ORGANOMETALLICS

Syntheses, Structures, and Electronic and Optical Properties of Platinum(II) Complexes of 1,3-Bis(imino)benzene-Derived Pincer Ligands

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Supporting Information



ABSTRACT: Six new Pt^{II} complexes of 5-substituted 1,3-bis(*N*-methylimino)benzene (bIBH)-derived ligands have been synthesized by direct reactions with $K_2Pt^{II}Cl_4$ in glacial acetic acid. The ethenylene groups in the two styryl-substituted complexes undergo E-Z photoisomerization, as revealed by ¹H NMR spectroscopy. The UV–vis spectra of the styryl-/aryl-substituted complexes show intense high-energy bands due to ligand-based $\pi \to \pi^*$ transitions and a number of weaker bands at lower energies in the 300–500 nm region. Time-dependent density functional theory (TD-DFT) calculations indicate that the latter absorptions have mixed intraligand $\pi \to \pi^*$ and Pt(d) $\to \pi^*$ metal-to-ligand charge-transfer (MLCT) character. Four of the new complexes give vibronically structured emission profiles in fluid solution at room temperature. The luminescence quantum yields and lifetimes in nondegassed dichloromethane are in the ranges 0.1–0.2% and 159–170 ns, respectively. In contrast, the styryl-substituted complexes are nonemissive, due to excited-state quenching by $E \to Z$ isomerization. DFT indicates that the emissive triplet state has mixed ligand-to-ligand charge-transfer and MLCT character, with a geometry distorted with respect to the symmetric ground state. Single-crystal X-ray structures have been determined for two of the complexes, showing N–Pt–N angles of ca. 159°. The complex of an unsubstituted bIB⁻ ligand is deep red and forms columns with short Pt…Pt distances of ca. 3.55 Å, indicating weak intermetallic interactions.

■ INTRODUCTION

Among complexes of the heavy d-block metals, square-planar platinum species have been investigated extensively, often due to their luminescent behavior.¹ Cyclometalated Pt^{II} complexes are especially efficient light emitters, because their strong ligand field destabilizes d–d excited states that otherwise can lead to nonradiative deactivation.² Complexes of symmetrical, NCN tridentate "pincer" cyclometalating ligands such as the monoanions derived from 1,3-bis(amino)benzene (bABH), 1,3-bis(imino)benzene (bIBH), and 1,3-bis(2-pyridyl)benzene (bPyBH) (Figure 1) offer great structural versatility, allowing tuning of electronic and optical properties.

Pt(bAB)X complexes have been studied extensively by van Koten and co-workers, including some 4-styryl derivatives which are luminescent in fluid solutions at room temperature when substituted with a terminal strong electron donor or acceptor.³ Unfunctionalized [Pt(bPipB)X]^{*n*+} (bPipBH = 1,3-bis(piperidylmethyl)benzene; n = 0, 1) complexes and [{Pt(bPipB)}₂(μ -Z)]²⁺ bimetallics, explored by Connick and colleagues, emit only in rigid media, although varying X/Z



Figure 1. General structures of Pt(bAB)X, Pt(bIB)X, and Pt(bPyB)X complexes (R = alkyl/aryl; X = halide, etc.).

allows control of the low-lying excited states.⁴ When X = a halide or pyridine and Z = 1,2-bis(4-pyridyl)ethane, emission emanates from spin-forbidden d-d states. For X = 4-phenylpyridine and Z = 4,4'-bipyridyl or (*E*)-1,2-bis(4-pyridyl)ethylene, the emissive state has ligand-centered (LC) ${}^{3}(\pi \rightarrow \pi^{*})$ character, whereas Z = pyrazine gives intense luminescence from a ${}^{3}MLCT$ state. Pt(bPyB)Cl and its

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derivatives, studied by Williams and co-workers, emit especially efficiently from states of mixed ${}^{3}LC/{}^{3}MLCT$ character in fluid solutions, where the LUMOs are based on the π -accepting pyridyl rings.^{2b,5}

Previous studies with Pt(bIB)X complexes have focused largely on catalytic properties,⁶ while their electronic/optical properties have received little attention. Related species with N-, P-, or S-based, typically saturated neutral electron donors have provided a wealth of functional materials.⁷ A recent report describes the incorporation of $[Pt(bIB)CNR]^+$ (R = ^tBu, 2,6- $Me_2C_6H_3$) pincer units into a thiophene-based polymer and changes in the ligand-to-metal charge-transfer (LMCT) absorption behavior as a function of redox state.⁸ Cycloplatinated complexes of benzophenoneimine, a bidentate relative of bIBH, are known to be luminescent in solution at room temperature.9 Also, Kanbara and co-workers have investigated the luminescence of Pt^{II} complexes of SCS-pincer ligands analogous to bIBH, based on 1,3-bis(thiocarbamoyl)benzene, some of which show room-temperature solution emission.10

The minor structural change of moving from saturated to unsaturated nitrogen donors in replacing bAB⁻ with bIB⁻ lends the pincer ligand some of the π -acceptor character of bPyB⁻. We explore herein the effects of the imine functionalities on the electronic and optical properties of Pt(bIB)Cl complexes in relation to their analogues containing bAB⁻, bPyB⁻, and similar ligands. The long-term aim of this work is to produce new Pt^{II} chromophores showing dichroic luminescence. While purely organic species displaying such behavior are relatively wellknown (often when dissolved in a liquid crystal medium),¹¹ only a few related studies with metal complexes have been reported.¹² Notably, Wang et al. reported very recently a liquid crystalline, dinuclear Pt^{II} complex that shows dichroic emission from aligned films.^{12e} In Pt(bIB) complexes, combining small R groups with extended 4-substituents enhances shape anisotropy, potentially affording dichroic properties. However, because preliminary studies with our new complexes give no evidence for dichroism, further discussion of this particular theme is confined to the Supporting Information.

EXPERIMENTAL SECTION

Materials and Procedures. The compound 4-(4-pentylcyclohexyl)benzeneboronic acid was synthesized by a published method.¹³ All other chemicals were used as supplied by Sigma Aldrich or Alfa Aesar. Products were dried at room temperature overnight in a vacuum desiccator ($CaSO_4$) or by direct attachment to a high-vacuum line for several hours prior to characterization.

General Physical Measurements. ¹H NMR spectra were recorded on Bruker UltraShield 500 or AV 400 spectrometers, and all shifts are quoted with respect to TMS. The fine splitting of phenyl ring AA'BB' patterns is ignored, and the signals are reported as simple "doublets", with "J values" (in Hz) referring to the two most intense peaks. Electrospray mass spectrometry was performed on a Micromass Platform II instrument, and MALDI mass spectra were recorded on a Shimadzu Axima Confidence instrument with dichloromethane as the solvent. In cases where clusters of peaks are observed due to the presence of various isotopes, the most intense peak is always quoted. Elemental and thermogravimetric analyses were performed by the Microanalytical Laboratory, University of Manchester. UV-vis spectra were obtained by using a Shimadzu UV-2401 PC spectrometer, and IR spectra were recorded with pure solids on a Varian Bio-Rad Excalibur series spectrometer. Abbreviations: Cy = cyclohexyl; st = strong; s = singlet; d = doublet; dd = doublet of doublets; t = triplet; q = quartet; m = multiplet.

Synthesis of 5-Bromoisophthalaldehyde (1). Isophthalaldehyde (2.00 g, 14.9 mmol) was dissolved in concentrated sulfuric acid (10 mL) and heated to 60 °C. *N*-Bromosuccinimide (3.18 g, 17.9 mmol) was added portionwise over 15 min, and the solution was heated at 60 °C for 3 h. The solution was poured onto ice, and the white precipitate was filtered off. The solid was washed thoroughly with water and hexane and then dried. Further purification was effected by multiple recrystallizations from hexane/ethyl acetate. Yield: 0.80 g (25%). $\delta_{\rm H}$ (400 MHz, CDCl₃): 10.06 (2H, s, 2CHO), 8.30 (1H, t, *J* = 1.4, C₆H₃), 8.26 (2H, d, *J* = 1.4, C₆H₃). ν (C==O): 1690 st cm⁻¹. Anal. Calcd for C₈H₅BrO₂: C, 45.1; H, 2.4. Found: C, 45.4; H, 2.3. *m*/*z* (-ES): 213 ([M - H]⁻).

Synthesis of 1,3-Bis(N-methylimino)benzene (2H). Isophthalaldehyde (200 mg, 1.49 mmol) and methylamine (33 wt % in ethanol, 421 mg, 4.52 mmol) were combined in ethanol (10 mL) and heated under reflux for 90 min. The solvent was evaporated to leave a pale yellow oil (232 mg). The ¹H NMR spectrum indicated negligible monoaldehyde impurity, and this material was used immediately without purification. $\delta_{\rm H}$ (400 MHz, CDCl₃): 8.29 (2H, q, J = 1.6, CHN), 7.97 (1H, t, J = 1.6, C_6H_4), 7.77 (2H, dd, ³J = 7.7, ⁴J = 1.7, C_6H_4), 7.44 (1H, t, J = 7.6, C_6H_4), 3.52 (6H, d, J = 1.7, 2Me). m/z(+ES): 161 ([M + H]⁺), 183 ([M + Na]⁺).

