ABSTRACT: Primary amines and benzothiophene-3-carboxaldehyde were reacted to give four large, bulky imine ligands. These imine ligands were reacted with a tetramethyl platinum dimer and by heteroatom-assisted C–H activation, both monometalated compounds and bismetalated compounds were synthesized. In all cases, five-membered platinacycles were formed. The compounds were characterized by NMR spectroscopy, and one bismetalated compound was characterized by single-crystal X-ray diffraction. The UV–vis absorption and emission spectra and the excited-state lifetimes were recorded for these complexes. Density functional theory (DFT) and time-dependent-DFT calculations were performed to aid in the assignment of the absorption and emission spectra of the newly synthesized complexes.

INTRODUCTION

Cyclometalated complexes, including platinum species are known for their interesting catalytic and photophysical properties.1,2 The properties of these cyclometalated compounds are also studied for their applications in a variety of fields, including sensors and devices.3,4 Generally cyclometalation is achieved by C–H activation of an ortho proton often by chelate assistance.5 Strong field ligands with carbon donors, the rigidity of the conjugated ring system, and the strong spin–orbit coupling of the heavy-metal center are explanations for the favorable photophysical properties of cyclometalated compounds, including long-lived excited triplet states.6–8 Thiophenes are also known for their photophysical properties and are implicated in a variety of applications, including solar cells and photodetectors.9–11 Benzothiophenes are thiophenes with an additional fused aromatic ring. Benzothiophene fragments are known in pharmaceuticals and dyes and thus have been studied.12–18 The additional size and conjugation may enhance the desirable properties of the cyclometalated complexes with benzothiophene-derived ligands. Bismetalated complexes are less studied than their monometalated analogues,19–21 however, perhaps with the additional strong field chelates, C^N ligands may improve the properties of these cyclometalated species.22 Computational studies on metal compounds have advanced a great deal in the last decade.23–25 Computational results for large compounds were computationally expensive, taking a great deal of time and results were often suspect, suggesting that synthesis precede computation.26 Recently, commercially available density functional theory (DFT) packages have become much more inviting and accessible with results allowing for the prediction of properties, such as assignment of electronic spectra bands in platinum compounds.27–30 We have undertaken the synthesis of several biscyclometalated platinum species, measured their photophysical properties, and used DFT computational results to aid in the assignment of the transitions in the electronic spectra.
RESULTS AND DISCUSSION

The four ligands (Figure 1) utilized in this study were synthesized by condensation reactions of the appropriate amine and aldehyde. The four ligands were characterized by $^1$H and $^{13}$C NMR spectroscopy. The monometalated compounds (Figure 1) were synthesized with one equivalent of ligand per platinum center, utilizing compound [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$], PtA, either by stirring the reactants in solution or in a microwave reactor, while bismetalated compounds (Figure 1) were synthesized with two equivalents of ligands per metal center in a solution of refluxing toluene. 18Bis, seemingly the compound with the bulkiest of ligands, could also be synthesized in methylene chloride at room temperature over a period of several days, whereas none of the other bismetalated species could be obtained under the same conditions. All compounds formed five-membered metalated platincycles, with the bis compounds forming two such metalacycles. The platinum metalacycle compounds were mainly characterized by 1D and 2D NMR and HRMS. An X-ray diffraction (XRD) study on a single crystal of 18Bis corroborated its molecular structure (Figure 2) as assigned using the NMR spectral data. Several pieces of data led to the

![Figure 1. Structures for ligands and monometalated and bismetalated compounds.](image)

![Figure 2. ORTEP of compound 18Bis (50% probability thermal ellipsoids). Selected bonds lengths (Å) and angles (°): Pt−N(11): 2.136 (4); Pt−N(12): 2.158 (4); Pt−C(122): 1.982 (6); Pt−C(11): 1.972 (7); C(11)−Pt−C(122): 99.4 (3); C(11)−Pt−N(12): 79.2 (2); C(122)−Pt−N(12): 170.69 (19); C(11)−Pt−N(11): 171.87 (19); C(122)−Pt−N(11): 77.9 (2); N(11)−Pt−N(12): 104.68 (14).](image)
NMR resonance assignments of the bis species. For example, no platinum-methyl resonances were observed once two chelate ligands were metalated. A few good diagnostic peaks are available in these compounds, one being the imine resonance at around 8.2 ppm.

