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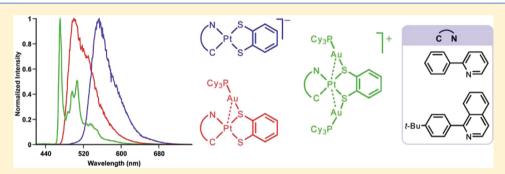




# Synthesis and Photophysical Properties of Cyclometalated Platinum(II) 1,2-Benzenedithiolate Complexes and Heterometallic Derivatives Obtained from the Addition of [Au(PCy<sub>3</sub>)]<sup>+</sup> Units

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Supporting Information



ABSTRACT: The cyclometalated compounds [Pt(C^N)(HC^N)Cl] [HC^N = 2-phenylpyridine (Hppy; 1a), 1-(4-tertbutylphenyl)isoquinoline (Htbpiq; 1b)] react with 1,2-benzenedithiol, t-BuOK, and Bu<sub>4</sub>NCl in a 1:1:2:1 molar ratio in CH<sub>2</sub>Cl<sub>2</sub>/ MeOH to give the complexes  $Bu_4N\lceil Pt(C^N)(bdt)\rceil \lceil bdt = 1,2$ -benzenedithiolate;  $C^N = ppy(Bu_4N2a)$ , tbpiq  $(Bu_4N2b)\rceil$ . In the absence of Bu<sub>4</sub>NCl, the same reactions afford solutions of K2a and K2b, which react with [AuCl(PCy<sub>3</sub>)] to give the neutral heterometallic derivatives  $[Pt(C^N)(bdt)\{Au(PCy_3)\}]$   $[C^N = ppy (3a), tbpiq (3b)]$ . The cationic derivatives  $[Pt(C^N)-Pt]$ (bdt){Au(PCy<sub>3</sub>)}<sub>2</sub>]ClO<sub>4</sub> [C^N = ppy (4a), tbpiq (4b)] are obtained by reacting 3a and 3b with acetone solutions of [Au(OClO<sub>3</sub>)(PCy<sub>3</sub>)]. The crystal structures of 3b and 4b reveal the formation of short Pt···Au metallophilic contacts in the range 2.929-3.149 Å. Complexes 3b, 4a, and 4b undergo dynamic processes in solution that involve the migration of the [Au(PCy<sub>3</sub>)]<sup>+</sup> units between the S atoms of the dithiolate. Complexes Bu<sub>4</sub>N2a and 2b display a moderately solvatochromic band in their electronic absorption spectra that can be ascribed to a transition of mixed ML'CT/LL'CT character (M= metal; L = bdt; L' = C^N; CT = charge transfer), while their emissions are assignable to transitions of the same orbital parentage but from triplet excited states. The successive addition of [Au(PCy<sub>3</sub>)]<sup>+</sup> units to the anions 2a and 2b results in an increase in the absorption and emission energies attributable to lower highest occupied molecular orbital energies. Additionally, the characteristics of the absorption and emission spectra of the heterometallic derivatives indicate a gradual loss of LL'CT character in the involved electronic transitions, with a concomitant increase of the L'C and ML'CT contributions.

### **■ INTRODUCTION**

Square-planar platinum(II) complexes are currently the subject of intensive research because of their interesting excited-state properties and their suitability for a number of advanced technological applications. Platinum(II) complexes with di- and triimine ligands, i.e., bi- and terpyridyls, have gained importance associated with their possible use as sensitizers for the photocatalyzed generation of hydrogen from water, systems for photoinduced charge separation, <sup>2,3</sup> and chemosensors.<sup>4</sup> Platinum(II) systems with cyclometalated aromatic ligands, such as 2-arylpyridines and related compounds, constitute a distinct set of complexes that have stimulated a considerable research effort, mainly because of their successful application as phosphors in light-emitting devices<sup>5-7</sup> and molecular sensors.<sup>8</sup>

One of the keys to the success of these compounds lies in the beneficial effects that cyclometalation induces on their stability and luminescence efficiencies. The strong  $\sigma$ -donor ability of the aromatic C-donor atom, combined with  $\pi$ -back-donation to the pyridine ring, results in a strong ligand field that ensures a higher energy for the nonemitting MC (d-d) states, which would otherwise provide thermally accessible pathways for the radiationless deactivation of emitting ligand-centered (LC)/ metal-to-ligand charge-transfer (MLCT) excited states. 5,6,9 Homoleptic complexes of the type  $[Pt(C^N)_2]$  were among the first reported platinum(II) complexes to display lumines-

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cence at room temperature in a fluid solution. 10 However, heteroleptic derivatives of the types [Pt(C^N)(L^X)], [Pt- $(C^N)(L^L)^+$ , and  $[Pt(C^N)X_2]^-$  have important advantages because variation of the ancillary ligands allows one to control the charge, solubility, and emission properties.<sup>6</sup> The most frequently employed ancillary ligands are  $\beta$ -diketonates, 11,12 although other monoanionic chelating O^O13 and O^N14 ligands have also been used to obtain neutral complexes. S-Donor ligands are relatively uncommon as ancillary ligands for cyclometalated platinum(II) complexes of the above-mentioned types. Several thioethers have been employed for the synthesis of cationic derivatives, 15,16 while neutral complexes have been reported with dithiocarbamates, <sup>17,18</sup> xanthates, dithiophosphates, <sup>19</sup> and monofunctional thiolates. <sup>14,19,20</sup> Only four anionic complexes of the type  $[Pt(C^N)(S^S)]^{-1}$ , containing maleonitriledithiolate 15 or sulfur-rich 1,2-dithiolates,<sup>21</sup> have been reported so far. The limited attention devoted to these complexes contrasts with the extensive studies carried out on the isoelectronic platinum(II) diiminedithiolates  $[Pt(N^N)(S^S)]^{2,22,23}$ 

The growing interest in heterometallic complexes, aggregates, and clusters has generated a highly active research field. One of the main motivations that fuel this area is the study of the nature of the metallophilic interactions that are commonly established between metal ions with closed- or pseudo-closed-shell electronic configurations (d<sup>10</sup>, d<sup>8</sup>, s<sup>2</sup>)<sup>24</sup> and their impact on the structures and photophysical properties. <sup>25</sup> In addition, a significant part of the recent research work within this field has been specifically devised to explore the coordination of additional metal centers as a method for modification of the emission properties. Notably, a variety of platinum(II) chalcogenido, <sup>26</sup> thiolato, <sup>27</sup> thione, <sup>28</sup> and alkynyl <sup>29,30</sup> complexes have been employed as metalloligands to generate diverse heterometallic systems, in which the bridging coordination mode of the ligands and/or the establishment of metallophilic interactions lead to critical changes in the luminescence.

