone. The mixture was stirred for 30 min in the dark, and the resulting precipitate was removed by vacuum filtration through Celite. The filtrate was stirred for 3 hours with tpy (0.049 g, 0.021 mmol), and the red solution was rotary-evaporated to dryness. The solid was dissolved in CH₂Cl₂, and diethyl ether was added to induce precipitation. Yield: 65 mg, 73%. Anal. Calcd. for $[C_{27}H_{27}N_4Pt](BF_4)$: C, 47.04; H, 3.95; N, 8.13. Found: C, 46.92; H, 3.85; N, 8.00. ¹H NMR (CDCl₃, δ): 1.09-1.25 (6H, m, CH₂), 2.27 (4, m, CH₂). 3.61 (2H, s, CH₂), 7.14 (2H, m, CH), 7.29 (1H, m, CH), 7.45 (2H, m, CH), 7.56 (2H, m, CH), 8.23 (2H, d with Pt satellites, J_{H-Pt}=42 Hz., CH), 8.28 (2H, m, CH), 8.53 (3H, m, CH), 8.64 (2H, d, CH).

 $[Pt(tpy)(pipNCH)](PF_6)_2$. Pt(pipNC)(DMSO)Cl (0.100 g, 0.021 mmol) and AgBF₄ (0.04 g, 0.021 mmol) were dissolved in 30 mL of acetone. The solution was allowed to stir for 30 min in the dark, and the resulting precipitate was removed by vacuum filtration through Celite. The filtrate was stirred for 3 hours with tpy (0.049 g,

0.021 mmol). Addition of concentrated HNO₃ (14 µL) caused the solution to turn from red to yellow. After addition of distilled H₂O (15 mL), the volume was reduced to ~15 mL by rotary evaporation. The mixture was filtered, and 2 mL of concentrated aqueous NH₄PF₆ was added to precipitate the product. The yellow solid was collected by vacuum filtration, washed with diethyl ether and dried under vacuum. The product was recrystallized by dissolving in CH₃CN and inducing precipitation with diethyl ether. Yield 0.17 g, 90%. Anal. Calcd. for $[C_{27}H_{28}N_4Pt](PF_6)_2$: C, 36.29; H, 3.16; N, 6.27. Found: C, 36.50; H, 3.18; N, 6.16. MS (ESI): m/z = 748 ((Pt(tpy)(pipNCH) • PF₆)⁺), m/z= 602 (Pt(tpy)(pipNC)⁺), m/z = 302 (Pt(pipNCH)²⁺). ¹H NMR (CD₃CN, δ): 1.4-1.7 (6H, m, CH₂), 2.81 (2H, m, CH₂), 3.33 (2H, m, CH₂), 4.47 (2H, d, CH₂), 6.9 (1H, broad, NH), 7.34 (2H, m, CH), 7.50 (1H, m, CH), 7.61 (2H, m, CH), 7.72 (1H, d with Pt satellites, J_{Pt-H}=34 Hz, CH), 8.12 (2H, d with Pt satellites, J_{Pt-H}=50 Hz, CH), 8.3-8.5 (9H, m, CH).

3,5-(CH₂Br)₂C₆H₃I. A modification of the method published by Duchêne and coworkers⁹ was used to prepare this compound. 3,5-dimethyliodobenzene (6.2 mL, 0.043 mol) was dissolved in CCl₄ (250 mL). *N*-bromosuccinimide (NBS, 19 g, 0.11 mol) and azobisisobutyronitrile (AIBN, ~25 mg) were added, and the mixture was allowed to reflux for 72 hour. Additional aliquots of AIBN (~25 mg) were added to the reaction mixture at 24 hours intervals. The mixture was allowed to cool to room temperature before filtration. The solvent was removed from the filtrate by rotary-evaporation to give a red-orange oil. The product was recrystallized by cooling an ethanol solution to -25° C to induce precipitation. The white solid was collected by vacuum filtration. Yield: 3.83 g, 23%. ¹H NMR (CDCl₃, δ): 4.38 (4H,s, CH₂), 7.38 (1H, s, CH), 7.67 (2H, s, CH).

3,5-((CH₂(C₅H₁₀N))₂)C₆H₃I (3,5-pip₂NCNI). A mixture of 3,5-(CH₂Br)₂C₆H₃I

(1.9 g, 5 mmol) and piperidine (4.9 mL, 50 mmol) in 300 mL of benzene was refluxed for 48 hours. The white solid was removed by filtration and discarded. The filtrate was reduced in volume by rotary-evaporation. The orange oil was dissolved in CH₂Cl₂, and hexanes were added to precipitate residual [C₅H₁₀NH₂]Br, which was removed by vacuum filtration. The filtrate was reduced in volume to give an oil that was used in the following syntheses without further purification. ¹H NMR (CDCl₃, δ): 1.45 (4H, d, CH₂), 1.58 (8H, m, CH₂), 2.36 (8H, d, CH₂), 3.42 (4H, s, benzylic CH₂), 7.18 (1H, s, CH), 7.35 (2H, s, CH).

Pt(PPh₃)₄. This compound was prepared according to the method published by Ugo and coworkers.¹⁰ All solutions were degassed with argon prior to use. PPh₃ (1.47 g, 5.6 mmol) was dissolved in ethanol (20 mL) and heated to 65°C. KOH (0.135g, 2.4 mmol) was dissolved in EtOH (4 mL) and H₂O (1 mL). The solution was heated to 65°C and cannula transferred to the solution of PPh₃. K₂PtCl₄ in H₂O (7 mL) was heated to 65°C and was added to the solution of PPh₃ over a 20-minute period. The solution turned yellow and was allowed to stir for ~1 hour. The mixture was cooled to room temperature and filtered under argon. The yellow product was washed with warm EtOH (15 mL), H₂O (60 mL), and room temperature EtOH (50 mL). Yield: 1.2 g, 80%. ¹H NMR (CDCl₃, δ): 7.15-7.5 (60H, m, CH).

 $Pt(PPh_3)_2(3,5-pip_2NCN)I$. The synthesis of this complex was adapted from a procedure by van Koten and coworkers for the preparation of $Pt(PPh_3)_2(3,5-Me_4NC(Br)N)I$.¹¹ A round bottom flask was charged with $Pt(PPh_3)_4$ (0.10 g, 0.08 mmol) under an argon atmosphere, and distilled toluene (20 mL) was added. 3,5-pip_NCNI

(0.028 g, 0.08 mmol) was dissolved in distilled toluene (150 mL), and the solution was bubble degassed for 5 minutes. The solution was cannula transferred to the flask containing Pt(PPh₃)₄, and the resulting mixture was refluxed under argon for 48 hrs. The solvent was removed by rotary-evaporation. The solid was dissolved in CH₂Cl₂ (5 mL), and hexanes (50 mL) were added to induce precipitation. The white solid was collected by vacuum filtration. Yield: 65 mg, 73%. ¹H NMR (CDCl₃, δ): 1.27-1.44 (12H, m, CH₂), 2.05 (8H, m, CH₂). 2.77 (4H, s, CH₂), 6.18 (1H, s, CH), 6.58 (2H, s with Pt satellites, J_{H-Pt}=58 Hz, CH), 7.2-7.35 (18H, m, CH), 7.5-7.6 (12H, m, CH).

[Pt(tpy)(3,5-pip₂NCN)](PF₆). A mixture of thallium hexafluorophosphate (0.031 g, 0.090 mmol) and Pt(PPh₃)₂(3,5-pip₂NCN)I (0.10 g, 0.090 mmol) in 40 mL of methanol was stirred for 30 minutes at room temperature. The resulting TlCl precipitate was removed by vacuum filtration through Celite. The filtrate was rotary-evaporated to dryness and the solid was dissolved in CH₂Cl₂. After addition of tpy (0.029 g, 0.090 mmol) and elemental sulfur (0.92g, 0.36 mmol), the filtrate was stirred for 72 hours. The solvent was removed by rotary-evaporation, the residue was dissolved in CH₂Cl₂. Diethyl ether was added to induce precipitation. The solid was washed with diethyl ether and dried under vacuum. Yield: 0.058 g, 77%. MS (ESI): m/z = 699.3 (Pt(tpy)(3,5-pip₂NCN)⁺), m/z = 428.1 (Pt(tpy)⁺). ¹H NMR (CD₃CN, δ): 1.49 (4H, m, CH₂), 1.62 (8H, m, CH₂), 2.61 (8H, m, CH₂), 3.65 (4H, s, CH₂), 7.11 (1H, s, CH), 7.41 (2H, s with Pt satellites, J_{H-Pt}=33 Hz, CH), 7.64 (2H, m, CH₂), 8.31-8.43 (9H, m, CH).

2-Acetylpyridinepyridinium hexafluorophosphate. This compound was prepared by the procedure of Kipp and coworkers.¹² Iodine (20.4 g, 0.74 mol) and 2-acetylpyridine (8.1 mL, 0.074 mol) were dissolved in pyridine (80 mL) and refluxed for
2.5 hours. The solution was cooled to room temperature and stirred for an additional 18 hours. The dark precipitate was collected by vacuum filtration and dissolved in hot tap water. Charcoal (4 g) was added to the solution, and the mixture was heated at 75°C for 10 min. The charcoal was removed by vacuum filtration and a solution of saturated aqueous NH_4PF_6 was added to precipitate the product. Yield (21.6 g, 85%). ¹H NMR (CD₃COCD₃, δ): 6.74 (2H,s, CH₂), 7.80 (1H, m, CH), 8.12 (2H, m, CH), 8.43 (2H, dd, CH), 8.8-8.9 (2H, m, CH), 9.20 (2H, d, CH).

6-phenyl-2,2'-bipyridine (phbpyH). This ligand was prepared by the procedure of Constable and coworkers.¹³ 2-Acetylpyridinepyridinium hexafluorophosphate (9.2 mmol) was dissolved in acetic acid (20 mL), and the solution was heated at 115°C for 10 min. Dimethylaminopropiophenone hydrochloride was added, and the solution was heated for an additional 5 hours. The black solution was rotary-evaporated to give a black oil that was treated with water (50 mL) and extracted with CH₂Cl₂ (3 x 50 mL). The organic layers were collected, dried over MgSO₄ and filtered. The filtrate was rotary-evaporated to dryness, and the product was purified by column chromatography using activated alumina (type F-20, 80-200 mesh) and eluting with 1:2 CH₂Cl₂:*n*-hexanes. The first fraction contained the product. Yield: 78%. MS (GCMS): m/z = 232. ¹H NMR (CDCl₃, δ): 7.32 (1H, m, CH), 7.48 (3H, m, CH), 7.75-7.9 (3H, m, CH), 8.16 (1H, d, CH), 8.37 (1H, d, CH), 8.62-8.7 (2H, m, CH).

