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

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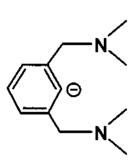
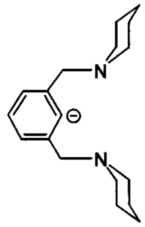
A new series of square planar Pt(II) complexes with the *mer*-coordinating tridentate ligand, pip_2NCN^- (pip_2NCNH = 1,3-bis(piperdylmethyl)benzene), has been prepared: Pt(pip_2NCN)Cl (**2**), Pt(pip_2NCN)Br (**3**), Pt(pip_2NCN)I (**4**), and [Pt(pip_2NCN)($CH_3N{=}C(CH_3)_2$)][CF_3SO_3] (**5**). The complexes have been fully characterized by ^{1}H NMR spectroscopy, elemental analysis, and UV–vis spectroscopy. The X-ray crystal structures of pip_2NCNBr (**1**), **2**, and **5** are reported. Compound **1**: triclinic, $P\bar{1}$, $a = 10.081(1)$ Å, $b = 10.153(2)$ Å, $c = 10.390(1)$ Å, $\alpha = 66.05(1)°$, $\beta = 79.07(1)°$, $\gamma = 64.51(1)°$, $V = 877.1(2)$ Å^3, $Z = 2$. Complex **2**: triclinic, $P\bar{1}$, $a = 9.897(2)$ Å, $b = 10.191(2)$ Å, $c = 19.174(4)$ Å, $\alpha = 75.09(3)°$, $\beta = 76.14(3)°$, $\gamma = 71.00(3)°$, $V = 1741.2(6)$ Å^3, $Z = 4$. Complex **5**: triclinic, $P\bar{1}$, $a = 10.709(2)$ Å, $b = 11.2321(10)$ Å, $c = 12.447(2)$ Å, $\alpha = 110.509(8)°$, $\beta = 112.417(10)°$, $\gamma = 91.066(9)°$, $V = 1276.1(3)$ Å^3, $Z = 2$. In 77 K 3:1 EtOH/MeOH glassy solution, these colorless complexes exhibit weak red-orange to red emissions originating from a lowest spin-forbidden ligand field excited state.

Introduction

There is growing interest in the spectroscopy and photochemistry of square planar platinum(II) complexes with *mer*-coordinating tridentate ligands.[1−3] 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).[2,3] In rigid media, these compounds often exhibit long-lived emission originating from metal-to-ligand charge transfer (MLCT) or terpyridyl ligand-localized $\pi-\pi^*$ 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 their photochemical properties. The present investigation was inspired by the studies of van Koten and co-workers[4−8] detailing the rich thermal chemistry of complexes with cyclometallating aryldiamine ligands, such as the 2,6-bis(dimethylaminomethyl)phenyl anion (Me_4NCN^-).



Me_4NCN^-



pip_2NCN^-

In the following, we report the synthesis and characterization of a new series of Pt(II) complexes based on the

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pip_2NCN^- ligand[9] and having 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 Section

K_2PtCl_4 was obtained from Pressure Chemical. 2,2′-Azobisisobutyronitrile (AIBN), 2-bromo-*m*-xylene, 1,5-cyclooctadiene, and methyl sulfide were obtained from Aldrich. All other reagents were obtained from Acros. Tetrahydrofuran (THF) was distilled from Na(s) and benzophenone, and ethanol was distilled from zinc metal and potassium hydroxide. All other chemicals were used as received. $PtCl_2(SMe_2)_2$,[10] $Pt(COD)Cl_2$ (COD = 1,5-cyclooctadiene),[11] $Pt(COD)I_2$,[12] and *m*-bis(bromomethyl)bromobenzene[13] were prepared according to literature procedures. Syntheses involving amines were carried out under an argon atmosphere using standard Schlenk techniques. Argon was predried 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, $CDCl_3$ (0.03% tetramethylsilane (TMS) (v/v)), were purchased from Cambridge Isotope Laboratories. Proton resonances were assigned with the aid of decoupling experiments. UV−vis 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 380 nm cutoff 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. Chromatography was carried out using a Biotage flash40i system with prepacked silica cartridges.