Our research group has reported the synthesis and structural characterization of an extensive series of heterodinuclear, trinuclear, and tetranuclear complexes derived from the addition of  $M^+$ ,  $[M(PPh_3)]^+$  (M = Ag, Au), or  $[Ag(PPh_3)_2]^+$ ions to palladium(II) and platinum(II) complexes of the type  $[M'\{S_2C=C(COMe)_2\}L_2]$  with M'=Pd, Pt and  $L=PPh_3$ , t-BuCN or  $L_2 = 1.5$ -cyclooctadiene (cod). More recently, we employed complexes of the types  $[M{S_2C=(t-Bu-fy)}_2]^{2-}$  and  $[M{S_2C=(t-Bu-fy)}(dbbpy)]$  (M = Pd, Pt; t-Bu-fy = 2,7-ditert-butylfluoren-9-ylidene; dbbpy = 4,4'-di-tert-butyl-2,2'-bipyridyl) as metalloligands toward [Au(PCv<sub>3</sub>)]<sup>+</sup> units to obtain heteronuclear complexes of the types  $[M{S_2C=(t-Bu \{y\}_{2}\{Au(PCy_{3})\}_{2}$ ,  $[M\{S_{2}C=(t-Bu-fy)\}(dbbpy)\{Au-fy\}\}_{2}$  $(PCy_3)$ }]<sup>+</sup>, and  $[M{S_2C=(t-Bu-fy)}(dbbpy){Au(PCy_3)}_2]^{2+}$ , with the main objective of evaluating the modification of their emission properties.<sup>33</sup> Although the results were encouraging, the heterometallic derivatives containing the diimine ligand dbbpy were only moderately stable in solution and in the solid state because of their tendency to dissociate  $[Au(PCy_3)]^+$  units.

For the present research, we turned our attention to platinum(II) complexes containing both cyclometalated and dithiolate ligands, which, given their anionic character, we considered particularly suited for the synthesis of stable heterometallic aggregates. In this paper, we report the synthesis and photophysical characterization of  $[Pt(C^N)(bdt)]^ [C^N] = 2$ -phenylpyridine (Hppy), 1-(4-tert-butylphenyl)-

isoquinoline] (Htbpiq); bdt =1,2-benzenedithiolate], and diand trinuclear platinum(II)/gold(I) derivatives resulting from coordination of the  $[Au(PCy_3)]^+$  units, and analyze the modifications of the excited-state properties as a consequence of the successive addition of Au centers.

### **■ EXPERIMENTAL SECTION**

General Considerations, Materials, and Instrumentation. Unless otherwise noted, all preparations were carried out at room temperature under atmospheric conditions. Synthesis-grade solvents were obtained from commercial sources. CH2Cl2, Et2O, and tetrahydrofuran (THF) were degassed and dried using a Pure Solv MD-5 solvent purification system from Innovative Technologies, Inc. The compounds  $[AuCl(PCy_3)]^{34}$  and [Pt(ppy)(Hppy)Cl] (1a)<sup>35</sup> were prepared following published procedures. All other reagents were obtained from commercial sources and used without further purification. NMR spectra were recorded on Bruker Avance 200, 300, or 400 spectrometers at 298 K. Chemical shifts are referred to internal tetramethylsilane (TMS; <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H}) or external 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P{<sup>1</sup>H}). The assignments of the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were made with the help of HMBC and HMQC experiments. Scheme 1 shows the atom numbering for the ppy and tbpiq ligands. The atoms of the nonmetalated Htbpiq ligand in 1b have been labeled with primes. For the variable-temperature NMR measurements, the 400 MHz spectrometer was employed. The temperature was calibrated using 4% methanol (MeOH) in CD<sub>3</sub>OD. Line-shape analyses of the temperature-dependent <sup>31</sup>P{<sup>1</sup>H} NMR spectra of **4a** and **4b** were carried out using the program gNMR 5.0; full details are given in the Supporting Information. Melting points were determined on a Reichert apparatus and are uncorrected. Elemental analyses were carried out with a Carlo Erba 1106 microanalyzer. IR spectra were recorded in the range 4000-200 cm<sup>-1</sup> on a Perkin-Elmer Spectrum 100 spectrophotometer using Nujol mulls between polyethylene sheets. High-resolution electrospray ionization mass spectrometry (ESI-MS) spectra were recorded on an Agilent 6220 Accurate-Mass time-of-flight (TOF) LC/MS. UV-vis absorption spectra were recorded on a Perkin-Elmer Lambda 750S spectrophotometer. Excitation and emission spectra were recorded on a Jobin Yvon Fluorolog 3-22 spectrofluorometer with a 450-W xenon lamp, doublegrating monochromators, and a TBX-04 photomultiplier. The solidstate measurements were made in a front-face configuration using polycrystalline samples between quartz coverslips; the solution measurements were carried out in a right-angle configuration using degassed solutions of the samples in 10-mm quartz fluorescence cells or 5-mm quartz NMR tubes. For the low-temperature measurements, a liquid-nitrogen Dewar with quartz windows was employed. Lifetimes were measured using an IBH FluoroHub TCSPC controller and a NanoLED pulse diode excitation source; the estimated uncertainty in the quoted values is  $\pm 10\%$  or better. Emission quantum yields were calculated by the relative method<sup>36</sup> for those compounds that are emissive in solution at room temperature, using [Ru(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> in a deaerated MeCN solution as the standard, for which the recently reevaluated absolute quantum yield is  $\Phi = 0.095$ .<sup>37</sup> The estimated uncertainty in the quoted  $\Phi$  values is  $\pm 20\%$  or better.

**X-ray Structure Determinations.** Crystals of **3b** and **4b**·CH<sub>2</sub>Cl<sub>2</sub> suitable for X-ray diffraction studies were obtained by the liquid–liquid diffusion method from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  or  $\text{CH}_2\text{Cl}_2/\text{pentane}$ , respectively. Numerical details are presented in Table 1. The data were collected on an Oxford Diffraction Xcalibur S diffractometer using monochromated Mo K $\alpha$  radiation in  $\omega$ -scan mode. The structures were refined anisotropically on  $F^2$  using the program SHELXL-97 (Sheldrick, G. M. University of Göttingen, Göttingen, Germany). Methyl H atoms were included as part of the rigid idealized methyl groups allowed to rotate but not tip; other H atoms were included using a riding model. Special features of refinement: The dichloromethane molecule in **4b**·CH<sub>2</sub>Cl<sub>2</sub> is disordered over two sites with relative occupation 0.65/0.35. Appropriate similarity restraints were used to improve the stability of refinement.