Synthesis of 1-Bromo-3,5-bis(*N*-methylimino)benzene (3H). This compound was prepared in a manner identical with that for 2H, by using 1 (100 mg, 0.469 mmol) and methylamine (33 wt % in ethanol, 133 mg, 1.43 mmol) to give a pale yellow oil (112 mg). The ¹H NMR spectrum indicated ca. 1% of monoaldehyde impurity, and this material was used immediately without purification. $\delta_{\rm H}$ (400 MHz, CDCl₃): 8.22 (2H, q, *J* = 1.7, CHN), 7.92 (2H, d, *J* = 1.4, C₆H₃), 7.86 (1H, t, *J* = 1.4, C₆H₃), 3.52 (6H, d, *J* = 1.7, 2Me). *m/z* (+ES): 239 ([M + H]⁺), 261 ([M + Na]⁺).

Synthesis of 5-Styrylisophthalaldehyde (4). 1 (500 mg, 2.35 mmol), K₃PO₄ (698 mg, 3.29 mmol), and Pd^{II}(OAc)₂ (5 mg, 0.022 mmol) were combined in an oven-dried Schlenk flask under a flow of argon. Styrene (293 mg, 2.81 mmol) was dissolved in anhydrous DMF (4 mL), and the solution was degassed with argon bubbling. The solution was added to the solids, and the mixture was heated at 140 °C for 24 h and then cooled to room temperature. The reaction mixture was poured into water (25 mL) and extracted with ethyl acetate (3 \times 20 mL), and the combined organic extracts were washed with brine, dried over MgSO4, and evaporated to give a yellow oil. This oil was purified by silica gel column chromatography, with hexane/ethyl acetate (96/4) as eluent, followed by reprecipitation from a dichloromethane solution with hexane to give a pale yellow solid. Yield: 124 mg (22%). $\delta_{\rm H}$ (400 MHz, CDCl₃): 10.14 (2H, s, CHO), 8.26 (2H, d, J = 1.5, C₆H₃), 8.24 (1H, t, J = 1.5, C₆H₃), 7.57-7.54 (2H, Ph), 7.43-7.38 (2H, Ph), 7.35-7.29 (2H, Ph + CH), 7.19 (1H, d, J = 16.4, CH). ν (C=O): 1686 st cm⁻¹. Anal. Calcd for C16H12O2.0.1H2O: C, 80.7; H, 5.2. Found: C, 80.7; H, 5.1. m/z (+MALDI): 236 ($[M]^+$). The retention of 0.1 equiv of H₂O is supported by thermogravimetric analyses.

Synthesis of 5-(4-Methoxystyryl)isophthalaldehyde (5). This compound was prepared and purified in a manner identical with that for 4, by using 1 (500 mg, 2.35 mmol), 4-methoxystyrene (378 mg, 2.82 mmol), K₃PO₄ (698 mg, 3.29 mmol), Pd^{II}(OAc)₂ (5 mg, 0.022 mmol), and anhydrous DMF (4 mL) to give a pale yellow solid. Yield: 106 mg (17%). $\delta_{\rm H}$ (400 MHz, CDCl₃): 10.13 (2H, s, CHO), 8.23 (2H, d, J = 1.4, C₆H₃), 8.21 (1H, t, J = 1.4, C₆H₃), 7.50 (2H, d, J = 8.7, C₆H₄), 7.27 (1H, d, J = 16.3, CH), 7.06 (1H, d, J = 16.3, CH), 6.94 (2H, d, J = 8.8, C₆H₄), 3.85 (3H, s, Me). ν (C=O): 1686 st cm⁻¹. Anal. Calcd for C₁₇H₁₄O₃: C, 76.7; H, 5.3. Found: C, 76.4; H, 5.1. *m/z* (+MALDI): 266 ([M]⁺).

Synthesis of 5-Styryl-1,3-bis(*N*-methylimino)benzene (6H). This compound was prepared in a manner identical with that for 2H, by using 4 (45 mg, 0.189 mmol) and methylamine (33 wt % in ethanol, 54 mg, 0.580 mmol) to give a pale yellow oil (50 mg). The ¹H NMR spectrum indicated ca. 3% of monoaldehyde impurity, and this material was used immediately without purification. $\delta_{\rm H}$ (500 MHz, CDCl₃): 8.33 (2H, q, *J* = 1.6, CHN), 7.96 (2H, d, *J* = 1.5, C₆H₃), 7.83 (1H, t, *J* = 1.4, C₆H₃), 7.52–7.50 (2H, Ph), 7.38–7.35 (2H, Ph),

7.29–7.24 (2H, Ph + CH), 7.14 (1H, d, J = 16.4, CH), 3.56 (6H, d, J = 1.6, 2Me). m/z (ES+): 263 ([M + H]⁺), 285 ([M + Na]⁺).

Synthesis of 5-(4-Methoxystyryl)-1,3-bis(*N*-methylimino)benzene (7H). This compound was prepared in a manner identical with that for 2H, by using 5 (22 mg, 0.083 mmol) and methylamine (33 wt % in ethanol, 23 mg, 0.248 mmol) to give an off-white solid (20 mg). The ¹H NMR spectrum indicated a negligible amount of monoaldehyde impurity, and this material was used immediately without purification. $\delta_{\rm H}$ (400 MHz, CDCl₃): 8.33 (2H, q, *J* = 1.6, 2CHN), 7.93 (2H, d, *J* = 1.6, C₆H₃), 7.80 (1H, t, *J* = 1.6, C₆H₃), 7.45 (2H, d, *J* = 8.8, C₆H₄), 7.21 (1H, d, *J* = 16.4, CH), 7.00 (1H, d, *J* = 16.3, CH), 6.91 (2H, d, *J* = 8.8, C₆H₄), 3.83 (3H, s, OMe), 3.55 (6H, d, *J* = 1.6, 2NMe). *m*/*z* (+ES): 293 ([M + H]⁺), 315 ([M + Na]⁺).

Synthesis of 5-(4-Methoxyphenyl)isophthalaldehyde (8). 1 (400 mg, 1.88 mmol), 4-methoxyphenylboronic acid (314 mg, 2.07 mmol), Pd^{II}(OAc)₂ (42 mg, 0.187 mmol), and Na₂CO₃ (498 mg, 4.70 mmol) were combined in a Schlenk flask under argon. Dimethoxyethane (5 mL), THF (5 mL), and water (5 mL) were combined and degassed with argon bubbling. The solvents were added to the solid reagents, and the mixture was heated under reflux for 24 h. The cooled solution was extracted with dichloromethane $(2 \times 30 \text{ mL})$, and the combined organic extracts were washed with water and dried over MgSO₄. Purification was effected by silica gel column chromatography, with hexane/ethyl acetate (95/5) as eluent, followed by reprecipitation from a dichloromethane solution with hexane to give a white solid. Yield: 165 mg (37%). $\delta_{\rm H}$ (400 MHz, CDCl₃): 10.15 (2H, s, CHO), 8.31 (2H, d, J = 1.5, C₆H₃), 8.28 (1H, t, J = 1.5, C₆H₃), 7.61 (2H, d, J = 8.9, C_6H_4), 7.03 (2H, d, J = 8.9, C_6H_4), 3.87 (3H, s, Me). ν (C=O): 1697 st cm⁻¹. Anal. Calcd for C₁₅H₁₂O₃: C, 75.0; H, 5.0. Found: C, 74.8; H, 4.9. m/z (+MALDI): 240 ([M]⁺).

Synthesis of 5-[4-(4-*n*-Pentylcyclohexyl)phenyl]isophthalaldehyde (9). This compound was prepared in a manner identical with that for 8, by using 1 (353 mg, 1.66 mmol), 4-(4-*n*pentylcyclohexyl)benzeneboronic acid (500 mg, 1.82 mmol), Pd^{II}(OAc)₂ (37 mg, 0.165 mmol), and Na₂CO₃ (439 mg, 4.14 mmol). Purification was effected by silica gel column chromatography, with hexane/ethyl acetate (98/2) as eluent, followed by reprecipitation from a dichloromethane solution with hexane to give a white solid. Yield: 215 mg (36%). $\delta_{\rm H}$ (400 MHz, CDCl₃): 10.17 (2H, s, 2CHO), 8.35 (2H, d, *J* = 1.5, C₆H₃), 8.31 (1H, t, *J* = 1.5, C₆H₃), 7.61 (2H, d, *J* = 8.4, C₆H₄), 7.36 (2H, d, *J* = 8.4, C₆H₄), 2.54 (1H, tt, *J* = 12.0, *J* = 3.2, CH^{Cy}), 1.97–1.86 (4H, m, 2CH₂^{Cy}), 1.56–1.43 (2H, m, CH₂^{Cy}), 1.38–1.20 (9H, C₄H₈ + CH^{Cy}), 1.14–1.02 (2H, m, CH₂^{Cy}), 0.90 (3H, t, *J* = 7.2, Me). ν (C==O): 1690 st cm⁻¹. Anal. Calcd for C₂₅H₃₀O₂: C, 82.8; H, 8.3. Found: C, 82.7; H, 8.4. *m/z* (+MALDI): 362 ([M]⁺).