pip_2NCNBr (1). The synthesis of this compound was originally reported by Schimmelpfennig and co-workers.[9] 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 h. The white solid was filtered off and discarded. The solvent was removed, leaving a yellow-orange oil. The oil was dissolved in CH_2Cl_2 and layered with hexanes. The volume was reduced by rotary evaporation until solid began to form, and the flask was placed in a freezer. The resulting off-white crystals were collected, washed with hexanes, and dried in vacuo. Yield 5.4 g, 53%. Anal. Calcd for $C_{18}H_{27}N_2Br$: C, 61.57; H, 7.75; N, 7.98. Found: C, 61.36; H, 7.66; N, 8.00. ^1H NMR ($CDCl_3$, δ): 1.46 (4H, d, CH_2), 1.58−1.64 (8H, m, CH_2), 2.47 (8H, d, CH_2), 3.57 (4H, s, benzylic CH_2), 7.24 (2H, d, CH), and 7.39 (1H, t, CH). UV−vis (MeOH) λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 265 (<330), 285 (<40).

$Pt(pip_2NCN)Cl$ (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 $PtCl_2(SMe_2)_2$ (1.0 g, 2.6 mmol) in 50 mL of THF. After 18 h, excess NaCl (>10 equiv) was added, and the dark brown mixture was stirred for an additional 2 h. 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 × 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 $C_{18}H_{27}N_2ClPt$: C, 43.08; H, 5.42; N, 5.58. Found: C, 42.98; H, 5.44; N, 5.43. ^1H NMR ($CDCl_3$, δ): 1.43 (4H, m, CH_2), 1.54−1.79 (8H, m, CH_2), 3.25 (4H, m, CH_2), 3.95 (4H, m, CH_2), 4.25 (4H, s with Pt satellites, J_{H-Pt} = 47 Hz, benzylic CH_2), 6.80 (2H, d, CH), and 6.98 (1H, t, CH).

$Pt(pip_2NCN)Br$ (3). The metathesis was accomplished by stirring 0.200 g (0.399 mmol) of **2** in 25 mL of acetone with excess KBr for 1 h. After removal of the solvent, the white solid was washed with H_2O, hexanes, and ether. Anal. Calcd for $C_{18}H_{27}N_2BrPt$: C, 39.56; H, 4.98; N, 5.13. Found: C, 39.33; H, 4.86; N, 5.14. ^1H NMR ($CDCl_3$, δ): 1.38 (4H, m, CH_2), 1.59−1.79 (8H, m, CH_2), 3.26 (4H, dd, CH_2), 4.06 (4H, dd, CH_2), 4.25 (4H, s with Pt satellites, J_{H-Pt} = 47 Hz, benzylic CH_2), 6.80 (2H, d, CH), and 6.99 (1H, t, CH).

$Pt(pip_2NCN)I$ (4). **Method A.** The metathesis was accomplished by stirring 0.100 g (0.200 mmol) of **2** in 25 mL of acetone with excess NaI(aq) for 3 h. After removal of solvent, the residue was treated with CH_2Cl_2 (50 mL) and water (50 mL). The organic layer was dried over $MgSO_4$ 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 μL (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 $Pt(COD)I_2$ (0.50 g, 0.90 mmol) in 50 mL of THF at −70 °C. The solvent was removed by rotary evaporation leaving a dark yellow residue. After the residue was dissolved in CH_2Cl_2, 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 ($CDCl_3$, δ): 1.32 (4H, m, CH_2), 1.46−1.85 (8H, m, CH_2), 3.25 (4H, m, CH_2), 4.25 (8H, m, aliphatic CH_2, benzylic CH_2), 6.81 (2H, d, CH), and 7.02 (1H, t, CH).