Additional diagnostic resonances due to protons on the chelate ligand are useful, including the \( \alpha \)-methyl and methine resonances. For example, the proton NMR spectrum of the 18Bis compound has the imine, methine, and \( \alpha \)-methyl resonances observed at 8.23 \( \delta (\text{Pt–H}) = 71 \text{ Hz} \), 6.06, and 1.80 ppm, respectively, all reasonable for platinum(II) compounds. The monometalated species also contain the ancillary methyl and dimethylsulfide ligands in the platinum coordination sphere, along with the chelate C=N ligand, allowing for additional diagnostic resonances in the NMR spectra to aid in characterization of these species. For example, the proton NMR spectrum of the 18Mono compound has the imine, methine, \( \alpha \)-methyl, and the platinum-methyl resonances observed at 8.74, 6.10, 1.91, 1.86, and 1.19 ppm, respectively, with \( \delta (\text{Pt–H}) \), \( \delta (\text{H–H}) \), \( \delta (\text{Pt–H}) \), \( \delta (\text{H–H}) \), and \( \delta (\text{Pt–H}) \) coupling constant values of 55, 6.5, 33, 6.5, and 78 Hz, respectively. Once again, these are all reasonable for platinum(II) compounds. The monometalated species have similar spectra to one another, as do the bismetalated species when compared to each other. The monometalated species 16Mono and 18Mono were slightly contaminated with small amounts of the corresponding bismetalated species, which forms to a small extent. It proved difficult to separate the small amount of bis-species from the monoplatinum compounds with our attempts often leading to decomposition of the compounds.

### PHOTOPHYSICAL MEASUREMENTS AND COMPUTATIONAL RESULTS

**Time-Dependent Density Functional Theory and Density Functional Theory Calculations.** The solid-state structure of 18Bis (Figure 2) has a distorted square planar platinum(II) metal center with two C=N chelate ligands. There are two inequivalent molecules in the asymmetric unit; Figure 2 shows one of these. The dihedral angles between the planes defined by the Pt atom and the carbon and nitrogen atoms of each ligand in a molecule are 10.2 and 13.1° for the two molecules. The XRD data was used as input for our DFT study (see below), and the results have good agreement giving a dihedral angle of 11.2° (Figure S1). The platinum-carbon and platinum–nitrogen bond lengths are typical for platinum(II) species.36,37

The photophysical properties of the compound were examined and are summarized in Table 1. The absorbance spectra (Figure 3) showed the lowest energy peak for the compounds to be between 390 and 560 nm. These peaks have extinction coefficients of around \( 10^4 \) to \( 10^5 \), thus, they were tentatively assigned as metal to ligand charge transfer (MLCT) peaks.7 The bathochromic shift of 170–190 nm for the corresponding emission spectra support the assignment. The emission spectra have their maximum peaks between 600 and 700 nm. Shoulders are observed at higher energy and lower energy depending on the compound with no definitive pattern for mono versus bis species. For example, the 16 and 18 mono/bis species pairs had similar emission maxima, while the 15 pair had the bis species emitting at a longer wavelength. Interestingly, the 14Mono had an additional emission peak at higher energy around 455 nm. This has been tentatively assigned to a fluorescence peak as it was determined to have an excited-state lifetime of 2.8 ns (\( \chi^2 = 0.94 \)).\textsuperscript{7,36,39} Computational results (vide infra) corroborate a possible emission from S\(_1\) to S\(_0\) at approximately that energy. 15Mono had a much smaller, similar emission band at around 400 nm. The other compounds did not have emission peaks with discernible features at higher energy. Generally, the bis species absorbed at a lower energy than the corresponding mono species, making the bathochromic shift slightly greater for the monospecies. 15Bis has its spectrum red-shifted somewhat more compared to.