Synthesis of 5-(4-Methoxyphenyl)-1,3-bis(*N*-methylimino)benzene (10H). This compound was prepared in a manner identical with that for 2H, by using 8 (61 mg, 0.254 mmol) and methylamine (33 wt % in ethanol, 72 mg, 0.762 mmol) to give a white solid (67 mg). The ¹H NMR spectrum indicated a negligible amount of monoaldehyde impurity, and this material was used immediately without purification. $\delta_{\rm H}$ (400 MHz, CDCl₃): 8.36 (2H, q, *J* = 1.6, 2CHN), 8.00 (2H, d, *J* = 1.5, C₆H₃), 7.89 (1H, t, *J* = 1.5, C₆H₃), 7.61 (2H, d, *J* = 8.9, C₆H₄), 6.97 (2H, d, *J* = 8.9, C₆H₄), 3.85 (3H, s, OMe), 3.55 (6H, d, *J* = 1.6, 2Me). *m*/*z* (+ES): 267 ([M + H]⁺), 289 ([M + Na]⁺).

Synthesis of 5-[4-(4-*n***-Pentylcyclohexyl)phenyl]-1,3-bis(***N***-methylimino)benzene (11H). This compound was prepared in a manner similar to that for 2H, by using 9 (140 mg, 0.386 mmol) and methylamine (40 wt % aqueous, 90 mg, 1.16 mmol) in ethanol (20 mL) to give a white solid. Yield: 150 mg (100%). ¹H NMR spectra indicated a negligible amount of monoaldehyde impurity, both initially and after 6 months of storage. \delta_{\rm H} (400 MHz, CDCl₃): 8.36 (2H, q,** *J* **= 1.6, 2CHN), 8.02 (2H, d,** *J* **= 1.5, C₆H₃), 7.93 (1H, t,** *J* **= 1.4, C₆H₃), 7.60 (2H, d,** *J* **= 8.3, C₆H₄), 7.28 (2H, d,** *J* **= 8.1, C₆H₄), 3.55 (6H, d,** *J* **= 1.6, 2Me), 2.51 (1H, tt,** *J* **= 12.1,** *J* **= 3.2, CH^{Cy}), 1.97–1.82 (4H, m, 2CH₂^{Cy}), 1.55–1.42 (2H, m, CH₂^{Cy}), 1.38–1.20 (9H, C₄H₈ + CH^{Cy}), 1.13–1.00 (2H, m, CH₂^{Cy}), 0.90 (3H, t,** *J* **= 7.2, Me). Anal. Calcd for C₂₇H₃₆N₂: C, 83.5; H, 9.3; N, 7.2. Found: C, 83.3; H, 9.7; N, 7.2.** *m/z* **(+ES): 389 ([M + H]⁺), 411 ([M + Na]⁺).**

Synthesis of [2,6-Bis(N-methylimino)phenyl]chloroplatinum (PtCl(2), 12). 2H (100 mg, ca. 0.62 mmol) and K₂Pt^{II}Cl₄ (236 mg, 0.569 mmol) were combined in glacial acetic acid (5 mL). The mixture was degassed by argon bubbling and heated under reflux, under an atmosphere of argon, for 48 h. On cooling, the precipitate was filtered off and washed with dichloromethane. The reaction filtrate and washings were evaporated and combined. The crude material was purified by silica gel column chromatography, with dichloromethane/ ethyl acetate (95/5) as eluent, to give a red solid. Yield: 53 mg (24%). $\delta_{\rm H}$ (400 MHz, CDCl₃): 8.27 (2H, (66%) q, $J_{\rm HH}$ = 1.3, (34%) d, ${}^{3}J_{\rm PtH}$ = 143.3, CHN), 7.40 (2H, (66%) d, $J_{\rm HH}$ = 7.7, (34%) dd, $J_{\rm HH}$ = 7.8, ${}^{4}J_{\rm PtH}$ = 7.8, C₆H₃), 7.10 (1H, (66%) t, $J_{\rm HH}$ = 7.7, (34%) dt, $J_{\rm HH}$ = 7.5, ${}^{5}J_{\rm PtH}$ = 2.8, C₆H₃), 3.89 (6H, (66%) d, $J_{\rm HH}$ = 1.4, (34%) dd, $J_{\rm HH}$ = 1.4, ${}^{3}J_{\rm PtH}$ = 32.6, 2Me). Anal. Calcd for C10H11ClN2Pt: C, 30.8; H, 2.8; N, 7.2. Found: C, 31.0; H, 2.4; N, 7.1. *m*/*z* (+MALDI): 353 ([M – Cl]⁺), 390 $([M]^+)$, 742 $([M_2 - Cl]^+)$. Diffraction-quality crystals were grown by slow evaporation of a dichloromethane solution.

Synthesis of [4-Bromo-2,6-bis(*N*-methylimino)phenyl]chloroplatinum (PtCl(3), 13). This compound was prepared and purified in a manner identical with that for 12, by using 3H (112 mg, ca. 0.47 mmol) and K₂Pt^{II}Cl₄ (177 mg, 0.426 mmol) in glacial acetic acid (6 mL) to give an orange solid. Yield: 60 mg (30%). $\delta_{\rm H}$ (400 MHz, CDCl₃): 8.24 (2H, (66%) q, $J_{\rm HH}$ = 1.5, (34%) d, $^{3}J_{\rm PtH}$ = 143.7, CHN), 7.53 (2H, (66%) s, (34%) d, $^{4}J_{\rm PtH}$ = 7.4, C₆H₂), 3.89 (6H, (66%) d, $J_{\rm HH}$ = 1.4, (34%) dd, $J_{\rm HH}$ = 1.4, $^{3}J_{\rm PtH}$ = 31.5, 2Me). Anal. Calcd for C₁₀H₁₀BrClN₂Pt: C, 25.6; H, 2.2; N, 60. Found: C, 25.9; H, 1.8; N, 5.8. *m*/*z* (+MALDI): 468 ([M]⁺), 901 ([M₂ - CI]⁺).

Synthesis of [4-Styryl-2,6-bis(N-methylimino)phenyl]chloroplatinum (PtCl(6), 14). This compound was prepared and purified in a manner similar to that for 12, by using 6H (50 mg, ca. 0.19 mmol) and K₂Pt^{II}Cl₄ (72 mg, 0.173 mmol) in glacial acetic acid (4 mL). The column was eluted with dichloromethane/ethyl acetate (95/5) and a red/orange solid obtained. Yield: 58 mg (68%). The reaction mixture and column were kept in the dark to obtain the pure E isomer; the Z isomer was generated later by exposure of the NMR solution to ambient light. $\delta_{\rm H}$ (400 MHz, CDCl₃): E isomer, 8.31 (2H, (66%) q, J = 1.4, (34%) d, ${}^{3}J_{\rm PtH} = 143.3$, CHN), 7.58 (2H, (66%) s, (34%) d, ${}^{4}J_{\rm PtH} = 7.5$, C₆H₂), 7.53–7.48 (2H, Ph), 7.39–7.34 (2H, Ph), 7.31–7.27 (1H, Ph), 7.09 (1H, d, J = 16.3, CH), 7.03 (1H, d, J = 16.2, CH), 3.91 (6H, (66%) d, J = 1.4, (34%) d, ${}^{3}J_{PtH} = 31.5$, 2Me); Z isomer, 8.16 (2H, (66%) q, J = 1.3, (34%) d, ${}^{3}J_{PH} = 144.2$, CHN), 7.30 (2H, (66%) s, (34%) d, ${}^{4}J_{PtH} = 7.5$, C₆H₂), 7.25–7.19 (5H, Ph), 6.63 (1H, d, J = 12.1, CH), 6.48 (1H, d, J = 12.1, CH), 3.86 (6H, (66%) d, J = 1.4, (34%) d, ${}^{3}J_{PtH} = 31.4$, 2Me). Anal. Calcd for C₁₈H₁₇ClN₂Pt: C, 44.0; H, 3.5; N, 5.7. Found: C, 44.0; H, 3.4; N, 5.7. m/z (+MALDI): 456 ([M - Cl]⁺). Diffraction-quality crystals were grown by layering of hexane on a dichloromethane solution.