 $Pt(phbpy)(pip_2NCN)$. A mixture of silver tetrafluoroborate (0.077 g, 0.40 mmol) and $Pt(pip_2NCN)Cl$ (0.20 g, 0.40 mmol) in 35 mL of acetone was stirred for 30 minutes at room temperature in the dark. The resulting precipitate was removed by vacuum filtration through Celite. After addition of phbpyH (0.093 g, 0.40 mmol), the filtrate was

stirred for 18 hours. The mixture was filtered, and aqueous HNO₃ (1 M) was added dropwise until the color of the filtrate changed from orange to bright yellow. After addition of water (25 mL), the volume was reduced to ~25 mL by rotary evaporation. The mixture was filtered, and aqueous NaOH (1 M) was added dropwise to precipitate the red product. The solid was collected by vacuum filtration, washed with ether and dried under vacuum. Yield 0.21 g, 78%. ¹H NMR (CDCl₃, δ): 0.1.25 (12H, m, CH₂), 2.30 (4H, m, CH₂), 3.63 (2H, m, CH₂), 3.96 (2H, m, CH₂), 6.90-7.12 (4H, m, CH), 7.30 (2H, m, CH), 7.44 (1H, d, CH), 7.65 (2H, m, CH), 7.87-8.00 (4H, m, CH), 8.36 (1H, d, CH).

[Pt(phbpy)(pip_2NCNH_2)](PF_6)_2. A mixture of silver tetrafluoroborate (0.039 g, 0.20 mmol) and Pt(pip_2NCN)Cl (0.10 g, 0.20 mmol) in 25 mL of acetone was stirred for 30 minutes at room temperature in the dark. The resulting precipitate was removed by vacuum filtration through Celite. After addition of phbpyH (0.046 g, 0.20 mmol), the filtrate was stirred for 18 hours. The mixture was filtered, and aqueous HNO₃ (1 M) was added dropwise until the color of the filtrate changed from orange to bright yellow. After addition of water (20 mL), the volume was reduced to ~20 mL by rotary evaporation. The mixture was filtered, and 1 mL of concentrated aqueous NH₄PF₆ was added to precipitate the product. The yellow solid was collected by vacuum filtration, washed with diethyl ether and dried under vacuum. The product was recrystallized by dissolving in CH₃CN and inducing precipitation with diethyl ether. Yield 0.14 g, 73%. Anal. Calcd. for $[C_{34}H_{40}N_4Pt](PF_6)_2$: C, 41.17; H, 4.07; N, 5.65. Found: C, 41.29; H, 4.09; N, 5.68. MS (ESI): m/z = 844.310 ((Pt(phbpy)(pip_2NCNH₂) • PF₆)⁺), m/z = 698.272 (Pt(phbpy)(pip_2NCNH)⁺), m/z = 349.638 (Pt(phbpy)(pip_2NCNH₂)²⁺). ¹H NMR (CD₃CN,

δ): 0.74-0.92 (4H, m, CH₂), 1.11-1.26 (2H, m, CH₂), 1.43 (2H, m, CH₂), 1.6 (4H, m, CH₂), 2.75-2.9 (4H, m, CH₂), 3.25-3.42 (4H, m, CH₂), 4.11 (4H, m, CH₂), 4.39 (4H, m, CH₂), 6.61 (1H, d with Pt satellites, J_{Pt-H}=63 Hz, CH), 7.10 (1H, dd, CH), 7.25-7.4 (4H, m, CH), 7.57 (2H, m, CH), 7.76 (1H, d, CH), 7.97 (2H, m, CH), 8.08-8.29 (3H, m, CH).

 $[Pt^{IV}(\eta^2-phbpy-C,N)(pip_2NCN)(OH)](OH)$. The exact coordination sphere around the platinum has not been confirmed, and the proposed structure is based on available analytical data (see discussion). A mixture of silver tetrafluoroborate (0.077 g, 0.40 mmol) and Pt(pip2NCN)Cl (0.20 g, 0.40 mmol) in 35 mL of acetone was stirred for 30 minutes at room temperature in the dark. The resulting precipitate was removed by vacuum filtration through Celite. After addition of phbpy (0.093 g, 0.40 mmol), the filtrate was stirred for 18 hours. Aqueous HNO₃ (1 M) was added dropwise until the orange solution turned bright yellow. After addition of water (20 mL), the volume was reduced to ~ 20 mL by rotary evaporation. The mixture was filtered, and concentrated aqueous NaOH was added dropwise until a red product precipitated. The solid was collected by vacuum filtration and dissolved in acetone. Hydrogen peroxide (50%) was added until the color of the solution changed from red to yellow (8-10 drops). The solution was stirred for 30 min and rotary-evaporated to dryness. The oily residue was dissolved in acetone (2 mL) and diethyl ether (75 mL) was added to induce precipitation. The pale-yellow solid was collected by vacuum filtration, washed with diethyl ether and dried under vacuum. Yield 0.100 g, 34%. Anal. Calcd. for [C₃₄H₃₉N₄OPt](OH): C, 55.80; H, 5.37; N, 7.66. Found: C, 56.19; H, 5.00; N, 7.45. MS (ESI): *m/z* = 714.283 $(Pt^{IV}(phbpy)(\eta^2-pip_2NCN-C,N)(OH)^+), m/z = 357.645 (Pt^{IV}(phbpy)(\eta^2$ pip₂NCNH)(OH)²⁺). ¹H NMR (CD₃CN, δ): 1.0-1.2 (12H, m, CH₂), 1.45-1.7 (4H, m,

CH₂), 2.45 (2H, m, CH₂), 2.77 (2H, d, CH₂), 3.28 (1H, d, CH₂), 3.89 (1H, d, CH₂), 4.04 (1H, d, CH₂), 4.38 (1H, d with Pt satellites, J_{Pt-H}=38 Hz, CH₂), 5.58 (1H, s with Pt satellites, J_{Pt-H}=22 Hz, OH), 6.70 (1H, d with Pt satellites, J_{Pt-H}=42 Hz, CH), 7.15 (2H, m, CH), 7.30 (3H, m, CH), 7.68 (1H, m, CH), 7.87 (1H, d, CH), 8.23-8.35 (5H, m, CH), 8.53 (1H, d, CH).

X-ray crystallography. Yellow needles of $[Pt(tpy)(pipNC)](BF_4)$ were grown by slow vapor diffusion of diethyl ether into a methylene chloride solution. Single crystals of $[Pt(tpy)(pipNCH)](PF_6)_2$ were obtained as yellow rectangular blocks by slow vapor diffusion of diethyl ether into an acetonitrile solution. Orange-red plates of Pt(phbpy)(pip₂NCN) were grown by cooling an acetone/diethyl ether/pentane solution to -20°C. Yellow triangular shaped plates of $Pt(phbpy)(pip_2NCNH_2)](PF_6)_2 \cdot 2CH_2Cl_2$ were grown by slow vapor diffusion of diethyl ether into a methylene chloride solution. For X-ray examination and data collection, suitable crystals of [Pt(tpy)(pipNC)](BF₄) and $[Pt(tpy)(pipNCH)](PF_6)_2$ were each mounted on cryo-loops with paratone-N, and intensity data were collected using a SMART6000 CCD diffractometer. A suitable crystal of $Pt(phbpy)(pip_2NCN)$ was mounted on the tip of a glass fiber with paratone-N, and intensity data were collected using a standard Siemens SMART 1K CCD diffractometer. A suitable crystal of Pt(phbpy)(pip_NCNH₂)](PF₆)₂ • 2CH₂Cl₂ was mounted on the tip of a glass fiber with epoxy resin, and intensity data were collected using a Bruker SMART APEX CCD diffractometer. Graphite-monochromated Mo Ka radiation, $\lambda = 0.71073$ Å, was used for the X-ray source. The data frames were processed using the program SAINT.¹⁴ Intensities were corrected for Lorentz, polarization and decay effects. Absorption and beam corrections based on the multi-scan technique were

applied using SADABS.¹⁵ The structures of [Pt(tpy)(pipNC)](BF₄),

 $[Pt(tpy)(pipNCH)](PF_6)_2$ and $Pt(phbpy)(pip_2NCN)$ were solved by a combination of the Patterson method in SHELXTL¹⁶ and the difference Fourier technique, and the models were refined by full-matrix least squares on F^2 . The structure of $Pt(phbpy)(pip_2NCNH_2)](PF_6)_2 \cdot 2CH_2Cl_2$ was solved by a combination of direct methods in SHELXTL and the difference Fourier technique, and the model was refined by fullmatrix least squares on F^2 . Non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms bonded to nitrogen atoms for Pt(tpy)(pipNCH)](PF₆)₂ and Pt(phbpy)(pip₂NCNH₂)](PF₆)₂ • 2CH₂Cl₂ were located directly, whereas the remaining H atoms for all complexes were either located directly or calculated based on geometric criteria and treated with a riding model. Hydrogen atom isotropic displacement parameters were assigned as 1.2 times U_{eq} of the adjacent atom. Pt(phbpy)(pip₂NCN) and Pt(phbpy)(pip₂NCNH₂)](PF₆)₂ • 2CH₂Cl₂ crystallize with two independent molecules in the asymmetric unit. In crystals of $Pt(phbpy)(pip_2NCNH_2)](PF_6)_2 \cdot 2CH_2Cl_2$, one CH_2Cl_2 is disordered over two positions in a ratio of 54:46. Restraints were applied to three CH₂Cl₂ molecules so they would refine similar to the molecule consisting of Cl1-C69-Cl2. In crystals of $Pt(tpy)(pipNCH)](PF_6)_2$, the protonated piperidyl ligand is disordered over two principal conformations, with the occupancy of the major conformer being 80%. Also one PF₆⁻ anion is disordered with two fluorine sites (F11 and F12) set at 50% occupancy; the displacement parameters were refined isotropically. Crystallographic data are

summarized in Tables 9.1 and 9.2.