#### Table 1. Photophysical Data for Platinum Compounds

| complex | absorption \( \lambda_{\text{max}}/\text{nm} \) \( (\varepsilon/M\text{-}cm^{-1}) \times 10^3 \) | emission \( \lambda_{\text{max}}/\text{nm} \) | lifetime \( \chi^2 \) ns |
|---------|--------------------------------------|-----------------|--------|
| 14Mono  | 435 (2.4), 382 (5.6) | 642, 598, 455 | 165 (1.03) |
| 15Mono  | 464 (4.6) | 652, 551 | 158 (1.01) |
| 16Mono  | 431 (3.7), 413 (3.9) | 676, 606 | 203 (1.19) |
| 18Mono  | 435 (3.4), 416 (3.8), 380 (5.3) | 668, 596 | 234 (1.13) |
| 14Bis   | 515 (7.9), 431 (6.5), 413 (6.6) | 750, 680 | 281 (0.942) |
| 15Bis   | 560 (3.1), 454 (5.5), 415 (8.5) | 748, 731, 636 | 207 (1.04) |
| 16Bis   | 511 (9.7), 434 (8.0), 413 (8.3) | 752, 679 | 261 (1.02) |
| 18Bis   | 517 (1.2), 434 (8.7), 415 (9.4) | 734, 671 | 458 (1.02) |

Notes: \( \lambda_{\text{excitation}} = 405 \text{ nm} \), \( \lambda_{\text{excitation}} = 450 \text{ nm} \), \( \lambda_{\text{excitation}} = 365 \text{ nm} \).
to the others. Perhaps this can be attributed to its structural features in that it does not have a “spacer” between the naphthyl ring and the nitrogen. The lifetime measurements of the emission peaks listed in Table 1 yielded values of 150–450 ns, which are on the low end for phosphorescence, which is expected for such compounds with MLCT bands; thus, our assignment is not unreasonable, given the data and the preponderance for such behavior for platinum(II) species, given their large spin–orbit coupling. In order to help consolidate these tentative MLCT and phosphorescence assignments, a detailed time-dependent DFT (TD/DFT) study was undertaken for 18Bis, the species for which an XRD structure determination has been obtained (vide supra).

DFT and TD-DFT were run on the 18Bis compound as the results of the calculation could be directly compared to our crystallographic data. The structure of bismetalated 18Bis was optimized and confirmed to represent an energetic minimum by harmonic frequency analysis. The agreement of the diffraction data bond lengths in the Pt(II) coordination sphere to theory was analyzed for a few different types of calculations (gas phase and solution phase, Table 2). The different calculation methodologies had very little impact on the optimized coordination environment for a single molecule, and the bond lengths appear to be systematically slightly longer in solution than those observed in the solid state. The calculation does reproduce the longer Pt–N versus Pt–C bond length, which is observed experimentally (Table 2).

In addition to analyzing the observed cis isomer (Figure 4) of 18Bis, the structure and thermodynamics of the trans isomer were examined (Tables S1 and S2, Figure S2). Using the X-ray crystallographic structure as a rough starting point for representative bond distances, molecular mechanics were then used to generate reasonable input geometries for the trans isomer. Attempts were made to optimize the structure with either trans or cis orientations of the N-α-methyls relative to the plane defined by the Pt(II) coordination sphere. The only structure which converged to a local minimum with no negative frequencies featured the former trans isomer, with the two different N-α-methyls pointed above or below the plane defined by the Pt(II) coordination sphere as is also seen experimentally in the observed cis isomer of 18Bis. The data in solution indicate a greater thermodynamic stability for the cis isomer. Interestingly, the only structure which would converge if the N-α-methyls were both pointed in the same direction was a transition state featuring a single negative frequency which consisted of a rocking motion of one of the naphthalene ring which appeared to be a bond rotation away from the trans orientation of the two N-α-methyls. As expected, the stronger trans influence of the C donor ligand leads to a significantly increased C–Pt bond length in the hypothetical trans isomer and also a shorter N–Pt bond length.