Synthesis of [4-(4-Methoxystyryl)-2,6-Bis(N-methylimino)phenyl]chloroplatinum (PtCl(7), 15). This compound was prepared and purified in a manner similar to that for 12, by using 7H (49 mg, ca. 0.17 mmol) and K₂Pt^{II}Cl₄ (63 mg, 0.152 mmol) in glacial acetic acid (4 mL). The column was eluted with dichloromethane/ethyl acetate (95/5) and an orange solid obtained. Yield: 45 mg (57%). The reaction and column were kept in the dark to obtain the pure E isomer; the Z isomer was generated later by exposure of the NMR solution to ambient light. $\delta_{\rm H}$ (400 MHz, CD₂Cl₂): *E* isomer, 8.32 (2H, (66%) q, J = 1.2, (34%) d, ${}^{3}J_{PtH} = 143.5$, CHN), 7.60 (2H, (66%) s, (34%) d, ${}^{4}J_{PtH} = 7.4$, C₆H₂), 7.45 (2H, d, J = 8.9, C₆H₄), 7.06 (1H, d, J = 16.3, CH), 6.93 (1H d, J = 16.4, CH), 6.89 (2H, d, J = 8.8, C_6H_4), 3.83 (6H, (66%) d, J = 1.4, (34%) d, ${}^3J_{PtH} = 31.7$, 2Me), 3.81 (3H, s, OMe); Z isomer, 8.20 (2H, (66%) q, J = 1.3, (34%) d, ${}^{3}J_{PtH} =$ 143.4, CHN), 7.35 (2H, (66%) s, (34%) d, ${}^{4}J_{PtH} = 7.6$, C₆H₂), 7.16 $(2H, d, J = 8.3, C_6H_4), 6.75 (2H, d, J = 8.8, C_6H_4), 6.56 (1H, d, J =$ 12.1, CH), 6.40 (1H, d, J = 12.0, CH), 3.79 (6H, (66%) d, J = 1.4, (34%) d, ³J_{PtH} = 32.8, 2Me), 3.76 (3H, s, OMe). Anal. Calcd for $C_{19}H_{19}ClN_2OPt:$ C, 43.7; H, 3.7; N, 5.4. Found: C, 43.6; H, 3.6; N, 5.3. m/z (+MALDI): 522 ([M]⁺), 486 ([M - Cl]⁺), 1008 ([M₂ -Cl]+).

Synthesis of [4-(4-Methoxyphenyl)-2,6-bis(N-methylimino)phenyl]chloroplatinum (PtCl(10), 16). This compound was prepared and purified in a manner similar to that for **12**, by using **10H** (67 mg, ca. 0.25 mmol) and K₂Pt^{II}Cl₄ (96 mg, 0.231 mmol). The column was eluted with dichloromethane/ethyl acetate (95/5) and an orange solid obtained. Yield: 51 mg (45%). $\delta_{\rm H}$ (400 MHz, CDCl₃): 8.31 (2H, (66%) q, *J* = 1.4, (34%) d, ³*J*_{PtH} = 143.9, CHN), 7.58 (2H, (66%) s, (34%) d, ⁴*J*_{PtH} = 7.3, C₆H₂), 7.44 (2H, d, *J* = 8.7, C₆H₄), 6.97 (2H, d, *J* = 8.7, C₆H₄), 3.90 (6H, (66%) d, *J* = 1.4, (34%) d, ³*J*_{PtH} = 31.0, 2Me), 3.85 (3H, s, OMe). Anal. Calcd for C₁₇H₁₇ClN₂OPt: C, 41.2; H, 3.5; N, 5.7. Found: C, 41.1; H, 3.2; N, 5.7. *m/z* (+MALDI): 460 ([M - Cl]⁺), 956 ([M₂ - Cl]⁺).

Synthesis of {4-[4-(4-*n*-Pentylcyclohexyl)phenyl]-2,6-bis(*N*-methylimino)phenyl}chloroplatinum (PtCl(11), 17). This compound was prepared and purified in a manner similar to that for 12, by using 11H (30 mg, ca. 0.08 mmol) and K₂Pt^{II}Cl₄ (29 mg, 0.070 mmol) in glacial acetic acid (3 mL). The column was eluted with dichloromethane/ethyl acetate (99/1) and a yellow solid obtained. Yield: 18 mg (42%). $\delta_{\rm H}$ (400 MHz, CDCl₃): 8.32 (2H, (66%) q, *J* = 1.4, (34%) d, ³J_{PtH} = 144.0, CHN), 7.61 (2H, (66%) s, (34%) d, ⁴J_{PtH} = 6.7, C₆H₂), 7.44 (2H, d, *J* = 8.3, C₆H₄), 7.28 (2H, d, *J* = 8.2, C₆H₄), 3.91 (6H, (66%) d, *J* = 1.4, (34%) d, ³J_{PtH} = 31.1, 2Me), 2.51 (1H, tt, *J* = 12.3, *J* = 3.1, CH^{Cy}), 1.96–1.85 (4H, m, 2CH₂^{Cy}), 1.54–1.42 (2H, m, CH₂^{Cy}), 0.90 (3H, t, *J* = 7.2, Me). Anal. Calcd for C₂₇H₃₅ClN₂Pt: C, 52.5; H, 5.7; N, 4.5. Found: C, 52.0; H, 5.7; N, 4.5. *m/z* (+MALDI): 618 ([M]⁺), 1201 ([M₂ - Cl]⁺).

X-ray Crystallography. Crystal structures of the complexes 12 and 14 have been obtained. Data were collected on a Bruker APEX CCD X-ray diffractometer by using Mo K α radiation (λ = 0.710 73 Å) and processed by using the Bruker SAINT¹⁴ and SADABS¹⁵ software packages. The structures were solved by direct methods by using SHELXS-97¹⁶ and refined by full-matrix least squares on all F_0^2 data by using SHELXL-97.17 All other calculations were carried out by using the SHELXTL package.¹⁸ All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in idealized positions by using the riding model, with thermal parameters 1.2 times those of aromatic parent carbon atoms and 1.5 times those of methyl parent carbons. For 14, atoms C9 and C10 are disordered over two sites with occupancies 0.590(15)/0.410(15); restraints were applied to this group, and the absolute configuration was determined by refining the Flack parameter. Crystallographic data and refinement details are presented in Table 1.

Luminescence Measurements. Steady-state emission and excitation spectra were determined by using a PerkinElmer LS50 B fluorimeter operating in fluorescence mode. The spectra were corrected for both the excitation source and the emission spectral response. Luminescence quantum yields $\phi_{ ext{lum}}$ were determined upon 350 nm excitation in nondegassed dichloromethane solutions relative to quinine sulfate (1 M H₂SO₄), which has $\phi_{\text{lum}} = 0.58$ at 293 K.¹⁹ Time-resolved luminescence measurements were recorded by using an Edinburgh instruments mini-Tau system by time-correlated singlephoton counting using an EPL 405 ps pulsed diode laser as the excitation source and a 100 nm bandpass interference filter (450-550 nm) to select the visible emission. Lifetimes τ were obtained by tail-fit on the data obtained, and the quality of fit was judged by minimization of reduced χ^2 and residuals squared. The fits gave χ^2 values of between 1.622 (for 12) and 1.007 (for 17). Fitting to a biexponential decay provided no improvement in all cases, indicating that there is only one emissive species on the nanosecond time scale. The respective estimated experimental errors for the ϕ_{lum} and τ values are $\pm 20\%$ and ±10%.

Theoretical Studies. All DFT and TD-DFT calculations were carried out by using the Gaussian 03 suite of programs.²⁰ Structure optimization of complexes **12**, **14**, and **16** were conducted at the B3LYP²¹ level by using the SDD²² basis set and pseudopotential on Pt and Def2-SVP²³ on all other atoms. TD-DFT calculations at these optimized geometries were conducted with a CPCM²⁴ solvent model (dichloromethane) at the same level, apart from **14**, for which MPW1PW91²⁵ was used instead. The first 60 excited states were calculated, covering wavelength ranges of 179–388 nm (**12**), 191–421 nm (**14**), and 193–423 nm (**16**). A TD-DFT calculation of the first 10