Table 1. Crystallographic Data for 3b and 4b·CH<sub>2</sub>Cl<sub>2</sub>

	3b	$4b \cdot CH_2Cl_2$
formula	$C_{43}H_{55}AuNPPtS_2$	$C_{62}H_{90}Au_2Cl_3NO_4P_2PtS_2$
fw	1073.03	1734.78
T (K)	100.2(2)	100.2(2)
λ (Å)	0.71073	0.71073
cryst syst	triclinic	monoclinic
space group	$P\overline{1}$	$P2_1/n$
a (Å)	11.9157(2)	24.0411(4)
b (Å)	12.0728(2)	11.0278(2)
c (Å)	14.8775(2)	24.6578(4)
$\alpha$ (deg)	79.1084(11)	90
$\beta$ (deg)	85.5256(11)	90.042(3)
γ (deg)	70.3669(12)	90
V (Å <sup>3</sup> )	1979.23(5)	6537.28(19)
Z	2	4
$ ho_{ m calcd}~({ m Mg~m^{-3}})$	1.801	1.763
$\mu  \left( \mathrm{mm}^{-1} \right)$	7.409	6.892
R1 <sup>a</sup>	0.0231	0.0236
wR2 <sup>b</sup>	0.0521	0.0434

 ${}^{a}\text{R1} = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|$  for reflections with  $I > 2\sigma(I)$ .  ${}^{b}\text{wR2} = [\sum [w(F_{o}^{\ 2} - F_{c}^{\ 2})^{2}] / \sum [w(F_{o}^{\ 2})^{2}]^{0.5}$  for all reflections;  $w^{-1} = \sigma^{2}(F^{2}) + (aP)^{2} + bP$ , where  $P = (2F_{c}^{\ 2} + F_{o}^{\ 2}) / 3$  and a and b are constants set by the program.

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Preparations on a larger scale than that described here should be avoided.

1-(4-tert-Butylphenyl)isoquinoline (Htbpiq). The following procedure is based on the method described for some quinoline derivatives.<sup>39</sup> A mixture of 1-chloroisoquinoline (850 mg, 5.20 mmol), 4-tert-butylphenylboronic acid (930 mg, 5.22 mmol), Ba(OH)<sub>2</sub>·8H<sub>2</sub>O (3.3 g, 10.5 mmol), 2,6-di-tert-butyl-4-methylphenol (30 mg, 0.14 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (140 mg, 0.12 mmol), and THF (18 mL) was placed in a Carius tube and stirred at 75 °C for 20 h under a N, atmosphere. The solvent was removed under a vacuum, and the residue was extracted using a 1:1 mixture of CH<sub>2</sub>Cl<sub>2</sub> and H<sub>2</sub>O (140 mL). The organic phase was decanted and dried over anhydrous MgSO<sub>4</sub>. Evaporation of the solvent under reduced pressure led to a yellow solid, which was chromatographed on silica gel using 4% AcOEt in n-hexane as the eluent. Yield: 868 mg, 64%. Mp: 110 °C. HRMS (ESI+, m/z). Exact mass calcd for  $C_{19}H_{19}N$  [M + H]<sup>+</sup>: 262.1590. Found: 262.1595. Error: 1.88 ppm. IR (Nujol, cm<sup>-1</sup>): 1581 (w), 1547 (w), 1019 (m), 973 (w), 841 (w), 825 (m), 800 (w), 679 (w), 585 (w), 520 (w), 466 (w), 452 (w), 434 (w). <sup>1</sup>H NMR (400.9 MHz, CDCl<sub>3</sub>):  $\delta$  8.60 (d,  ${}^{3}J_{HH}$  = 5.6 Hz, 1 H, Iq3), 8.18 (d,  ${}^{3}J_{HH}$  = 8.4 Hz, 1 H, Iq8), 7.87 (d,  ${}^{3}J_{HH}$  = 8.6 Hz, 1 H, Iq5), 7.64–7.72 (m, 3 H, Iq6, Ph2), 7.62 (d,  ${}^{3}J_{HH}$  = 5.6 Hz, 1 H, Iq4), 7.49–7.59 (m, 3 H, Ph3, Iq7), 1.41 (s, 9 H, t-Bu).  ${}^{13}C\{{}^{1}H\}$  APT NMR (100.8 MHz, CDCl<sub>3</sub>):  $\delta$  160.8 (Iq1), 151.6 (Ph4), 142.2 (Iq3), 136.8 (Iq4a), 136.7 (Ph1), 130.0 (Iq6), 129.6 (Ph2), 127.7 (Iq8), 127.0 (Iq7), 126.9 (Iq5), 126.7 (Iq8a), 125.3 (Ph3), 119.6 (Iq4), 34.7 (CMe<sub>3</sub>), 31.3 (CMe<sub>3</sub>).

[Pt(tbpiq)(Htbpiq)Cl] (1b). The following procedure is based on the method described for 1a.<sup>35</sup> K<sub>2</sub>[PtCl<sub>4</sub>] (450 mg, 1.08 mmol), Htbpiq (580 mg, 2.22 mmol), and a previously degassed 3:1 (v/v) mixture of 2-ethoxyethanol and H<sub>2</sub>O (40 mL) were placed in a Carius tube under a N<sub>2</sub> atmosphere, and the resulting solution was stirred at 80 °C for 4 days. The gradual precipitation of an orange solid was observed. The solvent was removed under reduced pressure, and the residue was chromatographed on silica gel using 2% AcOEt in CH<sub>2</sub>Cl<sub>2</sub> as the eluent. Crystallization from CH<sub>2</sub>Cl<sub>2</sub>/n-pentane afforded orange crystals of 1b·<sup>1</sup>/<sub>3</sub>CH<sub>2</sub>Cl<sub>2</sub>·<sup>2</sup>/<sub>3</sub>H<sub>2</sub>O. Yield: 565 mg, 69%. Mp: 177 °C. Anal. Calcd for C<sub>38.3</sub>H<sub>39</sub>Cl<sub>1.67</sub>N<sub>2</sub>O<sub>0.67</sub>Pt: C, 58.10; H, 4.96; N, 3.54. Found: C, 58.12; H, 4.96; N, 3.75. IR (Nujol, cm<sup>-1</sup>): 1620 (w), 1581 (w), 1265 (w), 1020 (m), 828 (m), 466 (w), 451 (w). <sup>1</sup>H NMR (400.91 MHz, CDCl<sub>3</sub>): δ 9.51 (d with satellites, <sup>3</sup> $J_{HH}$  = 6.4 Hz, <sup>3</sup> $J_{HPt}$  =