TD-DFT and DFT calculations were run on 18Bis to interrogate the nature of the observed electronic transitions in the UV-vis. DFT calculations on the frontier orbital manifold (HOMO – 5/LUMO + 5) show electron density concentrated largely on the platinum 5dxy/dxz orbitals in addition to the ligand π system in the HOMO manifold, while the LUMO manifold is of a more pronounced ligand π* character. Transitions between these orbitals which make up the observed visible absorption spectrum are generally of a mixed MLCT/ILCT character with electron density moving between the low-lying metal d orbitals and different parts of the ligand π* system (Figure S3, Chart S1, and Table S3). TD-DFT calculations simulate the major experimentally observed absorbance features (Figure 5). The large oscillator strength transitions, which make up the observed absorbance features, are principally described by a single major orbital transition (Figure S4). The (hole/particle) natural transition orbitals (NTOs) of these transitions are shown below which are well described by the principal contributing orbital transitions from comparison to DFT (Figure 6, Figure S5, and Table 3).42

**CONCLUDING REMARKS**

The reactions of [Pt2Me3(μ-SMe)2] with a variety of benzo thiophene-derived iminic ligands were conducted and sets of monometalated and bismetalated species were

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**Table 2. Comparison of Solid-State SCXRD Pt Coordination Sphere Bond Lengths and DFT Gas-Phase and Solution-Phase Minimum Energy Geometries for 18Bis**

| bond  | SCXRD (Å) | gas phase (Å) | DCM solution (Å) |
|-------|-----------|---------------|------------------|
| Pt–C1 | 1.9720    | 1.9901        | 1.9979           |
| Pt–C2 | 1.9528    | 1.9912        | 1.9974           |
| Pt–N1 | 2.1619    | 2.2406        | 2.2503           |
| Pt–N2 | 2.1387    | 2.2337        | 2.2467           |

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**Figure 4.** Gas-phase geometry-optimized structure of 18Bis calculated at LACVP***/***B3LYP DFT level of theory.

**Figure 5.** Observed UV–vis absorbance spectrum and simulated UV–vis spectrum from TD-DFT calculations for 18Bis. The vertical excitations are broadened with a Gaussian function for visualization as described in experiment.
synthesized. The photophysical properties of the resulting compounds were recorded and analyzed. Tentative assignments due to intermediate values of the excited-state lifetime of the MLCT bands were reinforced with TD/DFT calculations. The TD/DFT calculations were invaluable in corroborating the tentative assignment.

Table 3. TD-DFT-Calculated Vertical Excitations of High Oscillator Strength Transitions and Coefficients of Principle Contributing Orbital Transition

| \( S_n \) | excitation energy (nm) | oscillator strength | principal contributing transitions | coefficient of principal contributing transition |
|---|---|---|---|---|
| \( S_1 \) | 572 | 0.008 | HOMO to LUMO | 0.93 |
| \( S_2 \) | 443 | 0.052 | HOMO − 1 to LUMO | 0.99 |
| \( S_3 \) | 388 | 0.136 | HOMO − 4 to LUMO | 0.98 |
| \( S_4 \) | 351 | 0.060 | HOMO − 5 to LUMO | 0.97 |
| \( S_{14} \) | 306 | 0.164 | HOMO − 1 to LUMO + 3 | 0.94 |

EXPERIMENTAL SECTION

General. The solvents and reagents were purchased from Sigma-Aldrich unless otherwise noted. \( K_2PtCl_4 \) was purchased from the Pressure Chemical Company. NMR spectra were recorded at Bard College using Varian MR-400 MHz spectrometer (\(^1H, 400\) MHz; \(^{13}C, 100.6\) MHz) and referenced to SiMe\(_4\) (\(^1H, 13^C\)). Shifts are given in ppm and coupling constant \( J \) values in Hz. Abbreviations used: \( s = \) singlet; \( d = \) doublet; \( t = \) triplet; \( m = \) multiplet. Electrospray mass spectra were performed at Vassar College using an LC/MSD-TOF spectrometer. Elemental analyses have been included. Although several of these results are outside the range viewed as establishing analytical purity, they are provided to illustrate the best values obtained to date. A conscientious effort has been made to obtain pure compounds, where the values for the combustion analysis would fall within a range close to the theoretical values; however, the carbon values were at times high due to the presence of grease or solvents that could not be removed successfully from these organometallic compounds.