Table 1. Crystallographic Data and Refinement Details forComplexes 12 and 14

	12	14
formula	$C_{10}H_{11}ClN_2Pt$	$C_{18}H_{17}ClN_2Pt$
М	389.75	491.88
cryst syst	monoclinic	tetragonal
space group	$P2_{1}/c$	P41212
a/Å	9.6323(9)	10.0609(13)
b/Å	16.5241(16)	10.0609(13)
c/Å	6.7869(7)	31.897(6)
$lpha/{ m deg}$	90	90
$\beta/{ m deg}$	109.008(2)	90
γ/deg	90	90
$U/Å^3$	1021.34	3228.6(8)
Ζ	4	8
T/K	100(2)	100(2)
μ/mm^{-1}	13.958	8.854
cryst size/mm	$0.16\times0.15\times0.03$	$0.30\times0.20\times0.20$
appearance	amber plate	orange prismatic
no. of rflns collected	8727	18 629
no. of indep rflns (R_{int})	2422 (0.0301)	3315 (0.0591)
no. of rflns with $I > 2\sigma(I)$	2182	2982
goodness of fit on F ²	1.034	1.165
final R1, wR2 $(I > 2\sigma(I))$	0.0203, 0.0414	0.0341, 0.0646
final R1, wR2 (all data)	0.0248, 0.0424	0.0410, 0.0661
peak, hole/eÅ ⁻³	0.963, -0.653	1.068, -1.112

triplet excited states of **12** was also performed, at the B3LYP/Def2-SVP/SDD level, without a CPCM. The geometry of the lowest triplet excited state was optimized at the same level. Frequency calculations of the ground state S_0 and the first triplet excited state T_1 at the appropriate geometries were performed to give the zero-point corrections. Quasi-restricted orbitals (QROs)²⁶ were generated for T_1 by using the geometry of the ground state and the ORCA suite of programs.²⁷ The UV–vis absorption spectra were simulated by using the GaussSum program.²⁸

RESULTS AND DISCUSSION

Synthesis. Six new Pt^{II} pincer complexes (12–17) have been synthesized, with various 4-substituents (Scheme 1). The key intermediate 5-bromoisophthalaldehyde (1) was prepared by a new and facile method, adapted from a literature procedure.²⁹ One-step, regioselective bromination of isophthalaldehyde, using *N*-bromosuccinimide (NBS) in sulfuric acid, gave 1 in a moderate yield (25%) after recrystallization. The ¹H NMR spectrum of the crude material revealed a high yield of 1, while the isolated yield reflected difficulties in removing minor impurities. Previous syntheses of 1 include the reduction of either dimethyl 5-bromoisophthalate or 5-bromoisophthalic acid to 3,5-bis(hydroxymethyl)bromobenzene followed by oxidation³⁰ or lithiation of 1,3,5-tribromobenzene and then reaction with DMF.³¹

5-Styrylisophthaladehydes (4 and 5) were accessed via Heck reactions of 1 with styrene or 4-methoxystyrene, using a $Pd^{II}(OAc)_2$ catalyst,³² with isolated yields of ca. 20%. 5-Phenyl derivatives (8, 9) were prepared by Suzuki–Miyaura couplings of 1 with boronic acids, giving isolated yields of ca. 35%. The elongating groups are intended to aid alignment within liquid crystal matrices, especially the cyclohexylphenyl group (in 9), which is a common mesogenic subunit.

The proligands (2H, 3H, 6H, 7H, 10H, and 11H) were formed by reacting the isophthalaldehydes with methylamine in ethanol under reflux. Most of these compounds are unstable

Article

Scheme 1. Syntheses of the NCN Pincer Proligands and Their Pt^{II} Complexes^a



^aReagents and solvents: (a) NH₂Me/ethanol; (b) K₂Pt^{II}Cl₄/acetic acid.

toward hydrolysis to mono- and dialdehydes in the solid state (or as oils), with ¹H NMR spectra showing CHO signals after 2 days of exposure to a moist environment. Rapid filtration of solutions through silica plugs results in extensive hydrolysis. Therefore, these proligands were used immediately without purification, with ¹H NMR spectra of the crude materials indicating only trace impurities. In contrast, a pure sample of 11H was obtained without purification, as confirmed by elemental analyses. This sample showed no evidence of hydrolysis after 6 months of storage under ambient conditions, consistent with the increased hydrophobicity expected for 11H. A previous report notes the susceptibility of (N-arylimino)benzene compounds toward hydrolysis in ethanol;³³ greater hydrolytic susceptibility of (N-methylimino)benzenes is anticipated due to increased basicity, which facilitates the formation of an amine leaving group.

The new Pt pincer complexes 12–17 were synthesized by direct cyclometalation of the proligands by reacting with $K_2Pt^{II}Cl_4$ in acetic acid for 2 days under reflux, as reported for similar compounds by Fossey and Richards.^{6a} These reactions were regioselective, and no other complexes were produced. Reactions attempted using Pt^{II}Cl₂(DMSO)₂ or Pt^{II}Cl₂(EtCN)₂ in solvents such as dichloromethane and methanol were

unsuccessful. Alternative strategies⁷ to direct metalation include oxidative addition from halogenated starting materials,³⁴ transmetalation,³⁵ or the "ligand introduction route" recently conceived by Takenaka et al.^{6d} For relative ease of synthesis of the relevant starting materials, direct metalation is preferred, despite moderate reported yields. **12–17** were isolated in yields of 24–68%, based on K₂Pt^{II}Cl₄. Decreased solubility in acetic acid of the more extended complexes **14–17** aids precipitation, preventing further reactions with the solvent, and giving relatively higher yields.

The new compounds were characterized by ¹H NMR spectroscopy and CHN elemental analyses. Satisfactory CHN analyses of the proligands apart from **11H** were elusive, due to facile hydrolysis (see above). Compound **1** and all of the proligands were characterized also by electrospray mass spectrometry, while the MALDI technique proved superior for the precursors **4**, **5**, **8**, and **9**. MALDI also gives good results for the complexes, with the molecular ion being clearly observed in most cases and $[M_2 - Cl]^+$ being common.

¹**H NMR Spectroscopy.** All of the compounds give spectra consistent with their structures in CDCl_3 or CD_2Cl_2 . Converting the aldehyde precursors into imines causes the methine singlet signal to shift upfield by ca. 1.8 ppm and



Figure 2. $E \rightarrow Z$ isomerization of the ethenylene group in **15** upon exposure to ambient light monitored by ¹H NMR spectroscopy in CD₂Cl₂ over time intervals of ca. 2 h. All except the initial (red) trace are offset steadily to the left to improve clarity; apparent changes in the signal positions are therefore not real.

become a quartet due to coupling to the methyl protons. The aromatic signals of the attached rings also shift upfield slightly by ca. 0.3-0.4 ppm on imine formation. ¹H NMR spectra reveal that the ethenylene groups of aldehyde precursors 4 and 5 and proligands 6H and 7H are present in the *E* configuration only, as indicated by coupling constants of ca. 16 Hz.

Complexation is confirmed in the ¹H NMR spectra by the loss of an aromatic signal and the presence of distinctive ¹⁹⁵Pt satellites straddling the imine methine signals (${}^{3}J_{PtH} = 143-144$ Hz). The resolution of the quartet fine structure within these satellites is poor, and the methine signals show only very slight shifts on complexation (≤ 0.05 ppm). Pt satellites are also observed for the *N*-methyl proton signals (${}^{3}J_{PtH} = 31-33$ Hz) and the remaining aromatic signals (${}^{4}J_{PtH} \approx 7-8$ Hz), with the latter also shifting upfield by ca. 0.3–0.4 ppm on complexation, indicating substantial increases in shielding.

 $E \rightarrow Z$ photoisomerization of the ethenylene moieties in complexes 14 and 15 is detected by ¹H NMR spectroscopy. When the complexes are prepared in the dark, they are isolated as their E isomers almost exclusively. Representative spectra for 15 (Figure 2) show the appearance of new signals at higher field upon exposure to ambient light, especially the ethenylene doublets with $J \approx 12$ Hz. Signal integration reveals that, after 20 h of exposure, ca. 67% of the sample is in the Z form. Analogous behavior is observed for 14. $E \rightarrow Z$ isomerization in Pt^{II} complexes of 4-styryl-2-phenylpyridine (sppy) has been noted previously by Yin et al.³⁶ and for the substituted Pt(bAB)X complexes of van Koten and co-workers.³ It is noteworthy that photoisomerization does not occur in the precursors or proligands, being apparently stimulated by platination. Previous reports of ethenylene photoisomerization facilitated by the presence of heavy metals, particularly rhenium, attribute the effect to intramolecular energy transfer from a ³MLCT to a ³LC state of the (E)-ethenylene moiety.³⁷ Interest in this phenomenon is stimulated by the potential utility of molecular photoswitches.

Electronic Spectroscopy. Both absorption and emission spectra have been recorded for the new Pt^{II} complexes 12–17 in dichloromethane; the resulting data are shown in Table 2, with representative spectra in Figures 3 and 4.