~13 Hz, 1 H, Iq3), 9.08 (d with satellites,  ${}^{3}J_{\rm HH} = 6.7$  Hz,  ${}^{3}J_{\rm HPt} = \sim 16$  Hz, 1 H, Iq3'), 8.68 (d,  ${}^{3}J_{\rm HH} = 8.6$  Hz, 1 H, Iq8), 8.20 (dd,  ${}^{3}J_{\rm HH} = 8.2$  Hz,  ${}^{4}J_{\rm HH} = 1.6$  Hz, 1 H, Ph2'/Ph6'), 7.97 (d,  ${}^{3}J_{\rm HH} = 8.2$  Hz, 1 H, Iq5'), 7.80—7.91 (m, 3 H, Iq6', Iq8', Ph6), 7.76 (d,  ${}^{3}J_{\rm HH} = 8.2$  Hz, 1 H, Iq5), 7.74 (d,  ${}^{3}J_{\rm HH} = 6.8$  Hz, 1 H, Iq4'), 7.67 (t,  ${}^{3}J_{\rm HH} = 7.2$  Hz, 1 H, Iq6), 7.53—7.63 (m, 2 H, Iq7', Iq7), 7.50 (dd,  ${}^{3}J_{\rm HH} = 8.2$  Hz,  ${}^{4}J_{\rm HH} = 1.8$  Hz, 1 H, Ph3'/Ph5'), 7.30—7.38 (m, 2 H, Ph2'/Ph6', Iq4), 7.22 (dd,  ${}^{3}J_{\rm HH} = 8.2$  Hz,  ${}^{4}J_{\rm HH} = 1.7$  Hz, 1 H, Ph3'/Ph5'), 7.09 (dd,  ${}^{3}J_{\rm HH} = 8.4$  Hz,  ${}^{4}J_{\rm HH} = 2.0$  Hz, 1 H, Ph5), 6.28 (d with satellites,  ${}^{4}J_{\rm HH} = 2$  Hz,  ${}^{3}J_{\rm HPt} = 25$  Hz, 1 H, Ph3), 1.21 (s, 1 H, t-Bu'), 1.05 (s, 1 H, t-Bu).  ${}^{13}{\rm C}\{{}^{1}{\rm H}\}$  APT NMR (100.81 MHz, CDCl<sub>3</sub>):  $\delta$  167.6 (Iq1), 164.3 (Iq1'), 152.6 (Ph4), 152.0 (Ph4'), 145.8 (Iq3'), 143.1 (Ph2), 142.9 (Ph1), 142.8 (Iq3), 137.3 (Iq4a), 135.7 (Iq4a'), 134.6 (Ph1'), 132.0 (Iq6'), 131.7 (Ph2'/Ph6'), 131.1 (Iq6), 129.6 (Ph2'/Ph6'), 129.5 (Iq8a'), 129.1 (Iq8'), 128.4 (Iq7'), 128.3 (Ph6), 128.0 (Ph3), 127.7 (Iq7), 127.3 (Iq5), 126.8 (Iq6'), 126.4 (Iq8), 125.1 (Iq8a), 124.8, 123.9 (Ph3'/Ph5'), 121.8 (Iq4'), 119.6 (Ph5), 118.9 (Iq4), 34.7 (CMe<sub>3</sub>), 34.4 (CMe<sub>3</sub>), 31.1 (CMe<sub>3</sub>), 30.9 (CMe<sub>3</sub>).

Bu<sub>4</sub>N[Pt(ppy)(bdt)] (2a). 1,2-Benzenedithiol (55  $\mu$ L, 0.48 mmol), t-BuOK (105 mg, 0.93 mmol), and Bu<sub>4</sub>NCl (117 mg, 0.42 mmol) were dissolved in MeOH (12 mL), and the mixture was added to a solution of 1a (216 mg, 0.40 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40 mL). After stirring for 90 min, a turbid red-orange solution was obtained. The solvent was removed under reduced pressure, and the residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> (30 mL) and filtered through anhydrous MgSO<sub>4</sub>. Partial evaporation of the filtrate (4 mL) and the slow addition of Et<sub>2</sub>O (20 mL) led to the precipitation of a red solid, which was filtered off, washed with Et<sub>2</sub>O (2  $\times$  3 mL), and recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O to give 2a. Yield: 235 mg, 80%. Anal. Calcd for C33H48N2PtS2: C, 54.15; H, 6.61; N, 3.83; S, 8.76. Found: C, 53.96; H, 6.95; N, 3.92; S, 8.41. Mp: 186 °C. <sup>1</sup>H NMR (300.1 MHz, CDCl<sub>3</sub>):  $\delta$  9.22 (dd, <sup>3</sup> $J_{HH}$  = 5.4 Hz,  ${}^{3}J_{HPt} = 24$  Hz, 1 H, py6), 7.93 (dd,  ${}^{3}J_{HH} = 6.6$  Hz,  ${}^{3}J_{HPt} = 29.4$ Hz, 1 H, Ph3), 7.69 (t,  ${}^{3}J_{HH}$  = 7.5 Hz, 1 H, py4), 7.61 (d,  ${}^{3}J_{HH}$  = 8.1 Hz, 1 H, py3), 7.46 (d,  ${}^{3}J_{HH}$  = 6.9 Hz, 1 H, Ph6), 7.40 (m, 1 H, bdt), 7.30 (m, 1 H, bdt), 6.99 (m, 2 H, Ph4, Ph5), 6.88 (m, 1 H, py5), 6.55 (m, 2 H, bdt), 2.77 (m, 8 H, NCH<sub>2</sub>), 1.10 (m, 8 H, CH<sub>2</sub>), 0.91 (m, 8 H, CH<sub>2</sub>), 0.62 (m, 12 H, Me, Bu<sub>4</sub>N). <sup>13</sup>C{<sup>1</sup>H} NMR (75.45 MHz, CDCl<sub>3</sub>): δ 167.1 (py2), 158.0 (Ph2), 149.8 (py6), 148.8 (C1/C2, bdt), 144.5 (C1/C2, bdt), 143.8 (Ph1), 135.9 (py4), 134.2 (Ph3), 130.5 (C3/C6, bdt), 130.1 (Ph5), 128.7 (C3/C6, bdt), 123.3 (Ph6), 121.8 (py5), 121.1 (Ph4), 120.2 (C4/C5, bdt), 119.9 (C4/C5, bdt), 118.4 (py3), 57.9 (NCH<sub>2</sub>), 23.8 (CH<sub>2</sub>), 19.2 (CH<sub>2</sub>), 13.6 (Me, Bu<sub>4</sub>N).