Computational Details. Calculations were carried out using TD-DFT and DFT implemented in the Jaguar 9.1 suite of ab initio quantum chemistry programs. Geometry optimizations were performed with the B3LYP functional using a mixed basis set consisting of LANL2DZ with an effective core potential for the Pt atom and the 6-31-G** for all other atoms. X-ray crystallographic data was used as a starting point for geometries, which were confirmed to be energetic minima by vibrational analysis. In the case of the TD-DFT calculations, the UV–vis absorbance spectrum was simulated by optimization of the first 30 excited states and the use of a Poisson–Boltzmann implicit solvent model of dichloromethane to improve energetic agreement to the experimental UV–vis spectra. The resulting vertical excitation energies are convoluted with a Gaussian function of 20 nm half width for the purposes of visualization. Initial geometry guess was generated for the trans isomer using crystallographic data molecular mechanics as implemented in Avogadro version 1.2.0 using the UFF force field. Figures of molecular structure output from calculations were generated using CrystalMaker software. Initial geometry guess was generated using either crystallographic data molecular mechanics as implemented in Avogadro version 1.2.0 using the UFF force field.

Photophysical Measurements. Steady-state emission spectra were recorded using a PTI QM-40 instrument with a PMT detector, which is sensitive up to 850 nm. In these experiments, the concentration of the platinum complexes ranged from \( 2 \times 10^{-8} \) to \( 1 \times 10^{-6} \) M. The luminescence lifetimes of the complexes were measured by time-correlated single-photon counting following excitation with a 365, 405, or 450 nm LED in methylene chloride. Samples were de-gassed for 5 min.

X-ray Diffraction. 18Bis was crystallized by slow diffusion of pentane into an acetone solution. XRD data were collected on a Bruker APEX 2 CCD platform diffractometer [\( \text{Mo Kα (l = 0.71073 Å)} \)] at 125 K with crystals mounted on a nylon loop with Paratone-N cryo-protectant oil. After scaling with SADABS with Friedel opposites not treated as equivalent for scaling purposes, the structure of 18Bis was solved using direct methods (SHELXS-97) and standard difference map techniques and was refined by full-matrix least-squares procedures on F2 with SHELXL-97. All non-hydrogen atoms were refined anisotropically.

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Preparation of Compounds. Platinum dimer, cis-[Pt₂Me₄(μ-SMe₂)₂], PtA, was prepared as reported elsewhere. Please see the Supporting Information section for additional experimental details, including NMR spectra, UV–vis spectra, and emission spectra.

Ligand 14 [([C₅H₅]S)CH−NCH(C₅H₅)]₂. Benzothiophene-3-carboxaldehyde (0.3246 g, 0.0017 mol) and 1-naphthylmethylene (0.3175 g, 0.002 mol) were dissolved in 30 mL of ethanol. The resulting solution was heated under reflux for 4 h. The solvent was removed with a rotary evaporator, and the resulting tan solid was washed with pentane and dried under vacuum. The product was characterized by 1H NMR and 13C NMR spectroscopy. Yield: 91% (0.46 g, 0.0015 mol). 1H NMR (400 MHz, CDCl₃): δ 5.31 (s, 2H, CH₂), (7.24–8.83, aromatics), and 8.68 (s, 1H, CH=N). 13C NMR (CDCl₃): δ 62.8, 122.3, 123.9, 125.0, 125.2, 125.5, 125.6, 126.0, 127.7, 128.6, 132.9, and 156.7. (2H−2D-NOESY-NMR-cross peaks: (5.51, 1.87)-(CH to −SMe₂)2, {7.13–8.03 aromatics}, and 8.75 (s, δ(1H−2D-NOESY-NMR-cross peaks: (2H−2D-NOESY-NMR-cross peaks: (1.24, 2.01)-(PtCH₃ to SMe₂), (8.87, 5.54)-(CH to CH=N). Elemental analysis % calcld for [C₃₂H₂₃NPS₂]: C, 82.45; H, 4.05; N, 0.26. Found: C, 82.45; H, 4.05; N, 0.24. ESI-HR-MS (m/z): found, 543.0559; calcld for [C₃₂H₂₃NPS₂(CH₃)₂]⁻, 543.0528.