Table 2. Photophysical Data for Complexes 12–17 in Dichloromethane at 293 K

complex	absorption $\lambda_{\rm max}$ nm (ε , 10 ³ M ⁻¹ cm ⁻¹)/ $E_{\rm max}$ eV ^a	emission λ_{max} nm/ E_{max} eV ^b	ϕ_{lum} $(\times 10^3)^c$	r, ns^d
12	400 (4.1)/3.10	562/2.21	1.26	160
	386 (4.4)/3.21	606/2.05		
	339 (4.3)/3.66	$662/1.87^{e}$		
	295 (6.1)/4.20			
	254 (16.3)/4.88			
13	416 (4.1)/2.98	564/2.20	1.41	165
	401 (3.8)/3.09	609/2.04		
	343 (3.4)/3.61	$664/1.87^{e}$		
	330 (3.4)/3.76			
	302 (4.6)/4.11			
14	425 (5.8)/2.92	f		
	316 (38.9)/3.92			
15	427 (5.8)/2.90	f		
	297 (31.0)/4.17			
16	420 (4.4)/2.95	572/2.17	1.36	159
	406 (4.1)/3.05	611/2.03		
	350 (4.2)/3.54			
	338 (4.2)/3.67			
	259 (42.7)/4.79			
17	418 (4.8)/2.97	567/2.19	1.70	170
	405 (4.6)/3.06	609/2.04		
	349 (4.6)/3.55			
	257 (46.7)/4.82			

^{*a*}Solutions ca. 2 × 10⁻⁶–3 × 10⁻⁴ M. The ε values are the averages from measurements made at three or four different concentrations (with ε showing no significant concentration dependence). ^{*b*}Emission maxima on excitation at 400 nm. ^{*c*}Luminescence quantum yields determined relative to quinine sulfate in 1 M H₂SO₄ on 350 nm excitation ($\phi = 0.58$).¹⁹ ^{*d*}Luminescence lifetime determined on 405 nm excitation with a picosecond pulsed diode laser, using a 450–550 nm bandpass interference filter. ^{*e*}Shoulder. ^{*f*}Not observed.

Absorption. The absorption spectra of 12–17 (Figure 3) display two structured bands between 300 and 500 nm with moderate ε values (ca. $3-6 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$), except for the styryl derivatives 14 and 15, for which a more intense band



Figure 3. UV-vis absorption spectra in dichloromethane at 293 K of 12 (red), 13 (orange), 14 (green), 15 (light blue), 16 (dark blue), and 17 (purple), showing (a) entire spectra and (b) expansion of the low-energy region.

obscures the higher energy part. The $E_{\rm max}$ value of the lowest energy absorption decreases steadily as the 4-substituent changes in the order H > Br > aryl > styryl. On the basis of literature precedents, such low-energy bands are attributable to Pt(d) $\rightarrow \pi^*$ MLCT transitions,^{36,38} leading to the observed yellow/orange colors.

14 and 15 show intense absorptions ($\varepsilon \approx (3-4) \times 10^4$ M⁻¹ cm⁻¹) centered at ca. 300 nm, with quite different band shapes probably due to differing proportions of Z and E isomers. The analogous bAB⁻ complexes show similarly intense bands at ca. 350 nm, attributed by DFT to have mixed ligand-based $\pi \to \pi^*$ and MLCT character, with none at lower energies.^{3,39} Styryl-substituted phenylpyridine Pt^{II} complexes have two low-energy bands at ca. 300–350 and 400 nm, thought to have $\pi \to \pi^*$ and MLCT origins, respectively.³⁶ The intensity and position of the 300 nm bands of 14 and 15, and their absence in the other complexes, indicate stilbene-based $\pi \to \pi^*$ character, consistent with the presence of an intense band at 294 nm in stilbene itself.⁴⁰ 16 and 17 give similarly intense bands at ca. 250 nm due to biphenyl-based $\pi \to \pi^*$ transitions.

Previously, Milum et al. presented the only UV–vis analysis of Pt^{II} complexes of bIB^- ligands, although their complexes differ markedly from ours.⁸ The appearance of an intense band at ca. 450 nm on complexation was ascribed to LMCT absorption, but DFT calculations show that the responsible transition is substantially thiophene-based. In the $Pt^{II}(bAB)X$ complexes investigated by Connick et al., halide coligands give colorless solutions with the lowest energy absorption bands at 260–285 nm ascribed to MLCT transitions and long tails to lower energy due to d–d and spin-forbidden charge-transfer

(CT) transitions.^{4a} Pt^{II}(bPyB)Cl complexes show low-energy bands at 350–440 nm attributed to CT transitions, with weak bands at lower energy still due to direct population of triplet intraligand CT (³ILCT) states.^{5a,b} Such spin-forbidden bands have been reported also for other Pt^{II} complexes^{38a,c,d} but are not observed with **12–17**.

Emission. Except for 14 and 15, the new complexes are luminescent in fluid solution at room temperature (Table 2, Figure 4a). The emission bands cover the region ca. 550–750



Figure 4. (a) Emission and (b) excitation spectra in dichloromethane at 293 K of 12 (red), 13 (green), 16 (blue), and 17 (magenta).

nm and show some vibrational fine structure with a spacing of ca. 1100–1300 cm⁻¹, indicating some ligand-based character. The emission energies decrease slightly as the 4-substituent changes in the order H > Br > $C_6H_4CyC_5H_{11} > C_6H_4OMe$. For the unsubstituted complex 12, the intensities of the apparent 0 \rightarrow 0 and 0 \rightarrow 1 peaks are similar ($I_{00}/I_{01} \approx 1$), indicating geometric differences between the ground and emissive excited states. I_{00}/I_{01} increases with the 4-substituent in the order H < Br < aryl, indicating less structural change on excitation for the more substituted complexes. The 0 \rightarrow 2 transitions appear also as shoulders in 12 and 13.

The excitation spectra (Figure 4b) broadly mirror the absorption spectra (Figure 3), with the lowest energy band being red-shifted for more substituted complexes, although the relative intensities of the peaks do not correlate. The measured ϕ_{lum} (0.1–0.2%) and τ values (159–170 ns) are indistinguishable for all of the complexes, the latter being consistent with triplet-state emission. Such relatively small ϕ_{lum} and τ values suggest effective excited-state quenching, which would be expected to decrease significantly in degassed solutions.

The nonemissive solution-state behavior of **14** and **15** is attributed to excited-state quenching by $E \rightarrow Z$ isomerization. Such quenching has been noted for Pt^{II} sppy complexes, although weak solution luminescence was observed.³⁶ Ir^{III} sppy complexes show similar behavior, with the intensity restored on hydrogenation of the ethenylene bond.⁴¹ The same kind of photoisomerization decreases the radiative lifetimes of Re^I complexes.⁴²

The room-temperature luminescence of 12, 13, 16, and 17 is a marked improvement on the Pt^{II}(bAB)Cl complex investigated by Connick et al., the ${}^{3}(d-d)$ luminescence of which is completely quenched in solution.⁴ Notably, styryl-functionalized Pt^{II}(bAB)Cl complexes are appreciably luminescent in degassed solutions at room temperature, but with lifetimes much shorter than those measured here (picosecond time scale).^{3,39} The relevant excited states in these Pt^{II}(bAB)Cl compounds have intramolecular charge-transfer nature at mostly higher energies, and solution luminescence occurs only when a strong electron donor/acceptor substituent is present. The emissive behavior of 12, 13, 16, and 17 indicates that the imine functionality introduces an excited state that is less susceptible to deactivation than in analogous Pt^{II}(bAB)Cl complexes and is different from those in the polar styryl derivatives. In comparison with highly luminescent Pt^{II}(bPyB) Cl complexes, ^{5a,b} 12, 13, 16, and 17 have similar emission profiles, but $\phi_{
m lum}$ and au are lower by several orders of magnitude. If the emissions originate from similar states, their decreased efficiencies could result from a weaker ligand field, influenced by decreased rigidity and a less appropriate geometry for the metal (see below), making deactivating d-d states more accessible. The origins of the emission in the new complexes are explored by using DFT calculations (see below).

Crystallography. Single-crystal X-ray structures have been solved for complexes **12** and **14**. Representations of their molecular structures are given in Figures 5 and 8, crystal packing diagrams in Figures 6, 7 and 9, and selected bond distances and angles in Table 3.

The geometric parameters about the Pt core in **12** and **14** are similar and resemble closely those in other Pt^{II}(bIB) complexes, ^{6a,b,e,8,34,43} revealing only a very slight asymmetry between the two sides of the molecules. The aryl rings and metallocycles



Figure 5. Representation of the molecular structure of 12 (50% probability ellipsoids).