$[Pt(pip_2NCN)(CH_3N{=}C(CH_3)_2)][CF_3SO_3]$ (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 min at room temperature. The resulting AgCl precipitate was removed by filtration through Celite. After addition of excess methylamine (approximately 0.3 mL of 40% aqueous solution), the filtrate was stirred for 1 h. The solvent was removed, and the off-white solid was dissolved in CH_2Cl_2 and filtered. The filtrate was rotary evaporated to dryness, and product was collected. Yield 0.106 g, 79%. Anal. Calcd for $[C_{22}H_{36}N_3Pt][CF_3SO_3]\cdot H_2O$: C, 39.20; H, 5.44; N, 5.96. Found: C, 39.24; H, 5.16; N, 6.10. ^1H NMR ($CDCl_3$, δ): 1.44−1.79 (10H, m, CH_2), 2.33 (3H, s, CH_3), 2.85 (3H, s, CH_3), 3.10−3.34 (8H, m, CH_2), 3.64 (3H, s, CH_3), 4.35 (4H, s with Pt satellites, J_{H-Pt} = 55 Hz, benzylic CH_2), 6.89 (2H, d, CH), and 7.03 (1H, t, CH).

X-ray Crystallography. Colorless plates of pip_2NCNBr were obtained by slow evaporation of a CH_2Cl_2/hexanes solution.

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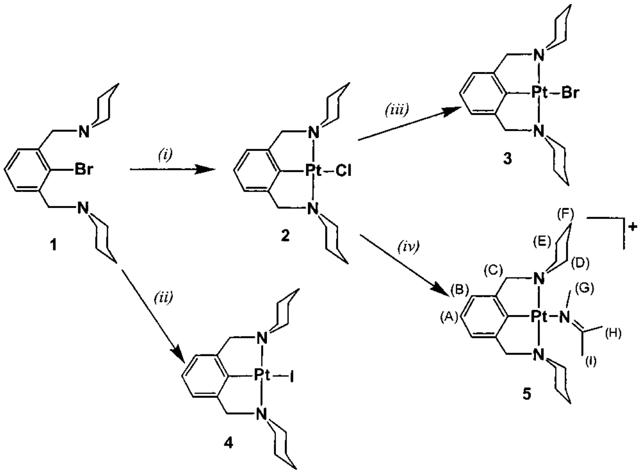
Table 1. Crystallographic Data for Compounds **1**, **2**, and **5**

formula	$C_{18}H_{27}BrN_2$ (**1**)	$C_{18}H_{27}ClN_2Pt$ (**2**)	$[C_{22}H_{36}N_3Pt)]$-$[CF_3SO_3]$ (**5**)
fw, g/mol	351.33	501.96	686.70
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	10.081(1)	9.897(2)	10.709(2)
b, Å	10.153(2)	10.191(2)	11.2321(10)
c, Å	10.390(1)	19.174(4)	12.447(2)
α, °	66.05(1)	75.09(3)	110.509(8)
β, °	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)
Z	2	4	2
T, 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
R1/wR2 [$I > 2\sigma(I)$]^a	0.0400/0.0797	0.0275/0.0566	0.0314/0.0723
R1/wR2 (all data)^a	0.0792/0.0935	0.0451/0.0630	0.0387/0.0761

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Colorless plates of Pt(pip$_2$NCN)Cl were similarly obtained. Diffraction data for crystals of pip$_2$NCNBr (**1**) and Pt(pip$_2$NCN)Cl (**2**) were collected at room temperature using a Siemens P3/PC diffractometer (Mo Kα radiation and graphite monochromator, $\lambda = 0.71073$ Å). Intensities were corrected for Lorentz, polarization, and absorption effects (empirical ψ-scans). A decay correction was applied to the data on the basis of three standard reflections monitored every 300 reflections. Colorless irregular chunks of [Pt(pip$_2$NCN)($CH_3N{=}C(CH_3)_2$)][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 Kα radiation and graphite monochromator, $\lambda = 0.71073$ Å). Data frames were processed using the Siemens SAINT program.[14] Intensities were corrected for Lorentz, polarization, and decay effects. Absorption and beam corrections based on the multiscan technique were applied using SADABS.[15] The structures were solved using SHELXTL v5.03[16] 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 on the basis of 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 CH_3 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 piperdyl 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 piperdyl ring. Crystallographic data are summarized in Table 1.