	[Pt(tpy)(pip ₂ NC)] (BF ₄)	[Pt(tpy)(pipNCH)](PF ₆) ₂
Fw, g/mol	689.43	893.56
Space group	$P2_1/c$	$P2_1/c$
a, Å	15.2579(4)	9.1439(3)
b, Å	13.3035(3)	17.8766(7)
<i>c</i> , Å	12.2249(3)	18.6797(7)
<i>α</i> , °	90	90
<i>β</i> , °	90.126(1)	94.335(1)
γ, °	90	90
$V, Å^3$	2481.45(11)	3044.68(19)
Ζ	4	4
<i>Т</i> , К	150(2)	150(2)
reflns collected	34326	42203
Ind reflns	6165	7586
R _{int}	0.0372	0.0414
GOF on F^2	1.033	1.052
$R_1/wR_2 \left[I \ge 2\sigma(I)\right]^a$	0.0209/0.0452	0.0241/0.0456
$\frac{R_1/wR_2}{(\text{all data})^{\text{a}}}$	0.0331/0.0506	0.0325/0.0607

Table 9.1. Crystallographic Data for $[Pt(tpy)(pip_2NC)](BF_4)$ and $[Pt(tpy)(pipNCH)](PF_6)_2$.

^a $R_1 \Sigma || F_0 |$ - $|F_c || / \Sigma |F_0|$, $wR_2 = [\Sigma w (F_0^2 - F_c^2)^2 / \Sigma w (F_0^2)^2]^{\frac{1}{2}}$.

	Pt(phbpy)(pip2NCN)	$[Pt(phbpy)(pip_2NCNH_2)] (PF_6)_2 \bullet 2CH_2Cl_2$
Fw, g/mol	697.77	1159.58
Space group	$P2_1/n$	$P2_1/c$
<i>a</i> , Å	17.5053(11)	26.1804(12)
b, Å	21.3856(13)	12.7526(6)
c, Å	17.7144(11)	26.2753(12)
α , °	90	90
<i>β</i> , °	118.630(1)	98.6640(10)
γ, °	90	90
$V, \text{\AA}^3$	5820.8(6)	8672.4(7)
Ζ	8	8
<i>Т</i> , К	150 (2)	100(2)
reflns collected	37882	69236
Ind reflns	14020	17721
R _{int}	0.0910	0.0719
GOF on F^2	0.960	1.015
$R_1/wR_2 [I \ge 2\sigma(I)]^a$	0.051/0.0881	0.0433/0.0786
$\frac{R_1/wR_2}{(\text{all data})^{\text{a}}}$	0.0983/0.0987	0.0849/0.0937

Table 9.2. Crystallographic Data for Pt(phbpy)(pip2NCN) and[Pt(phbpy)(pip2NCNH2)](PF6)2 • 2CH2Cl2.

^a $R_1 \Sigma || F_0 |- |F_c| |/\Sigma |F_0|, wR_2 = [\Sigma w (F_0^2 - F_c^2)^2 / \Sigma w (F_0^2)^2]^{\frac{1}{2}}.$

Results and Discussion.

Three complexes, $(Pt(tpy)(pipNC)^+, Pt(tpy)(3,5-pip_2NCN)^+$ and Pt(phbpy)(pip₂NCN) (Figure 9.3), have been prepared as models for the two-electron complex, $Pt(tpy)(pip_2NCN)^+$ (Figure 9.2),¹⁻³ reported in Chapter 8. The model complexes are expected to provide insight into the role of the piperidyl groups in facilitating two-electron transfer. Unlike $Pt(tpy)(pip_2NCN)^+$, which has two piperidyl groups capable of interacting with the platinum center, $Pt(tpy)(pipNC)^+$ has only one piperidyl group. This complex could stabilize a five-coordinate species, but would require solvent or another molecule to stabilize a six-coordinate product. Though six coordinate Pt(IV) is common, Goldberg and coworkers^{17,18} have prepared several five coordinate Pt(IV) complexes. The second model complex, $Pt(tpy)(3,5-pip_2NCN)^+$, has the same chemical formula as $Pt(tpy)(pip_2NCN)^+$. However, the positions of the piperidyl arms have been shifted from the 2 and 6 positions to the 3 and 5 positions. Consequently, the piperidyl groups are no longer expected to interact directly with the platinum(II) center upon oxidation. The third model complex, Pt(phbpy)(pip2NCN), has the same architecture as the two-electron reagent. However, one pyridyl nitrogen atom has been replaced with a carbon atom, resulting in a neutral complex. If the preorganized structure involves a Lewis acid-base interaction between the metal center and the piperidyl groups, this complex is expected to have a decreased tendency to preorganize because the metal center is expected to be less electrophilic.

Synthesis and Characterization. The synthesis of $Pt(pipNC)_2$ is shown in Scheme 9.1. The synthesis of $Pt(tpy)(pipNC)^+$ and $Pt(tpy)(pipNCH)^{2+}$ is shown in Scheme 9.2. The preparation of $Pt(tpy)(3,5-pip_2NCN)^+$ is illustrated in Scheme 9.3. The

syntheses of Pt(phbpy)(pip₂NCN), Pt(phbpy)(pip₂NCNH)⁺ and Pt(phbpy)(pip₂NCNH₂)²⁺ are shown in Scheme 9.4. The synthesis of the proposed platinum(IV) phenylbipyridyl complex, Pt(η^2 -pip₂NCN)(η^2 -phbpy)(OH)₂, is given in Scheme 9.5. Most of these complexes were characterized by elemental analysis, ¹H NMR spectroscopy, and mass spectrometry. The pipNCBr and pipNCH ligand precursors were synthesized by refluxing 2-bromobenzyl bromide and benzyl bromide, respectively, with excess piperidine, to give the product and the bromide salt of protonated piperidine. After dissolving the crude product in CH₂Cl₂, hexanes were added to precipitate [C₅H₁₀NH₂]Br, which was removed by vacuum filtration. The resulting oils were used in the syntheses of Pt(pipNC)₂ and Pt(pipNC)(DMSO)Cl without further purification.



Scheme 9.1. Synthesis of Pt(pipNC)₂.



(*i*) Pt(DMSO)Cl₂, NaCH₃CO₂, methanol; (*ii*) AgBF₄, tpy, acetone; (*iii*) HNO₃, NH₄PF₆, acetone.

Scheme 9.2. Synthesis of Pt(tpy)(pipNC)⁺ and Pt(tpy)(pipNCH)²⁺.



(*i*) Pt(PPh₃)₄, toluene; (*ii*) TIPF₆, tpy, S₈, methanol.

Scheme 9.3. Synthesis of $Pt(tpy)(3,5-pip_2NCN)^+$.





Scheme 9.4. Synthesis of Pt(phbpy)(pip₂NCN), Pt(phbpy)(pip₂NCNH)⁺ and Pt(phbpy)(pip₂NCNH₂)²⁺. The colors of the products are written in parentheses. The principle peaks in the mass spectra of two products are given as m/z.



Scheme 9.5. Synthesis of a platinum(IV) phenylbipyridyl complex. Two possible structures for the product are shown.

Preparation of Complexes with pipNC⁻. In an early attempt to prepare platinum(II) complexes with a single pipNC⁻ ligand, we investigated its reactivity with Pt(COD)Cl₂. We were surprised to find that we could only isolate starting materials and $Pt(pipNC)_2$ from the reaction. To confirm this result, we intentionally prepared Pt(pipNC)₂ in good yields (61%) by allowing two equivalents of pipNCBr to react with *N*-butyllithium and Pt(COD)Cl₂ (Scheme 9.1). The ¹H NMR spectrum (Figures 9.4) exhibits a singlet at 4.23 ppm (J_{H-Pt}=21 Hz) assigned to the benzylic protons. A doublet attributable to the α -protons of the aryl group occurs at 7.41 ppm with ¹⁹⁵Pt satellites (J_{H-Pt}=50 Hz), confirming that the pipNC⁻ ligand is bidentate. The spectrum is consistent with the presence of only one isomer (*cis* or *trans*) in solution. We tentatively assign the product as the *cis*-isomer, based on earlier work by Longoni *et al.*¹⁹ The *cis*-isomer of Pt(Et₂NC)₂ was prepared from cis-Pt(SEt₂)₂Cl₂ following a procedure similar to the one reported here; the trans-isomer was prepared from trans-Pt(SEt₂)₂Cl₂ using a Grignard reagent. The benzylic resonances for the *trans*-isomer show ¹⁹⁵Pt satellites with J_{H-Pt} equal to 44.0 Hz, whereas J_{H-Pt} for the *cis*-isomer (18.5 Hz) is similar to that observed for Pt(pipNC)₂.¹⁹

In an alternative strategy for attaching only one pipNC⁻ ligand to Pt(II), Pt(DMSO)Cl₂, pipNCH and sodium acetate were stirred in methanol at room temperature for four days (Scheme 9.2). After chromatography the cyclometallated product Pt(pipNC)(DMSO)Cl was obtained in reasonable yield (~40%). The reaction time can be reduced to 3 hours by refluxing the methanol solution, resulting in slightly lower yields (~30%). The ¹H NMR spectrum (Figures 9.5) exhibits a singlet at 4.28 ppm (J_{H-Pt}=45 Hz) assigned to the benzylic protons and a doublet at 7.92 ppm (J_{H-Pt}=47 Hz) confirming

that the pipNC⁻ ligand is bidentate. A pair of resonances occurs at 3.13 and 3.92 ppm due to the diastereotopic piperidyl protons, as previously noted for complexes with a tridentate pip₂NCN⁻.^{20,21} A singlet with ¹⁹⁵Pt satellites ($J_{H-Pt}=25 \text{ Hz}$) occurs at 3.55 ppm and is attributed to the DMSO methyl protons. The DMSO ligand is believed to be *trans* to the piperidyl group based on reactivity studies reported by van Koten and coworkers^{22,23} for related complexes, such as Pt(Me₂NC)(DMSO)Cl.

 $Pt(tpy)(pipNC)^+$ was synthesized by stirring an acetone solution of Pt(pipNC)(DMSO)Cl with a silver salt (*e.g.*, AgBF₄). After removal of the resultant silver chloride by filtration, one equivalent of tpy was added to the filtrate. The ¹H NMR spectrum of the product (Figures 9.6) shows a terpyridyl resonance at 8.23 ppm with distinct ¹⁹⁵Pt satellites (J_{H-Pt}=42 Hz) confirming that the tpy ligand is tridentate. A singlet at 3.61 ppm and the broad aliphatic resonances between 1.5 and 2.5 ppm confirm that the pipNC⁻ ligand is monodentate in solution, bonded to the platinum at the 2 position of the aryl ring. The ¹H NMR spectrum of the protonated complex (Figure 9.7) shows a broad resonance near 6.8 ppm attributable to the protonated piperidyl group. As expected, the benzylic resonance appears as a doublet, and the resonances associated with the diastereotopic piperidyl aliphatic protons form a characteristic pattern.