Bu<sub>4</sub>N[Pt(tbpiq)(bdt)] (2b). This purple compound was obtained as described for 2a, from 1b (250 mg, 0.33 mmol), bdt (42  $\mu$ L, 0.36 mmol), t-BuOK (82 mg, 0.73 mmol), and Bu<sub>4</sub>NCl (101 mg, 0.36 mmol). Yield: 250 mg, 90%. Anal. Calcd for C<sub>41</sub>H<sub>58</sub>N<sub>2</sub>PtS<sub>2</sub>: C, 58.76; H, 6.98; N, 3.34; S, 7.65. Found: C, 58.42; H, 7.06; N, 3.29; S, 7.60. Mp: 140 °C.  $^1\text{H}$  NMR (400.9 MHz, CDCl3):  $\delta$  9.12 (dd,  $^3J_{\rm HH}$  = 6.4 Hz,  ${}^{3}J_{HPt}$  = 29.2 Hz, 1 H, Iq3), 8.81 (d,  ${}^{3}J_{HH}$  = 8.5 Hz, 1 H, Iq8), 8.24 (dd,  ${}^{4}J_{HH} = 2.1 \text{ Hz}$ ,  ${}^{3}J_{HPt} = 47.6 \text{ Hz}$ , 1 H, Ph3), 7.99 (d,  ${}^{3}J_{HH} = 8.5 \text{ Hz}$ , 1 H, Ph6), 7.72 (dd,  ${}^{3}J_{HH} = 8.1 \text{ Hz}$ ,  ${}^{4}J_{HH} = 1.0 \text{ Hz}$ , 1 H, Iq5), 7.66 (td,  ${}^{3}J_{HH} = 8.1 \text{ Hz}, {}^{4}J_{HH} = 1.0 \text{ Hz}, 1 \text{ H}, \text{Iq6}), 7.54 \text{ (ddd, } {}^{3}J_{HH} = 8.5 \text{ Hz}, {}^{3}J_{HH}$ = 7.0 Hz,  ${}^{4}J_{HH}$  = 1.5 Hz, 1 H, Iq7), 7.46 (m, 1 H, bdt), 7.39 (m, 1 H, bdt), 7.16 (d,  ${}^{3}J_{HH}$  = 6.4 Hz, 1 H, Iq4), 7.11 (dd,  ${}^{3}J_{HH}$  = 8.4 Hz,  ${}^{4}J_{HH}$  = 2.1 Hz, 1 H, Ph5), 6.58 (m, 2 H, bdt), 2.87 (m, 8 H, NCH<sub>2</sub>), 1.37 (s, 9 H, t-Bu), 1.18 (m, 8 H, CH<sub>2</sub>), 0.97 (m, 8 H, CH<sub>2</sub>), 0.64 (t,  ${}^{3}J_{HH} = 7.3$ Hz, 12 H, Me, Bu<sub>4</sub>N).  $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$  NMR (75.45 MHz, CDCl<sub>3</sub>):  $\delta$  167.2 (Iq1), 159.8 (Ph2), 152.6 (Ph4), 149.5, 145.0 (C1/C2, bdt), 143.5 (Iq3), 142.6 (Ph1), 136.5 (Iq4a), 131.2 (Ph3), 130.6 (C3/C6, bdt), 129.9 (Iq6), 128.8 (C3/C6, bdt), 128.7 (Ph6), 127.3 (Iq7), 127.1 (Iq8), 127.0 (Iq5), 126.4 (Iq8a), 120.2 (C4/C5, bdt), 119.9 (C4/C5, bdt), 119.2 (Iq4), 118.2 (Ph5), 58.1 (NCH<sub>2</sub>), 35.0 (CMe<sub>3</sub>), 31.5 (CMe<sub>3</sub>), 24.0 (CH<sub>2</sub>), 19.3 (CH<sub>2</sub>), 13.6 (Me, Bu<sub>4</sub>N).

[Pt(ppy)(bdt){Au(PCy<sub>3</sub>)}] (3a). Method A. To a solution of [AuCl(PCy<sub>3</sub>)] (85 mg, 0.16 mmol) in acetone (10 mL) was added AgClO<sub>4</sub> (35 mg, 0.17 mmol). The resulting suspension was stirred for 5 min and filtered through Celite to remove the precipitate of AgCl. The clear filtrate was then added to a solution of 2a (120 mg, 0.16 mmol) in acetone (25 mL), and the mixture was stirred for 10 min. Partial evaporation of the solvent (6 mL) led to precipitation of a

yellow solid, which was filtered off, washed with acetone  $(2 \times 4 \text{ mL})$ , and vacuum-dried to give 3a. Yield: 124 mg, 78%. Method B. 1,2-Benzenedithiol (28  $\mu$ L, 0.24 mmol) and t-BuOK (60 mg, 0.53 mmol) were dissolved in MeOH, (6 mL) and the mixture was added to a solution of 1a (150 mg, 0.20 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (25 mL). After stirring for 60 min, a red solution was obtained. [AuCl(PCy<sub>3</sub>)] (117 mg, 0.23 mmol) was then added, and the mixture was stirred for 30 min, whereupon a color change to yellow was observed. The solvent was removed under reduced pressure, the residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> (40 mL), and the extract was filtered through anhydrous MgSO<sub>4</sub>. The solvent was removed under a vacuum, and the residue was stirred in n-pentane (40 mL) at 0 °C to give a yellow solid, which was filtered off and vacuum-dried to give 3a. Yield: 201 mg, 91%. Anal. Calcd for C<sub>35</sub>H<sub>45</sub>AuNPPtS<sub>2</sub>: C, 43.48; H, 4.69; N, 1.45; S, 6.63. Found: C, 43.38; H, 4.56; N, 1.60; S, 6.56. Mp: >270 °C. <sup>1</sup>H NMR (300.1 MHz, CDCl<sub>3</sub>):  $\delta$  9.07 (dd,  ${}^{3}J_{\text{HH}}$  = 5.9 Hz,  ${}^{3}J_{\text{HPt}}$  = 32 Hz, 1 H, py6), 7.97 (dd,  ${}^{3}J_{\text{HH}}$  = 7.4 Hz,  ${}^{3}J_{\text{HPt}}$  = 44 Hz, 1 H, Ph3), 7.80 (t,  ${}^{3}J_{\text{HH}}$  = 7.2 Hz, 1 H, py4), 7.72 (d,  ${}^{3}J_{HH} = 8.1$  Hz, 1 H, py3), 7.63 (m, 2 H, bdt), 7.54 (d,  ${}^{3}J_{HH}$  = 7.5 Hz, 1 H, Ph6), 7.06–7.17 (m, 2 H, Ph4, Ph5), 6.97–7.03 (m, 1 H, py5), 6.79–6.92 (m, 2 H, bdt), 1.47–1.76 (m, 18 H, Cy), 0.88–1.24 (m, 15 H, Cy). <sup>13</sup>C{<sup>1</sup>H} NMR (75.45 MHz, CDCl<sub>3</sub>): δ 167.0 (py2), 153.9 (Ph2), 150.2 (py6), 148.6 (C1/C2, bdt), 143.9 (Ph1), 137.0 (py4), 135.6 (C1/C2, bdt), 134.1 (Ph3), 132.2 (C3/C6, bdt), 130.4 (Ph5), 130.0 (C3/C6, bdt), 123.7 (C4/C5, bdt), 123.5 (Ph6), 122.7 (Ph4), 122.1 (py5), 121.8 (C4/C5, bdt), 118.8 (py3), 33.1 (d,  ${}^{1}J_{CP}$  = 28.1 Hz, C1, Cy), 30.3 (C2, Cy), 26.9 (d,  ${}^{3}J_{CP} = 12.1 \text{ Hz}, C3, Cy), 25.62 (C4, Cy). {}^{31}P\{{}^{1}H\} \text{ NMR (162.3 MHz,}$ CDCl<sub>3</sub>):  $\delta$  52.84 (s).