Scheme 1 [a]



[a] (i) THF, BuLi, −70 °C; Pt(SMe$_2$)$_2$Cl$_2$, 20 °C. (ii) THF, BuLi, −70 °C; Pt(COD)I$_2$, 20 °C. (iii) Excess NaBr, acetone, 20 °C. (iv) AgCF$_3$SO$_3$, acetone; NH$_2$CH$_3$(aq), 20 °C.

Results and Discussion

Synthesis. Procedures for synthesizing the pip$_2$NCNBr ligand precursor and the complexes were adapted from those developed by van Koten and co-workers[17] for related compounds. The syntheses of complexes **2**−**5** are shown in Scheme 1. The colorless complexes were characterized by ^{1}H 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, pip$_2$NCNH.

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 replacing the chloride ligand in **2** is to react a solution of the complex with a silver salt (e.g., AgCF$_3$SO$_3$). After removal of the silver chloride by filtration, the appropriate ligand is added to the filtrate.[18] 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 Bois[19] 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,[20] to our knowledge, this is the first example of a platinum complex with an *N*-isopropylidenemethylamine ligand.

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(14) *SMART v5.051* and *SAINT v5.A06* programs were used for data collection and data processing, respectively. Siemens Analytical X-ray Instruments, Inc., Madison WI.

(15) *SADABS* was used for the application of semiempirical absorption and beam corrections. G. M. Sheldrick, University of Goettingen, Germany, 1996.

(16) *SHELTX v5.03* was used for the structure solution and generation of figures and tables. G. M. Sheldrick, University of Goettingen, Germany, and Siemens Analytical X-ray Instruments, Inc., Madison, WI.

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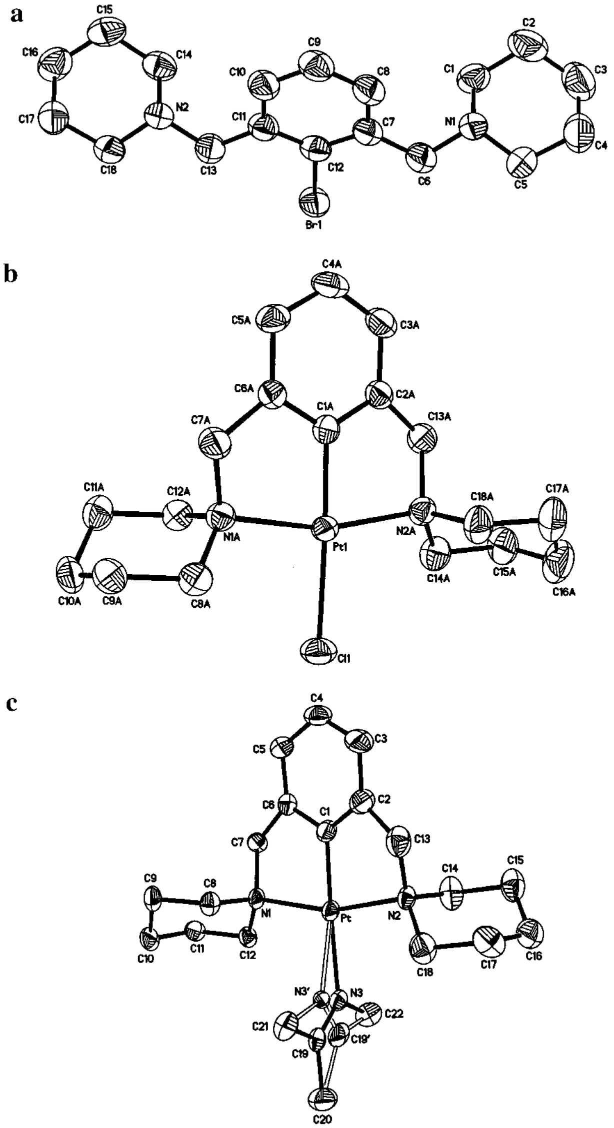