15Mono [PtCH₃S(CH₂)]([C₅H₅]S)CH−NCH(C₅H₅)]₂. Benzothiophene-3-carboxaldehyde (0.2168 g, 0.0001mol) and (S)-1-(2-naphthyl)-ethylenamine (0.228 g, 0.001mol) were dissolved in 30 mL of ethanol. The solution was heated and refluxed for 1.5 h and allowed to cool to room temperature. The solution was stirred overnight at room temperature under argon atmosphere. The solvent was removed with a rotary evaporator. The resulting orange powder was washed with pentane and dried under vacuum. The product was characterized by 1H NMR and 13C NMR spectroscopy. Yield: 83% (0.26 g, 8.3 × 10⁻⁴ mol). 1H NMR (400 MHz, CDCl₃): δ 1.69 (d, J(H−H) = 6.7 Hz, 3H, CH₃), 4.64 (q, J(H−H) = 6.7 Hz, 1H, CH), {7.23–8.94 aromatics}, and 8.68 (s, 1H, CH=N). 13C NMR (CDCl₃): δ 25.3, 70.6, 122.3, 124.8, 125.0, 125.2, 125.3, 125.4, 125.5, 125.9, 126.7, 127.8, 128.1, 132.6, 142.9, and 154.2. (2H−2D-NOESY-NMR-cross peaks: (5.51, 1.87)-(CH to CH₃)2, (8.87, 5.54)-(CH to CH≡N). Elemental analysis % calcld for [C₃₄H₂₇NPS₂(CH₃)₂]: found, 569.1797; calcld for [C₃₄H₂₇NPS₂(CH₃)₂]⁻, 569.1760.

16Mono [PtCH₃S(CH₂)]₂([C₅H₅]S)CH−NCH(C₅H₅)]₂. Benzothiophene-3-carboxaldehyde (0.3093 g, 0.0019 mol) and R-(+)-1-(1-naphthyl) ethylenamine (0.3264 g, 0.0019 mol) were dissolved in 30 mL of ethanol. The solution was heated and refluxed for 4.0 h and allowed to cool to room temperature. The solution was stirred overnight at room temperature under argon atmosphere. The solvent was removed with a rotary evaporator. The resulting white powder was washed with pentane and dried under vacuum. The product was characterized by 1H NMR and 13C NMR spectroscopy. Yield: 75% (0.01 g, 3.3 × 10⁻³ mol). 1H NMR (400 MHz, CDCl₃): δ 1.16 (s, δ(1H−2D-NOESY-NMR-cross peaks: (5.51, 1.87)-(CH to CH₃)2, (8.87, 5.54)-(CH to CH≡N), (1.24, 2.01)-(PtCH₃ to SMe₂), (8.87, 5.54)-(CH to CH≡N). Elemental analysis % calcld for [C₃₂H₂₃NPS₂(CH₃)₂]: found, 569.1760; calcld for [C₃₂H₂₃NPS₂(CH₃)₂]⁻, 569.1733.

Ligand 15 ([C₅H₅]S)CH−NCH(C₅H₅)]₂. Benzothiophene-3-carboxaldehyde (0.3477 g, 0.002 mol) and 1,2-naphthyl ethanolamine (0.3246 g, 0.0019 mol) were dissolved in 30 mL of ethanol. The resulting solution was heated under reflux for 4 h and then allowed to spin overnight at room temperature. A tan powder precipitate occurred, which was washed with pentane and dried under vacuum. The product was characterized by 1H NMR and 13C NMR spectroscopy. Yield: 90% (0.51 g, 0.0017 mol). 1H NMR (400 MHz, CDCl₃): δ 8.84 (s, 1H, CH=N), {6.91–9.02 aromatics}, and 13C NMR (CDCl₃): δ 117.5, 121.2, 122.4, 125.2, 125.3, 125.5, 126.3, 127.7, 128.9, 131.9, 134.1, 134.2, 134.9, 136.4, 140.8, 150.0, and 154.8. (2H−2D-NOESY-NMR-cross peaks: (5.51, 1.87)-(CH to CH₃)2, (8.87, 5.54)-(CH to CH≡N), (1.24, 2.01)-(PtCH₃ to SMe₂), (8.87, 5.54)-(CH to CH≡N). Elemental analysis % calcld for [C₃₂H₂₃NPS₂]: C, 82.45; H, 4.05; N, 0.26. Found: C, 82.45; H, 4.05; N, 0.26. ESI-HR-MS (m/z): found, 543.0559; calcld for [C₃₂H₂₃NPS₂(CH₃)₂]⁻, 543.0528.