Preparation of Pt(tpy)(3,5-pip_NCN)⁺. Oxidative addition of 3,5-pip_NCNI to $Pt(PPh_3)_4$ resulted in $Pt(PPh_3)_2(3,5-pip_2NCN)I$ in >70% yield (Scheme 9.3). Attempts to synthesize the bromide adduct from 3,5-pip_NCNBr were unsuccessful. The ¹H NMR spectrum of $Pt(PPh_3)_2(3,5-pip_2NCN)I$ (Figures 9.8) exhibits two singlets at 6.18 and 6.58 ppm, assigned to the aromatic protons of aryl group. The ¹⁹⁵Pt satellites for the downfield resonance (6.58 ppm, J_{H-Pt}=58 Hz) and the absence of satellites for the

benzylic resonance (2.77 ppm) confirm that the 3,5-pip₂NCN⁻ ligand is monodentate. By analogy to investigations by van Koten and coworkers,¹¹ the complex is tentatively assigned as the *trans*-isomer.

Metathesis was accomplished by reaction with TIPF₆ to remove iodide ligand, followed by addition of one equivalent of tpy and four equivalents of elemental sulfur. It is worth noting that attempts to remove the iodide with a silver salt (*e.g.*, AgBF₄) were less successful due to the slight solubility of the resulting AgI. The ¹H NMR spectrum of Pt(tpy)(3,5-pip₂NCN)⁺ (Figures 9.9) exhibits two singlets at 7.11 and 7.41 ppm (J_{H-Pt}=33 Hz) associated with the aryl group. A singlet at 3.65 ppm is attributed to the benzylic protons.

Preparation of Complexes with pip₂NCN⁻ and phbpy⁻. Pt(phbpy)(pip₂NCN) was prepared from the reaction of Pt(pip₂NCN)Cl with AgBF₄, followed by addition of one equivalent of phbpyH (Scheme 9.4). The mass spectrum of the orange product isolated from this reaction is consistent with the formation of Pt(phbpy)(pip₂NCNH)⁺. Reaction of this product with acid resulted in the bright yellow doubly protonated product. The red neutral Pt(phbpy)(pip₂NCN) complex was precipitated by addition of base. The ¹H spectrum of Pt(phbpy)(pip₂NCNH₂)²⁺ (Figure 9.10) shows a doublet at 6.61 ppm with distinct ¹⁹⁵Pt satellites (J_{H-Pt}=63 Hz), indicating that the phenyl group of the phbpy⁻ ligand is bonded to the metal center. The characteristically complex pattern of well-resolved aliphatic resonances is consistent with protonation of the piperidyl groups.

Reaction of Pt(phbpy)(pip_NCN) with Hydrogen Peroxide. When H₂O₂ is added to an acetone solution of Pt(phbpy)(pip₂NCN), the red solution turns pale yellow. After stirring for 30 minutes, a pale yellow solid was precipitated with diethyl ether. The

identity of the product remains uncertain, however the elemental analysis is consistent with addition of one H₂O₂ molecule to Pt(phbpy)(pip₂NCN). The electrospray mass spectrum (m/z = 714.283), is consistent with loss of OH⁻, raising the unappealing possibility of a hydroxide counterion (Scheme 9.5). To account for the presence of hydroxide ion, we propose that the product contains Pt(IV). Because hydroxide is usually found as a ligand rather than as a counterion, we prefer a structure in which one or more likely both hydroxide groups are bonded to platinum.

The ¹H NMR spectrum (Figure 9.11) is consistent with the neutral product depicted in Scheme 9.5. Three resonances exhibit distinct ¹⁹⁵Pt satellites. The resonance at 6.70 Hz ($J_{H-Pt}=42$ Hz) is attributed to the α -protons of the phenylbipyridine phenyl ring, confirming that it is bonded to the platinum center. The absence of ¹⁹⁵Pt satellites associated with the pyridyl resonances of the phbpy⁻ ligand suggests that the peripheral pyridine ring is not bonded to the platinum center. Therefore, we propose that the phbpy⁻ ligand is bidentate. The resonance at 5.58 ppm ($J_{H-Pt}=22$ Hz) is tentatively attributed to a coordinated hydroxyl proton, though this resonance was not present in spectra of freshly prepared product; it is possible that the chemical shift is sensitive to residual water concentration.

The four doublets with equal intensity between 3.3 and 4.6 ppm are attributed to the benzylic protons of the pip_2NCN^- ligand. The two doublets at 3.28 and 3.89 ppm are coupled ($J_{H-H}=11$ Hz), and the two at 4.04 and 4.38 ppm are coupled ($J_{H-H}=14$ Hz). Interestingly, only the furthest downfield of these resonances exhibits ¹⁹⁵Pt satellites (4.38 ppm, 38 Hz). The two coupled resonances at 4.04 and 4.38 ppm are attributed to two protons on the same benzylic carbon, and the average of the chemical shifts (4.21

ppm) is consistent with those observed for tridentate pip₂NCN⁻. Therefore, it is surprising that ¹⁹⁵Pt satellites are not observed for the resonance at 4.04 ppm. The difference in chemical shifts is consistent with protons that are in dramatically different environments. One possibility is that the plane of the aryl ring is significantly tilted with respect to the Pt-N(piperidyl) vector. In that case, the resonance at 4.38 ppm would be assigned to the proton that is *trans* or in an *anti* configuration with respect to the platinum; the resonance at 4.04 ppm would be attributable to the proton in the more gauche arrangement. In keeping with this interpretation, we propose that the other piperidyl group is locked in place through a strong hydrogen-bonding interaction with an axial hydroxide ligand, resulting in the canting of the pip_2NCN^2 aryl ring. This conformation accounts for the absence of ¹⁹⁵Pt satellites associated with the resonances at 3.28 and 3.89 ppm. It also would explain why the benzylic protons appear to be diastereotopic. The resulting complex is neutral with both the phbpy and pip₂NCN⁻ ligands being bidentate (Scheme 9.5). It is conceivable that one OH⁻ group dissociates in the electrospray experiment, accounting for the observed mass spectrum.

Crystal Structures. The structures of $[Pt(tpy)(pip_2NC)](BF_4)$, $[Pt(tpy)(pipNCH)](PF_6)_2$, $Pt(phbpy)(pip_2NCN)$ and $Pt(phbpy)(pip_2NCNH_2)](PF_6)_2 \cdot$ $2CH_2Cl_2$ were confirmed by single-crystal X-ray diffraction. ORTEP diagrams are shown in Figures 9.12 through 9.16, and relevant data are summarized in Tables 9.1 through 9.4. $Pt(phbpy)(pip_2NCN)$ and $Pt(phbpy)(pip_2NCNH_2)](PF_6)_2 \cdot 2CH_2Cl_2$ each crystallize with two independent molecules in the asymmetric unit cell. In crystals of $Pt(phbpy)(pip_2NCNH_2)](PF_6)_2 \cdot 2CH_2Cl_2$, one CH_2Cl_2 is disordered over two positions. In crystals of $[Pt(tpy)(pipNCH)](PF_6)_2$, the protonated piperidyl ligand is disordered over



Figure 9.4. ¹H NMR spectrum of Pt(pipNC)₂ in CDCl₃. Solvent and TMS resonances are labeled with *.



Figure 9.5. ¹H NMR spectrum of Pt(pipNC)(DMSO)Cl in CDCl₃. Solvent and TMS resonances are labeled with *.



Figure 9.6. ¹H NMR spectrum of Pt(tpy)(pipNC)⁺ in CDCl₃. Solvent and TMS resonances are labeled with *.



Figure 9.7. ¹H NMR spectrum of Pt(tpy)(pipNCH)²⁺ in CD₃CN. Solvent resonances are labeled with *.



Figure 9.8. ¹H NMR spectrum of Pt(PPh₃)₂(3,5-pip₂NCN)I in CDCl₃. Solvent and TMS resonances are labeled with *.



Figure 9.9. ¹H NMR spectrum of $Pt(tpy)(3,5-pip_2NCN)^+$ in CD_3CN . Solvent resonances are labeled with *.



Figure 9.10. ¹H NMR spectrum of $Pt(phbpy)(pip_2NCNH_2)^{2+}$ in CD₃CN. Solvent resonances are labeled with *.



Figure 9.11. ¹H NMR spectrum of $Pt(\eta^2-phbpy)(pip_2NCNH_2)(OH)^+$ in CD₃CN. Solvent resonances are labeled with *.

	[Pt(tpy)(pip ₂ NC)](BF ₄)	[Pt(tpy)(pipNCH)](PF ₆) ₂
Pt-C(16)	2.029(3)	2.028(3)
Pt-N(1)	2.019(2)	2.027(3)
Pt-N(2)	2.023(3)	2.033(3)
Pt-N(3)	1.991(2)	1.990(3)
N(1)-C(5)	1.392(4)	1.383(4)
N(2)-C(11)	1.388(4)	1.369(4)
N(3)-C(6)	1.339(4)	1.339(4)
N(3)-C(10)	1.343(4)	1.341(4)
C(5)-C(6)	1.479(4)	1.479(4)
C(10)-C(11)	1.475(4)	1.481(4)
C(16)-Pt-N(1)	100.72(11)	100.94(12)
C(16)-Pt-N(2)	98.27(10)	98.42(11)
C(16)-Pt-N(3)	174.23(10)	176.94(11)
N(1)-Pt-N(2)	160.99(10)	160.64(11)
N(2)-Pt-N(3)	80.48(10)	80.28(10)
N(1)-Pt-N(3)	80.53(10)	80.38(11)
C(5)-N(1)-Pt	113.53(19)	113.3(2)
C(11)-N(2)-Pt	113.3(2)	113.4(2)
C(6)-C(5)-N(1)	114.9(3)	115.6(3)
C(10)-C(11)-N(2)	115.2(3)	115.9(3)
C(6)-N(3)-Pt	117.62(19)	118.0(2)
C(10)-N(3)-Pt	117.1(2)	117.9(2)

Table 9.3. Selected Distances (Å) and Angles (°) for [Pt(tpy)(pip_2NC)](BF4) and
[Pt(tpy)(pipNCH)](PF6)2.