Figure 1. ORTEP diagrams of (a) **1**, (b) **2**, and (c) **5** with 50% probability ellipsoids. Anion and H-atoms omitted for clarity.

Table 2. Selected Distances (Å) and Angles (deg) for Compounds **2** and **5**

	Pt(pip$_2$NCN)Cl (**2**)	[C$_{22}$H$_{36}$N$_3$Pt)][CF$_3$SO$_3$] (**5**)
Pt−C(1)	1.910(4), 1.899(5)	1.919(5)
Pt−N(1)	2.115(4), 2.099(3)	2.108(3)
Pt−N(2)	2.101(4), 2.094(3)	2.104(3)
Pt−L^a	2.432(1), 2.420(2)	2.191(9), 2.150(14)
N(1)−C(7)	1.523(5), 1.511(6)	1.526(5)
N(2)−C(13)	1.523(5), 1.528(5)	1.509(6)
C(6)−C(7)	1.512(6), 1.505(6)	1.506(6)
C(2)−C(13)	1.484(6), 1.512(6)	1.527(8)
C(1)−Pt−N(2)	82.3(2), 82.5(2)	82.0 (2)
C(1)−Pt−N(1)	82.0(2), 82.4(2)	81.4 (2)
C(1)−Pt−L^a	177.50(13), 178.76(14)	175.4(5), 164.5(10)
N(2)−Pt−N(1)	164.29(13), 164.75(14)	163.21(14)
C(7)−N(1)−Pt	108.1(3), 107.1(2)	107.5(2)
C(13)−N(2)−Pt	106.5(3), 107.5(2)	105.7(3)
C(6)−C(7)−N(1)	109.4(4), 110.4(4)	109.2(3)
C(2)−C(13)−N(2)	110.2(4), 110.4(3)	108.6(4)
N(2)−Pt−L, N(1)−Pt−L^a	99.13(10), 96.53(10), 97.82(11), 97.36(11)	98.3(2), 98.6(3) 98.4(2), 96.8(3)

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

Crystal Structures. The structures of compounds **1**, **2**, and **5** were confirmed by single-crystal X-ray diffraction. ORTEP diagrams are shown in Figure 1, and relevant data are summarized in Tables 1 and 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.

In the crystal structure of the ligand precursor (**1**), the piperdyl rings adopt a chair conformation and are rotated away from the bulky Br substituent on the aromatic ring (Figure 1a). In the structures of complexes **2** (Figure 1b) and **5** (Figure 1c), each piperdyl 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 piperdyl ring. Thus, the piperdyl 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 piperdyl rings, the approximately square planar coordination geometries of the resulting complexes are very similar to those of related complexes with NCN$^-$ ligand systems.[6,21−27]

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 Me$_4$NCN$^-$ tridentate ligand: [Pt(Me$_4$NCN)(H$_2$O)](CF$_3$SO$_3$) (1.903(2) Å),[27] Pt(Me$_4$NCN)Br (1.90(1) Å),[22] and Pt(Me$_4$NCN)I (1.933(6) Å).[21] The Pt−Cl distances of 2.432(1) and 2.420(2) Å for **2** fall within the 2.43−2.41 Å range observed for related chloride substituted complexes.[24−26] Similarly, the Pt−N(piperdyl) 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.[21−24,26] For both complexes, the N(piperdyl)−Pt−N(piperdyl) 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.[26,27] For both **2** and **5**, these five-membered 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/C13 = 0.54/0.73 Å) the platinum coordination plane (defined by the four atoms directly bonded to Pt). To