[Pt(tbpiq)(bdt){Au(PCy<sub>3</sub>)}] (3b). This orange complex was prepared as described for 3a (method B), from 1,2-benzenedithiol (24 μL, 0.21 mmol), t-BuOK (48 mg, 0.43 mmol), 1b (150 mg, 0.20 mmol), and [AuCl(PCy<sub>3</sub>)] (103 mg, 0.20 mmol). Yield: 178 mg, 83%. Anal. Calcd for C<sub>43</sub>H<sub>55</sub>AuNPPtS<sub>2</sub>: C, 48.13; H, 5.17; N, 1.31; S, 5.98. Found: C, 47.75; H, 4.96; N, 1.29; S, 6.04. Mp: 249 °C. <sup>1</sup>H NMR (400.9 MHz,  $CD_2Cl_2$ ):  $\delta$  8.88 (d,  ${}^3J_{HH}$  = 8.7 Hz, 1 H, Iq8), 8.85 (dd,  ${}^{3}J_{HH} = 6.4 \text{ Hz}, {}^{3}J_{HPt} = 28.8 \text{ Hz}, 1 \text{ H, Iq3}, 8.12 (dd, {}^{4}J_{HH} = 1.9 \text{ Hz}, {}^{3}J_{HPt}$ = 55.4 Hz, 1 H, Ph3), 8.06 (d,  ${}^{3}J_{HH}$  = 8.4 Hz, 1 H, Ph6), 7.83 (d,  ${}^{3}J_{HH}$ = 8.0 Hz, 1 H, Iq5), 7.76 (t,  ${}^{3}J_{HH}$  = 7.2 Hz, 1 H, Iq6), 7.66 (t,  ${}^{3}J_{HH}$  = 7.6 Hz, 1 H, Iq7), 7.61 (d,  ${}^{3}J_{HH} = 8.0$  Hz, 1 H, bdt), 7.57 (d,  ${}^{3}J_{HH} = 8.0$ Hz, 1 H, bdt), 7.34 (d,  ${}^{3}J_{HH}$  = 6.4 Hz, 1 H, Iq4), 7.23 (dd,  ${}^{3}J_{HH}$  = 8.4 Hz,  ${}^{4}J_{HH} = 1.8$  Hz, Ph5), 6.90 (t,  ${}^{3}J_{HH} = 7.2$  Hz, 1 H, bdt), 6.80 (t,  ${}^{3}J_{HH}$ = 7.2 Hz, 1 H, bdt), 1.73–1.42 (br m, 18 H, Cy), 1.41 (s, 9 H, t-Bu), 1.20–0.80 (br m, 15 H, Cy).  $^{13}$ C $^{1}$ H $^{13}$ NMR (100.8 MHz, CDCl<sub>3</sub>):  $\delta$ 167.3 (Iq1), 155.5 (Ph2), 153.4 (Ph4), 150.5 (C1/C2, bdt), 143.4 (Iq3), 142.8 (Ph1), 136.9 (Iq4a), 134.9 (C1/C2, bdt), 132.6 (C3/C6, bdt), 131.2 (Ph3), 130.7 (Iq6), 130.1 (Iq7), 129.0 (Ph6), 128.0 (C3/ C6, bdt), 127.3 (Iq5 + Iq8), 126.4 (Iq8a), 124.1 (C4/C5, bdt), 121.5 (C4/C5, bdt), 119.8, 119.7 (Iq4, Ph5), 35.3 (CMe<sub>3</sub>), 33.2 (d,  ${}^{1}J_{PC} =$ 28 Hz, C1, Cy), 31.5 (CMe<sub>3</sub>), 30.4 (C2, C6, Cy), 27.0 (d,  ${}^{3}J_{PC} = 12$ Hz, C3, C5, Cy), 25.7 (C4, Cy). <sup>31</sup>P{<sup>1</sup>H} NMR (162.3 MHz,  $CD_2Cl_2$ ):  $\delta$  53.08 (br).