	Pt(phbpy)(pip2NCN)	$[Pt(phbpy)(pip_2NCNH_2)](PF_6)_2 \bullet 2CH_2Cl_2$
Pt-C(0)	2.019(7)/1.981(6)	2.017(5)/2.009(5)
Pt-C(16)	2.040(6)/2.022(6)	2.021(6)/2.042(6)
Pt-N(2)	2.078(6)/2.107(5)	2.095(4)/2.096(4)
Pt-N(3)	2.007(5)/2.013(5)	1.994(4)/2.004(5)
N(2)-C(11)	1.401(8)/1.368(8)	1.381(7)/1.370(7)
C(0)-C(5)	1.411(8)/1.419(9)	1.431(7)/1.444(7)
N(3)-C(10)	1.350(8)/1.361(8)	1.362(7)/1.347(7)
N(3)-C(6)	1.341(8)/1.331(8)	1.357(7)/1.354(7)
C(11)-C(10)	1.484(9)/1.476(10)	1.479(8)/1.475(8)
C(5)-C(6)	1.459(9)/1.485(8)	1.484(8)/1.460(8)
C(16)-Pt-N(2)	101.2(2)/101.3(2)	97.63(19)/100.75(19)
C(16)-Pt-N(3)	179.6(2)/178.4(2)	176.4(2)/179.8(2)
C(0)-Pt-C(16)	99.1(2)/98.4(2)	101.5(2)/98.5(2)
N(2)-Pt-N(3)	79.2(2)/78.8(2)	79.17(18)/79.11(18)
N(3)-Pt-C(0)	80.5(2)/81.5(2)	81.7(2)/81.7(2)
N(2)-Pt-C(0)	159.7(2)/160.2(2)	160.9(2)/160.7(2)
C(11)-N(2)-Pt	113.7(4)/113.5(5)	112.9(4)/113.0(4)
C(5)-C(0)-Pt	112.9(5)/113.3(4)	112.0(4)/111.6(4)
C(10)-C(11)-N(2)	114.6(6)/115.8(6)	116.3(5)/115.9(5)
C(6)-C(5)-C(0)	115.7(6)/115.3(6)	116.2(5)/116.6(5)
C(10)-N(3)-Pt	119.0(4)/118.3(5)	119.3(4)/118.4(4)
C(6)-N(3)-Pt	117.4(4)/117.2(4)	118.0(4)/117.6(4)

Table 9.4.Selected Distances (Å) and Angles (°) for $Pt(phbpy)(pip_2NCN)$ and
 $[Pt(phbpy)(pip_2NCNH_2)](PF_6)_2 \cdot 2CH_2Cl_2.$



Figure 9.12. ORTEP diagram of [Pt(tpy)(pip₂NC)](BF₄). Anion, solvent and H-atoms are omitted for clarity.



Figure 9.13. ORTEP diagram of [Pt(tpy)(pipNCH)](PF₆)₂. Both conformations of the disordered piperidyl group are shown. Anion, solvent and H-atoms (with the exception of those bonded to N(piperidyl)) are omitted for clarity.



Figure 9.14. ORTEP diagram of Pt(phbpy)(pip₂NCN). Anion, solvent and H-atoms are omitted for clarity.



Figure 9.15. ORTEP diagram of [Pt(phbpy)(pip₂NCNH₂)](PF₆)₂ • 2CH₂Cl₂. Anion, solvent and H-atoms (with the exception of those bonded to N(piperidyl)) are omitted for clarity.

two principal conformations and the occupancy of the major conformer is 80%. The complexes adopt distorted square planar structures that are qualitatively similar to those of other platinum(II) complexes with terpyridine $^{1,24-34}$ and phenylbipyridine ligand.³⁵⁻⁴³ The Pt-C(pipNCH) distances for Pt(tpy)(pipNC)⁺ (2.029(3) Å) and Pt(tpy)(pipNCH)²⁺ (2.028(3) Å) are similar to the Pt-C(phenyl) distances reported for Pt(phtpy)(Ph)⁺ (2.025) (2) Å), $Pt(tpy)(3.5-dmph)^+$ (2.042(4) Å), $Pt(tpy)(mes)^+$ (2.041(5) Å), and $Pt(phtpy)(mes)^+$ (2.023(6) Å) (Chapter 5),⁴⁴ as well as Pt(tpy)(pip₂NCNH₂)²⁺ (2.031(8) \text{ Å}) and $Pt(phtpy)(pip_2NCN)^{2+}$ (2.041(5), 2.047(5) Å) (Chapter 8).¹ The Pt-N1 and Pt-N2 distances for Pt(tpy)(pipNC)⁺ (2.019(2), 2.023(3) Å) and Pt(tpy)(pipNCH)²⁺ (2.027(3), 2.033(3) Å) are comparable to those of other platinum(II) terpyridyl complexes.²⁶⁻³² including those reported in Chapter 8: $Pt(tpv)(pip_2NCNH_2)^{2+}$ (2.030(8), 2.010(7) Å) and $Pt(phtpy)(pip_2NCN)^+$ (2.027(4), 2.035(4), 2.032(4), 2.029(4) Å).¹ The central Pt-N(tpy) distances for $Pt(tpy)(pipNC)^+$ (1.991(2) Å) and $Pt(tpy)(pipNCH)^{2+}$ (1.990(3) Å) are consistent with the strong trans-directing properties of a phenyl anion, as also observed for Pt(phtpy)(Ph)⁺ (1.9929(16) Å), Pt(tpy)(3.5-dmph)⁺ (1.992(3) Å), Pt(tpy)(mes)⁺ (1.987(4) Å), and Pt(phtpy)(mes)⁺ (1.998(4) Å) (Chapter 5).⁴⁴ but are significantly longer than the Pt-N(tpy) distances, when N(tpy) is opposite a weak trans-directing group such as in crystals of [Pt(4'-o-tolyl-tpy)Cl](BF₄) (1.935(9) Å),²⁶ [Pt(tpy)(1methylimidazole)](ClO₄) (1.943(7) Å)²⁴ and [Pt(4,4',4"-tri-*tert*-butyl-tpy)Cl](ClO₄) (1.935(6) Å).³³

The Pt-C(phbpy) and Pt-C(pip₂NCN) distances for Pt(phbpy)(pip₂NCN) (2.019(7), 1.981(6), 2.040(6), 2.022(6) Å) and Pt(phbpy)(pip₂NCNH₂)²⁺ (2.017(5), 2.009(5), 2.021(6), 2.042(6) Å) are consistent with the Pt-C(phenyl) distances observed for platinum(II) complexes with³⁵⁻⁴³ phbpy⁻ and^{1,24-34} pip₂NCN⁻ ligands, including [Pt(phbpy)(2-methylpyridine)](ClO₄) • CH₃CN (1.995(8) Å)⁴² and [Pt(phbpy)(*t*butylisocyanide)] (ClO₄) • 2CH₃CN (2.036(8) Å).³⁹ The Pt-N(phbpy) distances for the terminal pyridyl groups of Pt(phbpy)(pip₂NCN) (2.078(6), 2.107(5) Å) and Pt(phbpy)(pip₂NCNH₂)²⁺ (2.095(4), 2.096(4) Å) also are within the range observed for platinum(II) complexes with the phbpy⁻ ligand (2.063-2.177 Å).³⁵⁻⁴³ The central Pt-N(phbpy) distances for Pt(phbpy)(pip₂NCN) (2.007(5), 2.013(5) Å) and Pt(phbpy)(pip₂NCNH₂)²⁺ (1.994(4), 2.004(6) Å) are shorter than the terminal Pt-N(phbpy) distances, but marginally longer than the central Pt-N distance observed for Pt(tpy)(pipNC)⁺ (1.991(2) Å) and Pt(tpy)(pipNCH)²⁺ (1.990(3) Å). Overall, these values are consistent with the central Pt-N(phbpy) distances observed for [Pt(phbpy)(P(Ph)₂CH₂NHPh)](ClO₄) (2.013(4) Å),³⁵ and [Pt(phbpy)(2,6dimethylphenylisocyanide)](PF₆) • CH₃CN (1.998(6) Å).³⁹

As previously noted,²⁴⁻²⁶ the restricted bite angle of the tridentate terpyridine ligand precludes the 90° and 180° N-Pt-N bond angles of an idealized square planar complex. The N1-Pt-N3 and N2-Pt-N3 bond angles (Pt(tpy)(pipNC)⁺: 80.53(10), 80.49(10)°; Pt(tpy)(pipNCH)²⁺: 80.38(11), 80.28(10)°) are characteristically smaller than 90°. The strong trans-directing phenyl groups might be expected to aggravate the situation, because the long Pt-N2 bond distances necessitate even smaller N1-Pt-N2 bond angles (Pt(tpy)(pipNC)⁺, 160.99(10)°; Pt(tpy)(pipNCH)²⁺, 160.64(11)°). These angles are comparable to those observed for [Pt(tpy)(CH₃)](B(C₆H₅)₄) (160.6(3), 160.8(2)°),³⁰ Pt(phtpy)(Ph)⁺ (159.54(7)°), Pt(tpy)(3,5-dmph)⁺ (160.25(14)°), Pt(tpy)(mes)⁺ (159.41(18)°) and Pt(phtpy)(mes)⁺ (160.23(19)°) (Chapter 5).⁴⁴ The N2-Pt-N3, C0-Pt-N3 and C0-Pt-N2 bond angles for Pt(phbpy)(pip₂NCN) and Pt(phbpy)(pip₂NCNH₂)²⁺ also are comparable to literature values reported for related compounds.³⁵⁻⁴³ Interestingly the N2-Pt-N3 and C0-Pt-N3 angles of Pt(phbpy)(pip₂NCN) (79.2(2)/78.8(2)°, $80.5(2)/81.5(2)^{\circ}$) and Pt(phbpy)(pip₂NCNH₂)²⁺ (79.17(18)/79.11(18)°, $81.7(2)/81.7(2)^{\circ}$) are very similar to the N-Pt-N angles observed for the platinum(II) terpyridyl complexes, suggesting that the bite angles of phbpy⁻ and tpy ligands are very similar.

The dihedral angles formed by the Pt coordination plane, defined by Pt and the four atoms bonded to the Pt center, and the plane of the phenyl ring are 75.9° for $Pt(tpy)(pipNC)^{+}$, 66.9(1)° for $Pt(tpy)(pipNCH)^{2+}$, 80.6(2) and 80.7(2)° for Pt(phbpy)(pip₂NCN), and 86.8(2) and 85.9(2)° for Pt(phbpy)(pip₂NCNH₂)²⁺. This orientation of the phenyl groups, directs the piperidyl N atoms above and/or below the platinum coordination plane. In crystals of $Pt(phbpy)(pip_2NCN)$, there is a short interaction between the Pt center and one piperidyl nitrogen (PtB. N5B, 3.610(5) Å), for one of the complexes in the asymmetric unit. This distance is longer than those observed for both molecules in crystals of [Pt(phtpy)(pip₂NCN)](BF₄) (Pt1A···N4A, 3.512(5) Å; Pt1B···N5B, 3.195(5) Å), in keeping with the expectation that the metal center of the terpyridyl complex is more electrophilic. In crystals of $[Pt(phbpy)(pip_2NCNH_2)](PF_6)_2 \bullet$ 2CH₂Cl₂, the piperidyl H atoms bonded to nitrogen are directed toward the platinum center with intramolecular interactions of 2.45(6) Å (PtA···H5A) and 2.79(5) Å (PtA···H4A). Thus, it appears that the platinum center can act as a Brønsted base, as suggested by van Koten and coworkers,⁴⁵ as well as a Lewis acid. Interestingly, in yellow crystals of [Pt(tpy)(pipNCH)](PF₆)₂ the piperidyl N atom forms a hydrogen bond with the $CF_3SO_3^-$ counterion (H···F8, 2.23(5) Å; H···F10, 2.37(5) Å) and consequently is

directed away from the metal center. The fact that a hydrogen bonding interaction can compete with the N-H…Pt interaction suggests the strength of the latter is comparable to or weaker than the hydrogen bond.