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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°−13.7° angles observed for structures of other platinum complexes with related NCN$^-$ ligands,[6,22−29] except Pt(Me$_4$NCN)I which exhibits a dihedral angle of 9.5°.[21]

In crystals of **5**, the planar imine ligand lies nearly perpendicular to the platinum coordination plane, forming an 87.5(2)° dihedral angle (89.3(3)° for minor conformer). This orientation is consistent with steric as well as electronic considerations because 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, $[H(CH_3)N{=}C(CH_3)_2]$(BPh$_4$) (1.261(7) Å), $[(CH_3)_2N{=}C(CH_3)_2]$(BPh$_4$) (1.291(8) Å),[30] and $[(CH_3)_2N{=}C(CH_3)_2]$(ClO$_4$) (1.30(2) Å).[31] 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(Me$_4$NCN)(Hdptf)](CF$_3$SO$_3$) (2.16(1) Å) with an imine ligand (Hdptf = *N,N*′-di-*p*-tolylformamidine), though somewhat longer than observed for the deprotonated complex, Pt(Me$_4$NCN)(dptf) (2.132(6) Å).[23] 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)°).

^{1}H NMR Spectroscopy. A general labeling scheme for nonequivalent protons (A−I) is shown in Scheme 1 for complex **5**. The ^{1}H NMR spectra of complexes **2**−**5** exhibit a characteristic doublet and triplet between 6.8 and 7.1 ppm due to the protons on the phenyl ring (A, B). For complexes **2**, **3**, and **5**, the resonances near 4.3 ppm arising from the benzylic protons (C) exhibit distinct Pt satellites with J_{Pt-H} values of 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 piperdyl aliphatic proton resonances. These coupling constants are characteristic of values observed for related platinum(II) complexes.[4,22−24,26,28,32] 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 piperdyl rings. Similarly, the remaining aliphatic protons (E, F) are diastereotopic, accounting for the complexity of the splitting patterns further upfield.

Table 3. UV−Vis Absorption (MeOH) and 77 K Emission (3:1 EtOH/MeOH) Spectroscopic Data for **2**−**5**

cmpd	absorption λ_{max}, nm (ϵ, cm^{-1}M^{-1})	emission λ_{max}, nm	emission 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

[a] fwhm = full width at half-maximum of emission intensity.

A series of 2D NMR experiments was undertaken to assign the ^{1}H NMR spectrum of complex **5**. Resonances for the eight protons labeled D′ and D″ occur between 3.1 and 3.34 ppm. The 2D COSY 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 G and slightly weaker coupling to H. G and H are very weakly coupled. The ^{1}H NMR spectrum of *N*-isopropylidenemethylamine also shows three resonances (CDCl$_3$: CMe$_2$, 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 four-bond coupling between the *C*-methyl protons (<0.4 Hz).[33] 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 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 1.

Electronic Structures. UV−vis absorption and 77 K emission data for complexes **2**−**5** are summarized in Table 3 and Figure 2. 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 (7000−11000 cm^{-1}M^{-1}). The relatively large separation between these bands 1300−2100 cm^{-1} is consistent with two distinct spin-allowed charge-transfer transitions. The ligand precursor **1** (ϵ < 350 cm^{-1} M^{-1}) and *N*-isopropylidenemethylamine (ϵ < 100 cm^{-1} M^{-1})[34,35] 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,[36,37] whereas d → p transitions in platinum(II) complexes typically occur at shorter wave-

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(29) Pt(Me$_2$NCN)(PHPh$_2$)](CF$_3$SO$_3$) crystallizes with two molecules in the asymmetric unit (ref 28). Molecule 1 has a dihedral angle of 13.7°. The five-membered PtCCCN chelate rings are disordered in molecule 2, resulting in an unusually small dihedral angle of 5.9°.