[Pt(ppy)(bdt){Au(PCy<sub>3</sub>)}<sub>2</sub>]ClO<sub>4</sub> (4a). To a solution of [AuCl-(PCy<sub>3</sub>)] (117 mg, 0.23 mmol) in acetone (25 mL) was added AgClO<sub>4</sub> (47 mg, 0.23 mmol). The resulting suspension was stirred for 5 min and filtered through Celite to remove the precipitate of AgCl. The clear filtrate was added to a suspension of 3a (220 mg, 0.23 mmol) in acetone (65 mL). The mixture was stirred for 15 min and filtered through anhydrous MgSO<sub>4</sub> to remove a small amount of insoluble material. The solvent was removed under vacuum, and the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (3 mL). The slow addition of Et<sub>2</sub>O (30 mL) at 0 °C led to precipitation of a pale-yellow solid, which was filtered off, washed with  $Et_2O$  (2 × 3 mL), and vacuum-dried to give 4a. Yield: 246 mg, 69%. Anal. Calcd for C<sub>53</sub>H<sub>78</sub>Au<sub>2</sub>ClNO<sub>4</sub>P<sub>2</sub>PtS<sub>2</sub>: C, 41.24; H, 5.09; N, 0.91; S, 4.15. Found: C, 41.24; H, 5.48; N, 1.11; S, 3.80. Mp: 245 °C. <sup>1</sup>H NMR (400.91 MHz, CDCl<sub>3</sub>):  $\delta$  8.86 (dd, <sup>3</sup> $J_{\rm HH}$  = 5.8 Hz,  ${}^{3}J_{HPt} = 36 \text{ Hz}, 1 \text{ H, py6}), 8.15 \text{ (t, } {}^{3}J_{HH} = 5.8 \text{ Hz}, 1 \text{ H, py4}), 7.95 \text{ (d,}$  ${}^{3}J_{HH} = 6.0 \text{ Hz}, 1 \text{ H, py3}, 7.73 - 7.83 \text{ (m, 2 H, bdt)}, 7.64 \text{ (d, } {}^{3}J_{HH} = 6.3 \text{ (m, 2 H, bdt)}$ Hz, 2 H, Ph6), 7.61 (s with satellites,  ${}^{3}J_{HPt} = \sim 24$  Hz, 1 H, Ph3), 7.32 (m, 1 H, py5), 7.07-7.21 (m, 4 H, Ph4, Ph5, bdt), 1.5-1.78 (m, 36 H,

Cy), 0.88–1.24 (m, 30 H, Cy).  $^{13}$ C{ $^{1}$ H} NMR (75.45 MHz, CDCl<sub>3</sub>):  $\delta$  166.7 (py2), 151.72 (Ph2), 150.1 (py6), 144.1 (Ph1), 140.1 (py4), 139.3 (C1/C2, bdt), 134.5 (C, bdt), 133.5, 132.0 (Ph3, C1/C2, C3/C6, bdt), 130.6 (Ph5), 126.3, 126.1 (C4/C5, bdt), 124.7 (Ph6), 124.5 (Ph4), 123.7 (py5), 120.0 (py2), 33.2 (d,  $^{1}$ J<sub>CP</sub> = 28.3 Hz, C1, Cy), 30.5 (C2, Cy), 26.7 (d,  $^{3}$ J<sub>CP</sub> = 12.2 Hz, C3, Cy), 25.5 (C4, Cy).  $^{31}$ P{ $^{1}$ H} NMR (162.3 MHz, CDCl<sub>3</sub>):  $\delta$  54.94 (br).

[Pt(tbpiq)(bdt){Au(PCy<sub>3</sub>)}<sub>2</sub>]ClO<sub>4</sub> (4b). This yellow complex was obtained as described for 4a, from [AuCl(PCy<sub>3</sub>)] (91 mg, 0.18 mmol), AgClO<sub>4</sub> (37 mg, 0.18 mmol), and 3b (165 mg, 0.15 mmol). Yield: 219 mg, 86%. Anal. Calcd for C<sub>61</sub>H<sub>88</sub>Au<sub>2</sub>ClNO<sub>4</sub>P<sub>2</sub>PtS<sub>2</sub>: C, 44.41; H, 5.38; N, 0.85; S, 3.89. Found: C, 44.24; H, 5.64; N, 0.87; S, 3.57. Mp: 152 °C.  $^{1}$ H NMR (400.91 MHz, CDCl<sub>3</sub>):  $\delta$  8.86 (d,  $^{3}J_{HH}$  = 8.8 Hz, 1 H, Iq8), 8.70 (dd,  ${}^{3}J_{HH} = 6.4 \text{ Hz}$ ,  ${}^{3}J_{HPt} = 32 \text{ Hz}$ , 1 H, Iq3), 8.07 (d,  ${}^{3}J_{HH} =$ 8.4 Hz, 1 H, Ph6), 8.01 (d,  ${}^{3}J_{HH} = 8.4$  Hz, 1 H, Iq5), 7.89 (t,  ${}^{3}J_{HH} = 7.2$ Hz, 1 H, Iq6), 7.75–7.86 (m, 4 H, Ph3, Iq7, bdt), 7.57 (d,  ${}^{3}J_{HH} = 6.4$ Hz, 1 H, Iq4), 7.28 (dd,  ${}^{3}J_{HH} = 8.6$  Hz,  ${}^{3}J_{HH} = 1.8$  Hz, 1 H, Ph5), 7.15–7.20 (m, 2H, bdt), 1.44–1.79 (m, 36 H, Cy), 1.40 (s, 9 H, t-Bu), 0.78–1.19 (m, 30 H, Cy).  $^{13}$ C{ $^{1}$ H} NMR (100.81 MHz, CDCl<sub>3</sub>):  $\delta$ 167.5 (Iq1), 154.1 (Ph4), 151.6 (Ph2), 142.6 (Ph1), 142.4 (Iq3), 139.3 (C1/C2, bdt), 137.4 (Iq4a), 134.7 (C1/C2, bdt), 133.6 (C3/ C6, bdt), 132.3 (Iq6), 132.0 (C3/C6, bdt), 130.7 (Ph3), 129.7 (Ph6), 129.2 (Iq7), 127.9 (Iq5), 126.7 (Iq8), 126.2, 126.3 (C4/C5, bdt), 125.7 (Iq8a), 121.1 (Iq4, Ph5), 35.2 (CMe<sub>3</sub>), 33.1 (d,  ${}^{1}J_{CP} = 28.2 \text{ Hz}$ , C1, Cy), 31.3 (CMe<sub>3</sub>), 30.5 (C2, Cy), 26.7 (d,  ${}^{3}J_{\text{CP}} = 12.1$  Hz, C3, Cy), 25.5 (C4, Cy).  ${}^{31}\text{P}\{{}^{1}\text{H}\}$  NMR (162.3 MHz, CDCl<sub>3</sub>):  $\delta$  54.87

### ■ RESULTS AND DISCUSSION

**Syntheses.** The cyclometalated compounds  $[Pt(C^N)-(HC^N)Cl]$   $[HC^N] = Hppy$  (1a) or Htbpiq (1b) were chosen as precursors because they can be easily obtained in high yields. Their reactions with 1,2-benzenedithiol, t-BuOK, and  $Bu_4NCl$  in a 1:1:2:1 molar ratio in  $CH_2Cl_2/MeOH$  afforded the complexes  $Bu_4N[Pt(C^N)(bdt)]$  [bdt = 1,2-benzenedithiolate;  $C^N = ppy$   $(Bu_4N2a)$  or tbpiq  $(Bu_4N2b)$  in good yields (Scheme 1). Both derivatives are intensely colored compounds (red and violet, respectively) and stable in the solid state. However, they slowly decompose in solution in the presence of air and ambient light, as evidenced by the loss