Cyclic Voltammetry. Cyclic voltammograms of $Pt(tpy)(3.5-pip_2NCN)^+$ and Pt(tpy)(pipNC)⁺in acetonitrile (0.1 M TBAPF₆, 0.25 V/s) are shown in Figure 9.16 and Figure 9.17, respectively. $Pt(tpy)(pipNC)^+$ undergoes two reversible one-electron reduction processes at $E^{\circ}=-0.95$ V and $E^{\circ}=-1.47$ V vs. Ag/AgCl, with peak-to-peak separations (ΔE_p) of 69 and 68 mV, respectively. After the first sweep, an adsorption wave occurs near 0.5 V. $Pt(tpy)(3,5-pip_2NCN)^+$ undergoes two reversible one-electron reduction processes at E^o'=-0.91 V and E^o'=-1.44 V vs. Ag/AgCl, with ΔE_p values of 70 and 60 mV, respectively. These reduction processes are qualitatively similar to those observed for $Pt(tpy)(pip_2NCN)^+$ in acetonitrile solution (0.1 M TBAPF₆, 0.25 V/s). The latter complex exhibits two reversible one-electron ligand-centered reduction waves at $E^{\circ}=-0.98$ V and $E^{\circ}=-1.50$ V vs. Ag/AgCl, with ΔE_{p} values of 65 and 61 mV, respectively (Figure 8.7A).¹⁻³ In contrast to $Pt(tpy)(pip_2NCN)^+$, which undergoes a nearly reversible two-electron oxidation process at $E^{\circ}=0.40 \text{ V} (\Delta E_p=74 \text{ mV}, 0.25 \text{ V/s})$, neither of the two model complexes is oxidized at potentials ≤ 0.8 V. These observations establish that two piperidyl groups capable of interacting with the metal center are required for reversible two-electron oxidation to occur in these systems. The electrochemistry of $Pt(tpy)(3.5-pip_2NCN)^+$ suggests that the availability of through-space interactions of the piperidyl groups with the metal center are necessary for cooperative and reversible twoelectron reactivity. Evidently, the Pt(II)/Pt(III) couple for $Pt(tpy)(pipNC)^+$ is shifted to



Figure 9.16. Cyclic voltammogram of Pt(tpy)(3,5-pip₂NCN)⁺ in acetonitrile (0.1 M TBAPF₆, 0.25 V/s) vs. Ag/AgCl.



Figure 9.17. Cyclic voltammogram of Pt(tpy)(pipNC)⁺ in acetonitrile (0.1 M TBAPF₆, 0.25 V/s) vs. Ag/AgCl.

>0.8V, and therefore we also can confidently conclude that the two-electron oxidation of the $Pt(tpy)(pip_2NCN)^+$ does not involve formation of a stable Pt(III) (or Pt(IV)) five-coordinate complex or a six-coordinate complex with a solvent ligand. If an unstable Pt(III) species is formed in low concentrations at the electrode, it is presumably rapidly converted to the Pt(IV) product. In that case, $E^{on}=0.40$ V is approximately equal to the Pt(III)/Pt(IV) redox couple.

The cyclic voltammogram of Pt(phbpy)(pip₂NCN) was recorded in acetonitrile (0.1 M TBAPF₆, 0.25 V/s, Figure 9.18). This complex undergoes a one-electron ligandcentered nearly reversible reduction process at E° =-1.46 V vs. Ag/AgCl, with ΔE_p of 76 mV. The electrochemical properties of platinum(II) complexes with phbpy⁻ have not been previously reported. However, the 0.5 V cathodic shift of the reduction from the first terpyridine-centered reduction for $Pt(tpy)(pip_2NCN)^+$, is consistent with the phbpy being more electron rich than tpy. Pt(phbpy)(pip2NCN) also undergoes an oxidation process at E^o'=-0.14 V vs. Ag/AgCl (0.1 M TBAPF₆ in CH₃CN). The oxidation clearly involves transfer of considerably more charge than observed for the reduction, and the process is attributed to a net two-electron oxidation of the complex. The redox couple $(E^{\circ}=-0.14 \text{ V})$ is cathodicly shifted by ~0.54 V from the two-electron oxidation process observed for Pt(tpy)(pip_2NCN)⁺ (E^o=0.40 V), as expected for a more electron-rich metal center. Although the ratio (1.4) of the peak anodic current (i_{pa}) of the oxidation process to the peak cathodic current (i_{pc}) of the first reduction wave is less than 2.8, which is predicted for a Nernstian two-electron process, it exceeds the expected value of 1.0 for a one-electron process. In fact, the couple is clearly not electrochemically reversible as



Figure 9.18. Cyclic voltammogram of Pt(phbpy)(pip₂NCN)⁺ in acetonitrile (0.1 M TBAPF₆, 0.25 V/s) vs. Ag/AgCl.

indicated by the relatively large values of ΔE_p (ΔE_p =260 mV, 0.25 V/s), and therefore the value of i_{pc}/i_{pa} cannot be expected to approach the Nernstian limits.

The poor electrochemical reversibility of the oxidation process contrasts sharply with the behavior of Pt(tpy)(pip₂NCN)⁺. This result seems at first surprising because the complexes differ by only one atom and are expected to have very similar structures. However, both the structural and electrochemical data suggest that the platinum center in the phbpy⁻ complex is less electrophilic than in the tpy complex. Therefore, the interactions of the piperidyl groups with the metal are expected to be weaker in the phbpy⁻ complex, as suggested by the crystal structures of [Pt(phtpy)(pip₂NCN)](BF₄) (Pt1A···N4A, 3.512(5) Å; Pt1B···N5B, 3.195(5) Å) and Pt(phbpy)(pip₂NCN) (PtB···N5B, 3.610(5) Å). Consequently, we would anticipate that Pt(phbpy)(pip₂NCN) has a lower tendency to form preorganized five- or six-coordinate structures with weak Pt···N(piperidyl) interactions. If preorganization is necessary for facile two-electron transfer, then the phbpy⁻ complex would be expected to exhibit less reversible electrochemistry, as is observed.

UV-visible Absorption Spectroscopy. UV-visible absorption data for Pt(tpy)(pip₂NCN)](BF₄), Pt(phtpy)(pip₂NCN)](BF₄), Pt(tpy)(3,5-pip₂NCN)](PF₆), and Pt(tpy)(pipNC)](BF₄) in various solvents, are summarized in Table 9.5 and Figures 9.20 and 9.21. Data for several of the protonated complexes (Figure 9.19), as well as for Pt(tpy)(2,6-dmph)](BF₄) from Chapter 7, also are shown (Table 9.5). Pt(tpy)(pip₂NCN)](BF₄) is a red solid that dissolves to give red solutions, whereas Pt(tpy)(pipNC)](BF₄) is an yellow solid that dissolves to give red solutions. Pt(tpy)(3,5-pip₂NCN)](PF₆), like Pt(tpy)(dmph)](BF₄) discussed in Chapter 7, is an
orange solid that dissolves to give yellow solutions. The four protonated complexes, Pt(tpy)(pip₂NCNH₂)](PF₆)₃, Pt(phtpy)(pip₂NCNH₂)](PF₆)₃, Pt(tpy)(pip_NCH)](PF₆)₂, and Pt(phbpy)(pip₂NCNH₂)](PF₆)₂, are yellow solids that dissolve to give yellow solutions.

Each of the complexes exhibits an intense absorption between 270 and 280 nm. Transitions are observed in this region for Pt(pip₂NCN)Cl (275 nm (9050 cm⁻¹M⁻¹)) and Pt(pip₂NCN)(I) (276 nm (8150 cm⁻¹M⁻¹)),²⁰ as well as for platinum(II) terpyridyl complexes such as Pt(tpy)(Me)⁺ (274 nm (15900 cm⁻¹M⁻¹))⁴⁶ and Pt(4,4',4"-trichloro-2,2';6',2"-terpyridine)Cl⁺ (282 nm (33700 cm⁻¹M⁻¹)).³³ A series of absorptions is observed between 300 and 350 nm in the UV-visible spectra of the platinum(II) terpyridyl complexes The bands are similar to those observed for Pt(tpy)(Me)⁺ (314 nm, 10100 cm⁻¹M⁻¹),⁴⁶ Pt(tpy)Cl⁺(317 nm, 7200 cm⁻¹M⁻¹; 333 nm, 10100 cm⁻¹M⁻¹),⁴⁷ and Pt(4,4',4"-trichloro-2,2';6',2"-terpyridine)Cl⁺ (328 nm, 20600 cm⁻¹M⁻¹; 343 nm, 12300 cm⁻¹M⁻¹).³³ The latter have been assigned to terpyridine center π - π * transitions, and we make a similar assignment here.

A structured low-energy absorption band is observed between 400 and 445 nm ($\varepsilon = 1100-4600 \text{ M}^{-1} \text{ cm}^{-1}$) in the spectra of these complexes. The energy and intensity of these bands, are similar to those bands assigned as spin-allowed 5d(Pt) $\rightarrow \pi^*(\text{tpy})$ MLCT transitions in the UV-visible spectra of other platinum(II) terpyridyl complexes.^{32,33,47-49} However, due to the electron donating aryl group these transitions are shifted to lower energy than those observed for Pt(tpy)Cl⁺ (CH₃CN: 372 (1300), 398 nm (1200 cm⁻¹M⁻¹)).⁴⁹

Table 9.5. Room-Temperature UV-Visible Absorption data for $[Pt(tpy)(pip_2NCN)](BF_4)$,
 $[Pt(tpy)(pip_2NCNH_2)](PF_6)_3$, $[Pt(phtpy)(pip_2NCN)](BF_4)$,
 $[Pt(phtpy)(pip_2NCNH_2)](PF_6)_3$, $[Pt(tpy)(3,5-pip_2NCN)](PF_6)$,
 $[Pt(tpy)(pipNC)](BF_4)$, $Pt(tpy)(pipNCH)](PF_6)_2$, and
 $[Pt(phpy)(pip_2NCNH_2)](PF_6)_3$ and $[Pt(tpy)(2,6-dmph)](BF_4)$.