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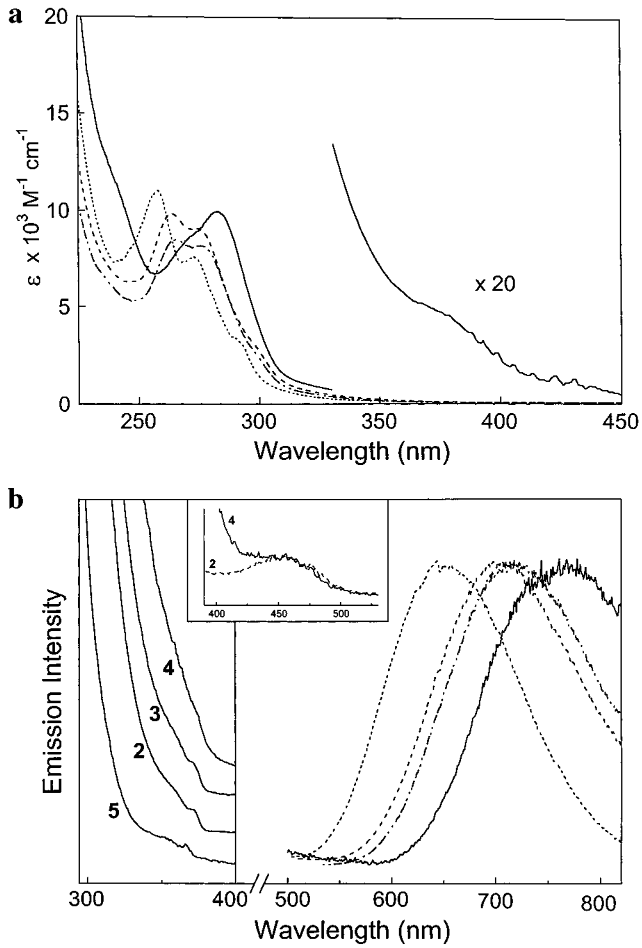
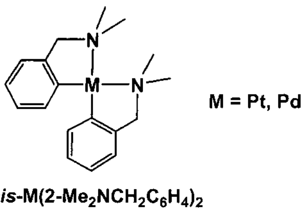


Figure 2. (a) Room-temperature UV−vis absorption spectra in methanol solution for compounds **2** (- - -), **3** (·· - -), **4** (—), and **5** (······). (b) 77 K corrected emission (λ_{ex} = 300 nm) and excitation spectra in 3:1 ethanol/methanol glassy solution for **2**−**5**. Inset shows 77 K excitation spectra of solid samples of **2** and **5**. Spectra have been arbitrarily scaled, and excitation spectra are offset for the purposes of comparison.

lengths.[36−40] Similar intense charge-transfer bands (260−305 nm) also are found in the absorption spectrum of the closely related complex, *cis*-$Pt(2\text{-}Me_2NCH_2C_6H_4)_2$.[41,42] van Koten and co-workers[41] 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.[42] For complexes **2**−**5**, the two bands shift to lower energy along the series **5** > **2** > **3** > **4**, as expected for predominantly Pt → phenyl(pip_2NCN) 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 $Pt(bpy)X_2$ (~1500 cm^{-1}, bpy = 2,2′-bipyridine)[43] and *trans*-$Pt(PPh_3)_2X_2$ (~3000 cm^{-1}).[37]



cis-$M(2\text{-}Me_2NCH_2C_6H_4)_2$

In the absorption spectra of **5**, **2**, and **3**, a weak shoulder (~3000 $M^{-1}cm^{-1}$) 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}).[44,45] 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 $M^{-1}cm^{-1}$) in the spectrum of the iodide complex. As expected from relative ligand field strengths, $Pt(Me_4NCN)Br$ exhibits a similar broad band at slightly shorter wavelength ($CHCl_3$: 365 nm, ~280 M^{-1} cm^{-1}).[41]