Гable	3.	Selecte	ed Inte	eraton	nic Di	stances	(Å)	and .	Angles
(deg)	fo	r Com	plexes	12 an	d 14				-

	12	14
Pt-C	1.897(3)	1.887(9)
Pt-N	2.035(3)	2.048(7)
	2.039(3)	2.037(7)
Pt-Cl	2.4179(8)	2.393(2)
C=N	1.294(4)	1.285(11)
	1.293(4)	1.291(11)
C-N	1.464(4)	1.453(10)
	1.456(4)	1.437(11)
C=C		1.33(3)
		$1.27(4)^{a}$
N-Pt-C	79.48(13)	79.4(3)
	79.62(13)	79.8(3)
N-Pt-Cl	98.90(8)	100.9(2)
	102.00(8)	99.9(2)
N-Pt-N	159.10(12)	159.2(3)
C-Pt-Cl	178.31(10)	177.5(2)
$C-C-C^{b}$		118.6(16)
		118.3(17)
		$114(2)^{a}$
		$116(3)^{a}$
$C-C-C^{c}$		107.2(13)
		132.1(12)
		105.4(11)
		136.1(12)
		$140.0(14)^{a}$
		$98.9(13)^a$
		$102.4(14)^{a}$
		$139.3(14)^{a}$

^{*a*}Incorporating the disordered C9B and/or C10B atoms. ^{*b*}Encompassing the ethenylene unit. ^{*c*}Incorporating two aromatic ring carbons and one ethenylene carbon.

are essentially coplanar, and the methyl groups are eclipsed with respect to the planar core. The chloride ligand is almost coplanar with the core in 12 (deviation ca. 0.04 Å), while a larger corresponding deviation (0.15 Å) is observed in 14. The geometries at Pt are distorted square planar, with N-Pt-C angles of ca. 79° and N-Pt-N angles of ca. 159° indicative of ring strain in the five-membered chelates, as in other NCNpincer complexes. Pt^{II}(bAB)X⁴⁴ and Pt^{II}(bPyB)X^{5b,45} complexes are less strained, with respective N-Pt-N angles of ca. 164 and 161° due to longer C-N distances. The C-Pt-Cl angle is almost 180° in both 12 and 14. In comparison with 12 and 14, the Pt-C distances are slightly longer in related complexes with N-tBu,6a N-phenyl,6a or N-benzyl6e groups in place of N-Me (1.915(6), 1.908(6), and 1.901(7) Å, respectively), giving smaller N-Pt-N angles (157.2(2), 157.9(2), and 159.29°, respectively). The Pt-Cl distances in 12 and 14 are as expected for NCN-pincer complexes. The Pt– N distances resemble those in other $bIB^{-6b,e,8,34,43}$ and bPyB⁻⁴⁵ complexes, while N-tBu complexes have slightly longer Pt-N distances (2.08-2.10 Å),^{6a} as do Pt^{II}(bAB)X species.44

12 stacks in columns parallel with the *c* axis. Adjacent complexes within each column are rotated mutually, giving a Cl-Pt…Pt-Cl torsion of ca. 82.8° (Figure 6), and avoiding close methyl contacts. The complexes are almost coplanar (dihedral angle ca. 1.3°), with an interplanar spacing of ca. 3.4 Å. Within the columns, Pt ions form a zigzag chain with an

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Figure 6. Structure of 12 viewed approximately along the *c* axis, showing the torsional relationship between adjacent complexes.

intermolecular Pt…Pt distance of 3.5469(4) Å and a Pt…Pt…Pt angle of $146.17(1)^{\circ}$ (Figure 7). Such "linear-chain" packing of



Figure 7. Packing diagram of **12**, showing the planarity of the complex units, the columnar structure, and zigzag close contacts between Pt atoms (dashed lines).

planar Pt^{II} complexes has been widely studied, due to interesting consequent electronic/optical properties.⁴⁶ The van der Waals radius of Pt is ca. 1.7–1.8 Å,⁴⁷ and weak Pt…Pt interactions can occur at distances of up to 3.60 Å.^{46a} Although the Pt…Pt separation in **12** is longer than in most reported linear-chain Pt complexes, interactions have been invoked in complexes with similar distances.⁴⁸ While solid-state UV–vis spectra are required to confirm the presence of Pt…Pt interactions in **12**, its red color is indicative.⁴⁹ For Pt^{II}Cl₂(2,2′bipyridyl)₂, the red polymorph shows close Pt…Pt contacts (3.45 Å),^{49a} while the yellow form has a much larger separation (4.44 Å).⁵⁰ Solutions of **12** appear orange-yellow, and color differences between solid and solution states are not observed for the other complexes. Close Pt…Pt interactions in the latter are inhibited by their 4-substituents; for example, the Pt…Pt distance in **14** is 3.9621(5) Å (see below).

In addition to intermetallic interactions and steric effects, the solid-state structure is also probably influenced by interligand interactions. In a series of linear-chain Pt α -diimines, Connick et al. noted that complexes are rotated successively through 120–180° within the columns.^{49c} Resultant sandwiching of

halide or pseudohalide ligands between adjacent diimines may accommodate weak intermolecular bonding between filled anionic ligand orbitals and diimine π^* orbitals. In 12, the proximity of the chloride ligands and imine groups is reminiscent of the α -diimine systems (Figure 6).

For 14 (Figure 8), the structure shows an (*E*)-ethenylene moiety, despite crystallization from a mixture of isomers in the



Figure 8. Representation of the molecular structure of 14 (50% probability ellipsoids).

presence of light. The disorder observed is common in (E)-stilbene (and (E)-azobenzene) compounds and occurs via a pedal motion.⁵¹ The proportion of the minor orientation in (E)-stilbene increases with temperature, with a maximum of ca. 20% at 373 K.^{51b} The proportion of the minor orientation in 14 is considerably larger (at 100 K), implying a smaller energy barrier between the two conformers. The dihedral angle between the two phenyl rings in 14 is ca. 17.1°. The molecular structure is similar to that of the nitro-substituted complex in the study on related bAB⁻ complexes,³ but the twisting is less severe in 14. The four other structures obtained in that previous study show distinctly bowed shapes.³ In contrast to the case for 12, 14 does not form columnar stacks but packs with a Cl-Pt…Pt-Cl torsion of ca. 108.7° for the closest associated complexes (Figure 9).



Figure 9. Packing diagram of complex 14 viewed approximately along the *b* axis. Hydrogens and disordered atoms are omitted for clarity.

Theoretical Studies. In order to rationalize their electronic/optical properties, TD-DFT calculations have been performed on complexes **12**, **14** (*E* isomer), and **16** by using Gaussian 03.²⁰

Structures. Selected optimized bond distances and angles are given in Table 4. The three structures show very similar, symmetrical coordination geometries. In comparison with the

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Table 4. Selected Interatomic Distances (Å) and Angles (deg) for the Optimized (B3LYP/Def2-SVP/SDD) Structures of 12, 14, and 16

	12	14	16
Pt-C	1.92	1.92	1.92
Pt-N	2.08	2.08	2.08
	2.08	2.08	2.08
Pt-Cl	2.42	2.42	2.42
C=N	1.31	1.31	1.31
	1.31	1.30	1.31
C-N	1.45	1.45	1.45
	1.45	1.45	1.45
C=C		1.35	
N-Pt-C	79.3	79.2	79.2
	79.3	79.2	79.2
N-Pt-Cl	100.7	100.9	100.8
	100.6	100.7	100.8
N-Pt-N	158.6	158.4	158.4
C-Pt-Cl	179.9	179.9	180.0
$C-C-C^{a}$		127.6	
		127.2	
$C-C-C^{b}$		122.6	
		118.1	
		123.6	
		118.8	

^{*a*}Encompassing the ethenylene unit. ^{*b*}Incorporating two aromatic ring carbons and one ethenylene carbon.

crystal structures of **12** and **14** (Table 3), the predicted bond distances are generally slightly longer, but the angles are very similar. Optimization of **14** gives a fully planar structure, unlike in the crystal, while the dihedral angle between the phenyl rings in **16** is ca. 39° .

Electronic Absorption. The computed and experimental UV–vis spectra of **12**, **14**, and **16** are shown in Figure 10, predicted transition energies in Table 5, and selected orbitals in Figures 11–13. The predicted profiles match the measured spectra reasonably well, but the λ_{max} values differ somewhat.

For 12, the two low-energy bands above 300 nm originate from five transitions, with the highest energy of these being the most intense. These transitions correspond to excitations from π orbitals based on the aryl and imine units as well as Pt(d) (HOMO-3 is d_z^2) and Cl(p) to bIB π^* orbitals with some Pt(d) contribution (Figure 11). Both of the involved LUMOs are antibonding across the imine fragment. These results indicate that the corresponding absorptions have mixed MLCT/ligandbased $\pi \rightarrow \pi^*$ character. Introducing the imine π^* orbitals redshifts the lowest energy absorption significantly with respect to the related bAB⁻ complexes.

In 14, the lowest energy band ($\lambda_{max} \sim 415 \text{ nm}$) comprises HOMO \rightarrow LUMO/LUMO+1 transitions. The HOMO is similar to that of 12, but the bIB⁻ π system also includes the styryl portion (Figure 12). The LUMO/LUMO+1 are based around only the PtNCN core and are again π antibonding with respect to the imine fragment. The styryl substituent effects substantial asymmetry in the LUMOs. TD-DFT reveals also multiple transitions in the range 300–400 nm; the most intense transition at $\Delta E = 3.76$ eV is HOMO \rightarrow LUMO+2, largely of stilbenyl $\pi \rightarrow \pi^*$ character, but with contributions from Pt, Cl, and imine orbitals (Figure 12).