Ligand 16 ([S]−[C₅H₅]S)CH−NCH(C₅H₅)]₂. Benzothiophene-3-carboxaldehyde (0.2168 g, 0.0001mol) and (S)-1-(2-naphthyl)-ethylenamine (0.228 g, 0.001mol) were dissolved in 30 mL of ethanol. The solution was heated and refluxed for 1.5 h and allowed to cool to room temperature. The solution was stirred overnight at room temperature under argon atmosphere. The solvent was removed with a rotary evaporator. The resulting orange powder was washed with pentane and dried under vacuum. The product was characterized by 1H NMR and 13C NMR spectroscopy. Yield: 43.8% (0.11 g, 3.3 × 10⁻³ mol). 1H NMR (400 MHz, CDCl₃): δ 1.33 (s, δ(1H−2D-NOESY-NMR-cross peaks: (5.51, 1.87)-(CH to CH₃)2, (8.87, 5.54)-(CH to CH≡N), (1.24, 2.01)-(PtCH₃ to SMe₂), (8.87, 5.54)-(CH to CH≡N). Elemental analysis % calcld for [C₃₂H₂₃NPS₂]: C, 82.45; H, 4.05; N, 0.26. Found: C, 82.45; H, 4.05; N, 0.26. ESI-HR-MS (m/z): found, 543.0559; calcld for [C₃₂H₂₃NPS₂(CH₃)₂]⁻, 543.0528.
8.2 × 10⁻³) were dissolved in 20 mL of acetonitrile. The resulting solution was heated under reflux for 1 h, cooled to room temperature, and then was allowed to stir overnight. The solvent was removed with a rotary evaporator, and the resulting orange solid was washed with pentane and dried under vacuum. The final product was characterized by ¹H NMR and ¹³C NMR spectroscopy. Yield: 95% (0.020 g, 2.7 × 10⁻³ mol). ¹H NMR (400 MHz, CDCl₃): δ 7.90 (d, J(H–H) = 6.6 Hz, 3H, α-CH₃), 1.86 (d, J(H–H) = 6.6 Hz, 3H, α-CH₃), 1.91 (m), 7.94 (d, J(Pt–H) = 33.2, 3H SMe₂), 6.10 (q, J(H–H) = 6.6 Hz, 1H, CH), 7.1–8.13 aromatics, and 8.74 (s, J(Pt–H) = 54.7 Hz, 1H, CH=≡N). ¹³C NMR (CDCl₃): δ 17.9, 20.9, 59.3, 118.7, 121.5, 122.8, 123.5, 124.0, 124.2, 125.4, 125.6, 126.5, 128.1, 130.7, 133.8, 138.3, 138.2, 138.3, and 161.3. (¹H–H)-2D-COSY-NMR-cross peaks: (6.10, 1.85)- (CH to α-CH₃). (¹H–H)-2D-NOESY-NMR-cross peaks: (6.10, 1.85)- (CH to α-CH₃). (¹H–H)-2D-NOESY-NMR-cross peaks: (6.10, 1.85)- (CH to α-CH₃). ESI-HR-MS (m/z): found, 796.1475, calcd for C₂₄H₂₅NPtS₂: C, 49.14; H, 4.30; N, 3.57. 

Ele- 

mental analysis % calcd for C₂₄H₂₅NPtS₂: C, 49.14; H, 4.30; N, 3.57.