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 2b). The emission profiles are characteristically broad and Gaussian in shape, with values for the emission band full-width at half-maximum (fwhm) between 3600 and 4000 cm^{-1}. The bands exhibit a large Stokes shift from the intense UV absorption features, and the onsets 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 > Cl^- > Br^- > I^-. 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.[46] The emission maxima (640−765 nm) and fwhm values are similar to the broad ligand field emissions reported for other platinum(II) complexes: *cis*-$Pt(NH_3)_2Cl_2$ (78 K, 590),[39] *trans*-$Pt(NH_3)_2Cl_2$ (78 K, 610 nm),[39] $Pt(bpy)Cl_2$ (250 K, 641 nm),[44] $Pt(bpy)I_2$ (300 K, 694 nm),[44] K_2PtCl_4 (5 K, 777 nm),[47] and K_2PtBr_4 (5 K, 804 nm).[47] The observed variation in emission energies for **2**−**5** also is consistent with relative ligand field strengths. For example,

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(42) Charge-transfer band maxima of *cis*-$Pt(2\text{-}Me_2NCH_2C_6H_4)_2$ in chloroform: 260 (19000), 272sh (15000), 290sh (11000), 305 nm (14500 M^{-1} cm^{-1}). Band maximum of cis-$Pd(2\text{-}Me_2NCH_2C_6H_4)_2$ in chloroform: 262 nm (24500 M^{-1} cm^{-1}). All features at longer wavelengths have ϵ < 1000 M^{-1} cm^{-1} (ref 41).

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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*-$Pt(NH_3)_2Cl_2$ and K_2PtCl_4 (3600 cm^{-1}). Similarly, the emission energy difference between the chloride (**2**) and bromide (**3**) complexes (~260 cm^{-1}) is less than that of K_2PtCl_4 and K_2PtBr_4 (430 cm^{-1}).[47] 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 2b). For solid samples of **2** and **4**, a spin-forbidden ligand field transition occurs near 460 nm in the 77 K excitation spectra, falling between the lowest energy absorptions reported for *trans*-$Pt(NH_3)_2Cl_2$ (407 nm)[39] and $[NBu_4]PtCl_4$ (560 nm).[36,46]

It is noteworthy that the emissions from the imine (**5**) and chloride (**2**) complexes occur at longer wavelengths than those of *cis*- and *trans*-$Pt(NH_3)_2Cl_2$. This result seemingly contradicts the notion that phenyl anion is a significantly stronger field ligand than imine and chloride.[48] However, it is evident that the orientation of the phenyl group in **2**−**5** is not optimized for π-back-bonding with the d_{xy} level, and therefore, favors low-energy $d_{xy} \rightarrow d\sigma^*$ excited states. This interpretation accounts for the preference of π-acceptor ligands to adopt a geometry favoring interaction with the high-lying d_{xy} level in Pt(II) complexes with NCN^- ligands,[7,23] such as **5**.[18] 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 $Pt(PEt_3)_2PhCl$ (<260 nm),[37,49,50] in which the phenyl rings are likely to be significantly tilted with respect to the coordination plane.[51] 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-phenylpyridine)[52] and $Pt(bph)(CH_3CN)_2$ (bph = biphenyl dianion),[53] respectively. The emissions from those complexes are believed to originate from triplet MLCT or ligand-centered excited states.[52,53] These considerations suggest the feasibility of tuning the orbital character of the lowest emissive states of $Pt(pip_2NCN)L$ complexes by varying the donor properties of the monodentate ligand (L).

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Supporting Information Available: Tables of crystallographic data, structure refinement details, atomic coordinates, interatomic distances and angles, anisotropic displacement parameters, and calculated hydrogen parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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