Compound	Absorption λ_{max} , nm (ϵ , cm ⁻¹ M ⁻¹)		
[Pt(tpy)(pip ₂ NCN)](BF ₄) ^a	270 (31000), 279 (31000), 310 (15000), 425 (1500), 455 (1300), 485sh (1000),550sh (300)		
[Pt(tpy)(pip ₂ NCNH ₂)](PF ₆) ₃ ^c	310 (10700), 330 (11050), 345 (8000), 387 (2050), 408 (1150)		
[Pt(phtpy)(pip ₂ NCN)](BF ₄) ^a	200 (38200), 316sh (21900), 430 (2100), 563sh (400)		
[Pt(phtpy)(pip ₂ NCNH ₂)](PF ₆) ₃ ^b	283(48200), 310 (25800), 325 (25700), 339sh (20450), 357sh (7600), 396sh (3050)		
$[Pt(tpy)(3,5-pip_2NCN)](PF_6)^b$	269, 279, 315, 343, 400sh, 420, 475		
[Pt(tpy)(pipNC)](BF ₄) ^a	270 (31000), 279 (31000), 320 (14000), 420 (1800), 445 (1700), 480sh (1000), 550sh (300)		
[Pt(tpy)(pipNCH)](PF ₆) ₂ ^b	268 (30200), 278sh (28500), 313 (13350), 333 (12400), 396 (2200), 409sh (2000)		
[Pt(phbpy)(pip ₂ NCNH ₂)](PF ₆) ₂ ^b	271 (28900), 318 (9900), 330sh (10400), 341 (10300), 393sh (1450)		
Pt(tpy)(2,6-dmph)](BF ₄) ^a	270 (26000), 278 (26000), 316 (11900), 332sh (7550), 345 (6150), 405 (1300), 430 (1150), 483sh (300)		

^a Recorded in CH₂Cl₂, ^b Recorded in CH₃CN, ^c Recorded in CH₃OH



Figure 9.19. Room-temperature UV-visible absorption spectra of [(Pt(tpy)(pip₂NCNH₂)](PF₆)₃ (----) in methanol, [Pt(tpy)(pipNCH)](PF₆)₂ (----) in acetonitrile, and [Pt(phbpy)(pip₂NCNH₂)](PF₆)₂ (-----) in acetonitrile.



Figure 9.20. Room-temperature UV-visible absorption spectra of $[(Pt(tpy)(3,5-pip_2NCN)](PF_6)(\dots)]$ in acetonitrile and $[Pt(tpy)(2,6-dmph)](BF_4)(\dots)$ in methylene chloride.



Figure 9.21. Room-temperature UV-visible absorption spectra of [Pt(tpy)(pip₂NCN)](BF₄) (----), and [Pt(tpy)(pipNC)](BF₄) (----), and [Pt(phtpy)(pip₂NCN)](BF₄) (----) in methylene chloride.

For all four complexes a weak shoulder (300-1000 cm⁻¹M⁻¹) is observed between 470 and 500 nm in the tail of the ¹MLCT absorption band. This feature is shifted 2000 to 4000 cm⁻¹ to the red of the ¹MLCT maximum, as might be expect for the corresponding ³MLCT transition. This assignment is in agreement with that made by Lai and co-workers for Pt(4,4',4"-tri-*tert*-butyl-2,2':6',2"-terpyridine)Cl]⁺ (465 nm, 57 cm⁻¹M⁻¹).³³ The apparent singlet-triplet MLCT splitting is similar to that observed for Pt(phbpy)(4-aminopyridine)⁺ (2000 cm⁻¹) (phbpy = 6-phenyl-2,2'-bipyridine).⁴² For comparison, typical singlet-triplet MLCT splittings for platinum(II)-diimine complexes are 2000-3000 cm⁻¹.⁵⁰

The UV-visible absorption spectra of $Pt(tpy)(pip_2NCN)^+$, $Pt(phtpy)(pip_2NCN)^+$ and $Pt(tpy)(pipNC)^+$ in methylene chloride exhibit a low-energy feature $(Pt(tpy)(pip_2NCN)^+$: 550sh nm (~300 cm⁻¹M⁻¹); $Pt(phtpy)(pip_2NCN)^+$: 563sh nm (~400 cm⁻¹M⁻¹); $Pt(tpy)(pipNC)^+$: 550sh nm (~300 cm⁻¹M⁻¹)) that is not observed in the spectra of $Pt(tpy)(3,5-pip_2NCN)^+$, or $Pt(tpy)(2,6-dmph)^+$, or the protonated complexes. In fact no previously reported platinum(II) terpyridyl complexes exhibit such low energy absorption bands. The possibility that this feature is due to a contaminant has been ruled out. The band is consistently observed in the spectra of samples that have been recrystallized several times. Also, when a methanol solution of $Pt(tpy)(pip_2NCNH_2)^{3+}$ is titrated with base, a shoulder grows in at ~530 nm (Figure 9.25). The solvent dependence of this band is consistent with a transition having significant charge-transfer character.

The low-energy band and the corresponding red color of $Pt(tpy)(pip_2NCN)^+$, $Pt(phtpy)(pip_2NCN)^+$ and $Pt(tpy)(pipNC)^+$ are proposed to be the result of the N(piperidyl) groups interacting with the platinum center. The ~550 nm feature is not

observed in the spectra of platinum(II) terpyridine complexes if the piperidyl groups are not present, as in $Pt(tpy)(2,6-dmph)^+$. Also, this band is not observed if the piperidyl groups are present, but cannot interact with the platinum center, as in $Pt(tpy)(3.5-pip_2NCN)^+$. Protonation the piperidyl groups, as in $Pt(tpy)(pip_2NCNH_2)^{3+}$, Pt(phtpy)(pip₂NCNH₂)³⁺, Pt(tpy)(pipNCH)²⁺, and Pt(phbpy)(pip₂NCNH₂)²⁺, results in yellow solutions that do not exhibit the low-energy band. We tentatively assign the lowenergy band to a $\sigma(Pt-N) \rightarrow \pi^*(tpy)$ ligand-to-ligand charge-transfer transition, resulting from the weak interaction of a piperidyl group with the metal center. In analogy to the d^6 rhenium(I) and platinum(IV) complexes,⁵¹⁻⁵⁵ the sp³ hybridized N(piperidyl) lone-pair orbital is expected to mix with the $6p_z(Pt)$ orbital giving rise to $\sigma(Pt-N)$ and $\sigma(Pt-N)^*$ combinations (Scheme 9.6). Evidently, the σ level lies at higher energy than the four filled d(Pt) levels. A possible alternative assignment derives from the expectation that weak interactions of the N(piperidyl) lone pair with the metal center will destabilize the $d_{z^2}(Pt)$ level. Thus, it is conceivable that the low-energy band is due to a MLCT transition of different orbital parentage than the shorter wavelength MLCT transition (400-500 nm). Regardless of the assignment, an increase in the energy of the d_{72} level is consistent with the electrochemical results. Coordination of the piperidyl groups of $Pt(tpy)(pip_2NCN)^+$ to the metal center, is expected to destabilize the occupied d_z2 level, favoring loss of both electrons from this orbital.

Emission Spectroscopy. The yellow salts of the protonated complexes, [Pt(tpy)(pip₂NCNH₂)](PF₆)₃, [Pt(phtpy)(pip₂NCNH₂)](PF₆)₃ and [Pt(phpy)(pip₂NCNH₂)](PF₆)₂, exhibit intense yellow emissions when irradiated with UV light at room temperature. In contrast, the red salts of the deprotonated complexes do



Scheme 9.6. Qualitative molecular orbital diagram depicting the sp³ hybridized N(piperidyl) orbital interacting with the $6p_z(Pt)$ orbital, giving rise to $\sigma(Pt-N)$ and $\sigma(Pt-N)$ * combinations.

Compound	Temperature	Sample Type	Emission (nm)
[Pt(tpy)(pip ₂ NCN)](BF ₄)	77K	Glassy Solution ^a	472, 507, 540, 583sh
[Pt(tpy)(pip ₂ NCNH ₂)](PF ₆) ₃	RT	Solution ^b	470, 501, 537sh, 583sh
	77 K	Glassy Solution ^a	468, 503, 536, 583,
[Pt(phtpy)(pip ₂ NCNH ₂)](PF ₆) ₃	RT	Solution ^b	497, 528, 575sh
	77 K	Glassy Solution ^a	492, 528, 567,
[Pt(phbpy)(pip ₂ NCNH ₂)](PF ₆) ₂	RT	Solution ^c	538
	RT	Solid	550
	77 K	Glassy Solution ^a	507sh, 529, 566, 615sh, 670sh
	77 K	Solid	523, 556, 603sh

Table 9.6. Emission data for [Pt(tpy)(pip₂NCN)](BF₄), [Pt(tpy)(pip₂NCNH₂)](PF₆)₃, [Pt(phtpy)(pip₂NCNH₂)](PF₆)₃, and [Pt(phbpy)(pip₂NCNH₂)](PF₆)₂.

^a Recorded in 4:1 EtOH:MeOH. ^b Recorded in CH₃CN. ^c Recorded in CH₂Cl₂.