In **16**, the two low-energy bands have origins similar to those in **12**, except that some of the HOMOs spread across both aryl



Figure 10. TD-DFT calculated (blue) and experimental (green) UVvis spectra of (a) **12**, (b) **14**, and (c) **16**. The ε axes refer to the experimental data only, and the vertical axes of the calculated data are scaled to match the main experimental absorptions. The oscillator strength axes refer to the individual calculated transitions (red).

rings (Figure 13). However, the LUMO/LUMO+1 are directly equivalent to those of **12**, with no electron density on the pendent ring. The observed red shifting of the lowest energy absorption on 4-substitution is therefore mostly due to destabilization of the HOMO. However, while TD-DFT does yield an increase in the λ_{max} of this band on moving from **12** to **16**, the observed further increase on moving to **14** is not predicted (Figures 3 and 10). The intense band at ca. 260 nm in the recorded spectrum of **16** (Table 2 and Figure 3) is predicted to encompass several transitions; the dominant one at $\Delta E = 4.53$ eV is of biphenyl $\pi \rightarrow \pi^*$ nature largely, but with significant contributions from Pt, Cl, and imine orbitals (Figure 13).

Electronic Emission. TD-DFT indicates that excitation to the lowest energy excited state T_1 of **12** has $\Delta E = 2.44 \text{ eV}/508$ nm (although f_{os} for all $S_0 \rightarrow T_n$ excitations are zero, correlating

Table 5. Data from TD-DFT Calculations Based on B3LYP/ Def2-SVP/SDD Geometries of 12, 14, and 16

complex	ΔE (eV)	f_{os}	major contribn	μ_{12} (D)
12	3.20	0.06	$HOMO \rightarrow LUMO$	2.19
	3.22	0.01	HOMO \rightarrow LUMO+1	0.90
	3.25	0.01	HOMO-3 → LUMO+1	1.09
	3.38	0.01	$HOMO-2 \rightarrow LUMO+1$	0.94
	3.84	0.19	$HOMO-2 \rightarrow LUMO$	3.64
	4.50	0.04	HOMO-4 \rightarrow LUMO+1	1.45
	4.96	0.28	HOMO-6 \rightarrow LUMO+1	3.87
			HOMO-1 \rightarrow LUMO+2	
	5.10	0.12	HOMO-6 \rightarrow LUMO	2.52
	5.68	0.35	HOMO-3 \rightarrow LUMO+3	4.04
			HOMO \rightarrow LUMO+4	
14	2.95	0.07	$HOMO \rightarrow LUMO$	2.57
	3.03	0.11	HOMO \rightarrow LUMO+1	3.14
	3.76	1.28	HOMO \rightarrow LUMO+2	9.47
	3.85	0.14	HOMO-4 \rightarrow LUMO	3.14
			HOMO-4 \rightarrow LUMO+1	
			HOMO $-3 \rightarrow$ LUMO	
	4.13	0.21	HOMO-4 \rightarrow LUMO+1	3.65
			$HOMO-3 \rightarrow LUMO$	
	5.11	0.31	HOMO-8 \rightarrow LUMO	4.02
			HOMO-8 \rightarrow LUMO+1	
			HOMO-6 \rightarrow LUMO	
	5.27	0.18	HOMO-8 \rightarrow LUMO	3.03
			HOMO-8 \rightarrow LUMO+1	
16	2.93	0.05	$HOMO \rightarrow LUMO$	2.20
	3.00	0.04	HOMO \rightarrow LUMO+1	1.80
	3.70	0.08	HOMO-4 \rightarrow LUMO	2.45
			$HOMO-2 \rightarrow LUMO+1$	
	3.90	0.12	$HOMO-4 \rightarrow LUMO$	2.85
			$HOMO-2 \rightarrow LUMO+1$	
	4.53	0.97	HOMO-6 \rightarrow LUMO+1	7.52
			HOMO \rightarrow LUMO+2	
	4.95	0.23	HOMO-8 \rightarrow LUMO+1	3.47
			$HOMO-1 \rightarrow LUMO+4$	
	5.08	0.43	$HOMO-8 \rightarrow LUMO$	4.70

with the observed absence of spin-forbidden absorption bands), with major contributions from the transitions HOMO-2 \rightarrow LUMO and HOMO \rightarrow LUMO+1 (orbitals shown in Figure 11). A geometry optimization of T_1 induces substantial asymmetry in the structure around the coordination site (Figure 14). This result correlates with the observed emission profile with $I_{00} \approx I_{01}$, indicating geometrical changes on excitation, and the discrepancy between the calculated vertical excitation and observed emission energies. The calculated difference in total energies between S₀ and T₁ now becomes 2.26 eV (549 nm), while frequency calculations to factor in zero-point corrections give the difference in energy between the lowest vibrational levels $(0 \rightarrow 0)$ as 2.15 eV (577 nm). The experimentally measured $0 \rightarrow 0$ emission at 2.21 eV (562 nm) lies between these two computed values, since the frequency calculations do not incorporate the effects of anharmonicity.

To describe the nature of T_1 , QROs²⁶ were calculated with triplet electronic configuration at the ground-state geometry: i.e., before the excited state has relaxed to its asymmetric geometry. The singly occupied QROs are shown in Figure 15. SOMO2 resembles very closely the LUMO derived by DFT for the ground-state singlet molecule, while SOMO1 includes occupancy of a d orbital that is different from those in

Figure 11. Contour surface diagrams of MOs involved in the lowenergy transitions of complex **12**, excluding HOMO-3, which is simply the d_{z^2} orbital (isosurface value 0.03 au).

Figure 12. Contour surface diagrams of MOs involved in the major electronic transitions of complex 14 (isosurface value 0.03 au).

HOMO-2 or HOMO (Figure 11). The TD-DFT results indicate that T_1 is formed by depopulation of Pt(d) and Cl(p)and subsequent population of bIB⁻ ligand π^* : i.e., the emissive state has mixed MLCT and ligand-to-ligand charge-transfer (LLCT) character. The emissive states of organometallic Pt^{II} complexes are often intermediate between MLCT and ligandbased.⁵² On comparison of 12 with theoretical studies on $Pt^{II}(bPyB)Cl$, the origins of T_1 are qualitatively quite similar, although the LUMO in the latter case is located mostly on the pyridyls with only a small contribution from the aryl ring.^{5c} For $Pt^{II}(bPyB)Cl$, TD-DFT provides a reasonable description of T_{1} , since only a small geometrical change occurs on excitation due to greater rigidity. The introduction of a low-energy π^* orbital including the imine groups (SOMO2) is the key to the different photophysical behaviors of Pt^{II}(bIB)Cl and Pt^{II}(bAB)Cl complexes.

Six new Pt^{II} NCN-pincer complexes of 1,3-bis(*N*-methylimino)benzene-derived ligands with various 5-substitu-

HOMO-6 -7.35 eV

Figure 13. Contour surface diagrams of MOs involved in the major electronic transitions of complex 16 (isosurface value 0.03 au).

Figure 14. DFT calculated geometry of the lowest energy excited state T_1 of **12**, showing selected bond distances (Å).

ents have been synthesized by direct metalation. ¹H NMR spectroscopy reveals $E \rightarrow Z$ photoisomerization of the ethenylene groups in the styryl-substituted complexes. UV-vis spectra show intense high-energy $\pi \rightarrow \pi^*$ bands in aryl and styryl-substituted complexes, and a number of lower energy transitions in the 300–500 nm region of mixed MLCT/ligand-based $\pi \rightarrow \pi^*$ origins, as indicated by TD-DFT calculations. Most of the complexes display vibronically structured emission profiles in nondegassed fluid solutions at room temperature, but the styryl-substituted complexes are nonemissive due to

Figure 15. Singly occupied QROs of complex 12 corresponding to the first triplet excited state, calculated at the ground state geometry (isosurface value 0.03 au).

complete quenching by $E \rightarrow Z$ isomerization. Luminescence quantum yields and lifetimes are in the ranges 0.1–0.2% and 159–170 ns, respectively. DFT calculations indicate that the emissive state is of mixed ³LLCT/³MLCT origin, and this state has a distorted geometry with respect to the very symmetric ground state. The photophysical properties of Pt^{II}(bIB)Cl and Pt^{II}(bAB)Cl complexes differ largely due to the presence of a low-energy π^* orbital including the imine groups in the former. Single-crystal X-ray structures of two of the complexes also reveal a symmetric PtNCN core, with N–Pt–N angles of ca. 159°. The unsubstituted complex packs in columnar stacks with short Pt…Pt distances of ca. 3.55 Å. Weak Pt…Pt interactions are tentatively invoked on the basis of this short distance and the deep red color associated with solid samples of this complex only.

ASSOCIATED CONTENT

S Supporting Information

CIF files giving crystallographic information for **12** and **14** and text, tables, and figures giving details relating to dichroic properties, Cartesian coordinates of theoretically optimized geometries for complexes **12**, **14**, and **16**, and lifetime data and fits. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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