The filtrate had its solvent removed via rotary evaporation, triturated with diethyl ether, and vacuum filtered. Yield: 65% (0.022 g, 2.7 × 10⁻³ mol) ¹H NMR (400 MHz, CDCl₃): δ 1.77 (d, J(H–H) = 6.7 Hz, 3H, CH₃), 5.47 (q, J(H–H) = 6.7 Hz, 1H, CH), [7.15–7.9 aromatics], and 8.32 (s, J(Pt–H) = 71.5 Hz, 1H CH=≡N). ¹³C NMR (CDCl₃): δ 21.4, 63.1, 118.2, 121.1, 122.4, 124.7, 125.8, 125.9, 126.3, 127.6, 128.2, 128.9, 132.8, 133.3, 137.2, 138.5, 141.9, 143.6, 164.2, and 166.2. (¹H–H)-2D-COSY-NMR-cross peaks, (5.49, 1.76)- (CH to α-CH₃). (¹H–H)-2D-NOESY-NMR-cross peaks, (5.46–1.75)- (CH to α-CH₃). ESI-HR-MS (m/z): found, 823.1675, calcd for C₄₂H₃₂N₂PtS₂. 823.1655. Elemental analysis % calcd for C₄₂H₃₂N₂PtS₂: C, 61.23; H, 3.96; N, 3.34. Found: C, 60.58; H, 3.66; N, 3.34.

**18Bis [Pt((R)-(C₈H₅S)CH=≡NCHCH₂(C₁₀H₇)₂)]**. PtA, [Pt₂(CH₃)₄(μ-S(CH₃)₂)₂] (0.0205 g, 3.56 × 10⁻³ mol) and **Ligand 18 [(R)-(C₈H₅S)CH=≡NCHCH₂(C₁₀H₇)₂] (0.0421 g, 1.33 × 10⁻³ mol)** were dissolved in 15 mL of toluene. The resulting solution was heated under reflux for 4 h under argon. The solution was allowed to stir at room temperature overnight. The resultant dark red precipitate was separated via vacuum filtration and washed with diethyl ether. Product was characterized by NMR spectroscopy. Yield: 72% (0.021 g, 2.54 × 10⁻³ mol). ¹H NMR (400 MHz, CDCl₃): δ 1.80 (d, J(H–H) = 6.5 Hz, 3H, CH₃), 6.06 (q, J(H–H) = 6.5 Hz, 1H, CH), and [7.12–8.33 aromatics] 8.23 (s, J(Pt–H) = 70.5 Hz, 1H, CH=≡N). ¹³C NMR (CDCl₃): δ 21.5, 60.8, 118.8, 122.2, 122.5, 124.5, 124.8, 125.1, 125.3, 126.1, 127.2, 129.1, 129.3, 131.0, 134.5, 137.3, and 165.5. (¹H–H)-2D-COSY-NMR-cross peaks, (6.04, 1.80)- (CH to CH₃), (¹H–H)-2D-NOESY-NMR-cross peaks, (6.04, 8.26)- (CH to CH=≡N). ESI-HR-MS (m/z): found, 824.1793, calcd for [C₄₂H₃₂N₂PtS₂]+, 824.1734. Elemental analysis % calcd for C₄₂H₃₂N₂PtS₂: C, 61.23; H, 3.91; N, 3.40. Found: C, 60.03; H, 3.70; N, 3.26.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c03993.

Molecular structures illustrating planes for both molecules in the asymmetric unit and planes in calculated structure; cis and trans isomer energy comparisons; gas-phase geometry-optimized structure of the trans isomer of 18Bis; coordination sphere bond lengths and DFT gas-phase and solution-phase minimum energy geometries for hypothetical trans isomer of 18Bis; orbitals at and below HOMO and orbitals at and above LUMO; energy levels and energy values determined for frontier and non-frontier orbitals; observed theoretical spectrum arising from four high oscillator strength transitions; and natural transition orbitals for the high oscillator strength transitions; NMR spectra; Uv–vis spectra; Emission Spectra (PDF).

**CCDC for compound 18Bis** (CIF)

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Notes

The authors declare no competing financial interest.

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