Figure 9.22. 77 K glassy solution 4:1 EtOH:MeOH emission spectra of Pt(tpy)(pip₂NCNH₂)³⁺ (---), Pt(phtpy)(pip₂NCNH₂)³⁺ (----) and Pt(phbpy)(pip₂NCNH₂)³⁺ (----). Emission intensities have been arbitrarily scaled.

not exhibit emission in the visible region; it is conceivable that they emit at longer wavelengths, though this possibility has not been investigated. The absence of emission from fluid solution samples is consistent with McMillin and coworkers' suggestion that the lowest excited states of platinum(II) terpyridyl complexes are quenched by interactions of the metal center with nucleophiles (e.g., solvent).⁵⁶ The deprotonated piperidyl groups are expected to be strong nucleophiles. Emission data are summarized in Table 9.6, and the emission spectra of 77 K 4:1 EtOH: MeOH glassy solutions of $Pt(tpy)(pip_2NCNH_2)^{3+}$, $Pt(phtpy)(pip_2NCNH_2)^{3+}$ and $Pt(phbpy)(pip_2NCNH_2)^{2+}$ are shown in Figure 9.22. These complexes each exhibit highly structured emission profiles, similar to those observed for previously reported platinum(II) terpyridyl complexes.^{26,33,46-48} There is disagreement surrounding the oribital character of the emissive state. The emissions are typically assigned to lowest ${}^{3}\pi$ - π * 26,33,46,48 or ${}^{3}MLCT$ excited states.⁴⁷ The 1200 to 1500 cm⁻¹ vibronic spacings observed for the emissions from Pt(tpy)(pip₂NCNH₂)³⁺ and Pt(phtpy)(pip₂NCNH₂)³⁺ are characteristic of a π - π * terpyridyl ligand-centered lowest excited state. The origin of the emission observed for $(Pt(tpy)(pip_2NCNH_2)^{3+})$ is only shifted by ~2000 cm⁻¹ from the phosphorescence observed for free terpyridine.⁵⁷ Also, the bandshapes and Franck-Condon factors, as indicated by the Huang-Rhys ratios⁵⁸ ($I_{10}/I_{00} \sim 0.85$), are similar to that of the free ligand $(I_{1,0}/I_{0,0} \sim 0.85)$. Based on the preceding and the fact that the origin of these emissions are independent of media ((Pt(tpy)(pip₂NCNH₂)³⁺: 460 nm for 77 K 4:1 EtOH:MeOH glassy solution and room temperature CH₃CN solution (vide infra)), we assign the emissions as originating from a predominantly spin-forbidden $\pi - \pi^*$ terpyridyl ligand-centered lowest excited state.

The 77 K glassy solution emission spectrum of $Pt(phbpy)(pip_2NCNH_2)^{2+}$ (Figure 9.22) is very similar to that of the platinum(II) terpyridyl complexes. The origin of the emission (20400 cm⁻¹) is red shifted ~1300 cm⁻¹ from that of $(Pt(tpy)(pip_2NCNH_2)^{3+})$ (21700 cm⁻¹). The room-temperature and 77 K solid state emission spectra of $[Pt(phbpy)(pip_2NCNH_2)](PF_6)_2$ are shown in Figure 9.23. The room-temperature spectrum is broad and asymmetric with an emission maximum of 550 nm. The 77 K spectrum is structured with maxima at 523 and 556 nm, as well as a shoulder at 603 nm. The vibronic spacings (1100-1400 cm⁻¹) are similar to those observed for 77 K 4:1 EtOH:MeOH glassy solution samples (1200-1400 cm⁻¹; Figure 9.22). These emission profiles are very similar to those of platinum(II) complexes with phbpy; those emissions have been uniformly assigned to lowest ³MLCT excited states.^{35,37,39-43,59,60} Though the energy of the lowest ³MLCT state is expected to be very sensitive to changes in the donor properties of the monodentate ligand, the emission energy for Pt(phbpy)(pip₂NCNH₂)²⁺ is very similar to those reported for other platinum(II) complexes with the phbpy ligand: Pt(phbpy)(PPh₃)⁺ (512, 544 nm; 77 K CH₃CN),⁴¹ Pt(phbpy)(CNC(CH₃)₃) (505, 538, 581sh nm; 77 K CH₃CN)⁴³ and Pt(4-(6-OR)C₆H₄)phbpy)Cl (R=C₁₂H₂₅; 495, ~530, ~570 nm, 77 K butyronitrile).⁴⁰ Therefore, we suggest the earlier ³MLCT assignments for these emissions may be in error, and we propose a lowest phbpy ligand-centered $\pi - \pi^*$ excited state as an alternative.

The room-temperature fluid-solution emission spectra of $(Pt(tpy)(pip_2NCNH_2)^{3+}, Pt(phtpy)(pip_2NCNH_2)^{3+}$ and $Pt(phbpy)(pip_2NCNH_2)^{2+}$ are shown in Figure 9.24. The emission profiles for $(Pt(tpy)(pip_2NCNH_2)^{3+} (\lambda_{max} = 470, 501, 537sh, 583sh nm)$ and $Pt(phtpy)(pip_2NCNH_2)^{3+} (\lambda_{max} = 497, 538, 75sh nm)$ are structured, whereas the profile of

Pt(phbpy)(pip₂NCNH₂)²⁺ ($\lambda_{max} = 538 \text{ nm}$) is broad. The energies of these emissions follow the same order as the 77 K glassy solutions, $\lambda_{max} = (Pt(tpy)(pip_2NCNH_2)^{3+} > Pt(phtpy)(pip_2NCNH_2)^{3+} > Pt(phtpy)(pip_2NCNH_2)^{2+}$.

Titration of $(Pt(tpy)(pip_2NCNH_2)^{3+}$ **with potassium** *tert*-**butoxide**. Roomtemperature UV-visible absorption and emission spectra recorded during the titration of $Pt(tpy)(pip_2NCNH_2)^{3+}$ with potassium *tert*-butoxide in methanol are shown in Figure 9.25. Addition of base causes the intensity of the 385 nm band to decrease, whereas a charge-transfer transition at ~530 nm grows in. This observation is consistent with the N(piperidyl) groups interacting with the platinum(II) center upon deprotonation, as discussed previously. The π - π * emission from Pt(tpy)(pip_2NCNH_2)^{3+} also loses intensity with addition of base. As suggested previously, the deprotonated complex is expected to be only weakly emissive because of quenching by the piperidyl groups.

77 K emission of Pt(tpy)(pip_NCN)⁺. Upon cooling a red 4:1 EtOH:MeOH solution of Pt(tpy)(pip_NCN) ⁺ to77 K, we were surprised to find that the resulting glassy solution is yellow and emissive. The 77 K emission spectrum is shown in Figure 9.26. The emission profile is nearly identical to that observed for Pt(tpy)(pip_NCNH₂)³⁺, and the emission is assigned to a lowest predominantly spin-forbidden ligand-centered π - π * excited state. The observation that the sample changes from red to yellow upon freezing is consistent with little, if any Pt…N(piperidyl) interaction occurring at low temperatures. This result is in keeping with the view that these interactions are weak and likely easily perturbed by changes in solvation. It is conceivable that freezing a different solvent mixture will result in a red colored glass.

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Figure 9.23. Room-temperature (——) and 77 K (-----) solid-state emission spectra of [Pt(phbpy)(pip₂NCNH₂)](PF₆)₂. Emission intensities have been arbitrarily scaled.



Figure 9.24. Room-temperature fluid solution emission spectra of Pt(tpy)(pip₂NCNH₂)³⁺ (---) in acetonitrile, Pt(phtpy)(pip₂NCNH₂)³⁺ (----) in acetonitrile, and Pt(phbpy)(pip₂NCNH₂)²⁺ (-----) in methylene chloride. Emission intensities have been arbitrarily scaled.



Figure 9.25. Room-temperature UV-visible absorption and emission (-----) spectra of a 96 μ M methanol solution of Pt(tpy)(pip₂NCNH₂)³⁺ titrated with 27 μ L aliquots (0.50 equivalents) of potassium *tert*-butoxide (0.18 M, methanol).



Figure 9.26. 77 K glassy solution 4:1 EtOH:MeOH emission spectra of $Pt(tpy)(pip_2NCN)^+$.

Conclusions and Future Directions. In this chapter, we investigated a series of model complexes in an effort to better understand the parameters that govern the cooperative two-electron oxidation observed for $Pt(tpy)(pip_2NCN)^+$. The electrochemistry of these complexes verifies that two piperidyl groups positioned over the axial sites of the platinum(II) center are required for reversible two-electron oxidation. Moreover, the poor electrochemical reversibility of the two-electron process observed for the neutral Pt(phbpy)(pip₂NCN) contrasts sharply with the behavior of $Pt(tpy)(pip_2NCN)^+$. The electrochemical and structural data suggest that the platinumcenter in the phbpy⁻ complex is less electrophilic than in the tpy complex. Therefore, the interactions of the basic piperidyl groups with the acidic metal are expected to be weaker in the phbpy⁻ complex. Consequently, Pt(phbpy)(pip₂NCN) has a lower tendency to form preorganized five- or six-coordinate structures with weak Pt...N(piperidyl) interactions, resulting in less reversible electrochemistry. UV-visible absorption data support the notion that a preorganized five- or six-coordinate structure is present in solution. The spectra of Pt(tpy)(pip₂NCN)⁺, Pt(phtpy)(pip₂NCN)⁺ and Pt(tpy)(pipNC)⁺ exhibit a band at ~550 nm assigned as a σ (Pt-N) $\rightarrow \pi^{*}$ (tpy) ligand-toligand charge-transfer transition, resulting from the weak interaction of a piperidyl group with the metal center.

In the short term, elemental analyses for Pt(3,5-pip₂NCN)(PPh₃)₂(I), [Pt(tpy)(3,5-pip₂NCN)](PF₆) and Pt(phbpy)(pip₂NCN) are needed to complete this project. Also, ¹H NMR and elemental analysis data for [Pt(phbpy)(pip₂NCNH)](BF₄) are necessary. UV-visible absorption data for Pt(phbpy)(pip₂NCN) and [Pt(tpy)(3,5-pip₂NCN)](PF₆) also should be recorded. It is expected that the LLCT band will be much less intense for the

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neutral Pt(phbpy)(pip₂NCN), than observed for Pt(tpy)(pip₂NCN)⁺. The temperature dependences of these absorptions also should be investigated. Variable temperature NMR studies of Pt(tpy)(pip₂NCN)⁺ in CD₃CN are complicated by the tendency of tpy to dissociate. However, the phbpy⁻ complex should be readily amenable to these experiments.

The scan rate dependence of the cyclic voltammogram of Pt(phtpy)(pip₂NCN)⁺ should be carefully investigated, in analogy to the study of Pt(tpy)(pip₂NCN)⁺ described in Chapter 8. A linear dependence of the peak current on square root of the scan rate is expected according to the Randles-Ševčik equation.⁶¹⁻⁶³ An electrochemical study of Pt(phbpy)(pip₂NCN) is more complicated since the apparent two-electron process is not Nernstian. However, it may be possible to use spectroelectrochemical and/or coulometric methods to determine the number of electrons transferred. It also may be possible to electrochemically or chemically (with an aprotic oxidant) oxidize the platinum(II) complex to generate a stable platinum(IV) product, Pt(phbpy)(pip₂NCN)²⁺. The identity of the hydrogen peroxide oxidized product also needs to be ascertained. The product is very soluble, and it seems likely that suitable crystals can be obtained for X-ray crystallography.

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