### Scheme 1

(i)  $H_2bdt$ , 2 t-BuOK,  $Bu_4NCl$  ( $Q = Bu_4N^*$ ) or  $H_2bdt$ , 2 t-BuOK ( $Q = K^*$ ). (ii)  $[Au(OClO_3)(PCy_3)]$  ( $Q = Bu_4N^*$ ) or  $[AuCl(PCy_3)]$  ( $Q = K^*$ ). (iii)  $[Au(OClO_3)(PCy_3)]$ .

of color. This decomposition is probably caused by a photooxidation process, which is common for platinum(II) diiminedithiolate complexes that display low-energy charge-transfer absorptions.  $^{40-42}$ 

We initially attempted coordination of [Au(PCy<sub>3</sub>)]<sup>+</sup> units to the anionic complexes Bu<sub>4</sub>N2a and Bu<sub>4</sub>N2b by reacting them with acetone solutions of [Au(OClO<sub>3</sub>)(PCy<sub>3</sub>)], which, in turn, were generated from [AuCl(PCy<sub>3</sub>)] and AgClO<sub>4</sub>.<sup>33</sup> Thus, the reaction of Bu<sub>4</sub>N2a with 1 equiv of [Au(OClO<sub>3</sub>)(PCy<sub>3</sub>)] in acetone gave the neutral complex 3a, which precipitated from the reaction mixture upon partial evaporation of the solvent and was therefore easily separated from the other reaction product, Bu<sub>4</sub>NClO<sub>4</sub>. When starting from Bu<sub>4</sub>N2b, this method afforded the analogous complex 3b, but its solubility in common solvents turned out to be very similar to that of Bu<sub>4</sub>NClO<sub>4</sub>, and hence the two products could not be conveniently separated. For this reason, we devised an alternative procedure to avoid the presence of Bu<sub>4</sub>N<sup>+</sup> salts, which consisted of the in situ generation of the potassium salt of the dithiolato complex (K2a and K2b) from 1a or 1b, 1,2-benzenedithiol, and t-BuOK, and its reaction with [AuCl(PCy<sub>3</sub>)]. Given the anionic nature of the dithiolato complexes, we expected that the S atoms would have sufficient coordinating ability to displace the chloro ligand from the gold precursor. This procedure allowed the preparation of both 3a and 3b in good yields. The cationic trinuclear derivatives  $[Pt(C^N)(bdt)\{Au(PCy_3)\}_2]ClO_4$   $[C^N = ppy]$ (4a), tbpiq (4b)] were prepared by reacting 3a or 3b with 1 equiv of [Au(OClO<sub>3</sub>)(PCy<sub>3</sub>)] in acetone. Unlike their mononuclear precursors, the heterometallic derivatives are stable in solution in the presence of air and ambient light.

**Crystal Structures.** The crystal structure of complex **3b** is shown in Figure 1. Selected bond distances and angles are listed in Table 2. The molecule consists of a  $[Pt(tbpiq)(bdt)]^-$  unit with one  $[Au(PCy_3)]^+$  unit bonded to the S atom trans to the arylic C atom. The other possible structural isomer, with the  $[Au(PCy_3)]^+$  unit bonded to the S atom trans to the N atom, was not present in the crystal. The Pt atom is in a slightly

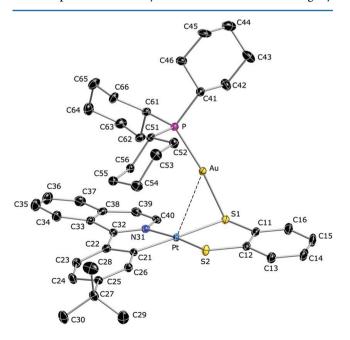


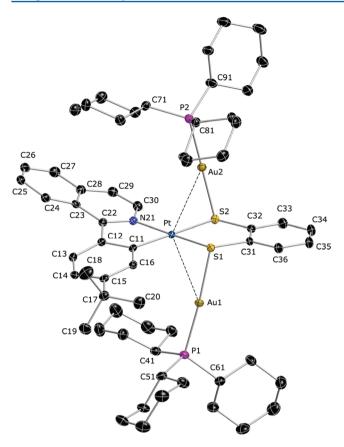
Figure 1. Thermal ellipsoid representation (50% probability) of the structure of complex 3b. H atoms have been omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 3b

Pt-C21	2.001(3)	Au-S1	2.3621(8)
Pt-N31	2.051(3)	S1-C11	1.774(3)
Pt-S2	2.2653(8)	S2-C12	1.752(3)
Pt-S1	2.3781(8)	N31-C32	1.346(4)
Pt-Au	2.92940(17)	N31-C40	1.363(4)
Au-P	2.2698(8)		
C21-Pt-N31	79.80(12)	C11-S1-Au	105.91(11)
C21-Pt-S2	94.42(10)	C11-S1-Pt	102.73(12)
N31-Pt-S1	97.54(8)	Au-S1-Pt	76.34(2)
S2-Pt-S1	88.23(3)	C12-S2-Pt	105.22(12)
P-Au-S1	172.68(3)		

distorted square-planar environment (the mean deviation from the plane C21-N31-Pt-S1-S2 is 0.015 Å); the most significant deviation from the ideal square-planar geometry arises from the narrow bite angle of the tbpiq ligand, namely,  $C21-Pt-N31 = 79.80(12)^{\circ}$ . The the third ligand is not planar because of the steric repulsion between the H atoms attached to C23 and C34, which leads to an angle of 22.6° between the isoquinoline and phenyl mean planes; a similar arrangement was found for the 1-phenylisoquinoline (piq) ligand in [Pt(piq)(Hpiq)Cl].<sup>43</sup> Of the two possible conformations, the tbpiq ligand adopts the one in which the tert-butylphenyl group bends away from the [Au(PCy<sub>3</sub>)]<sup>+</sup> unit reasonably to minimize the steric repulsions between the tert-butyl substituent and the phosphine. The bond distances Pt-C21 and Pt-N31 are similar to those found for cyclometalated complexes containing ppy and derivatives. 44 The Pt-S2 bond distance (trans to N) of 2.2653(8) Å is similar to that found in [Pt(bdt)(bpy)] (2.250 and 2.244 Å;<sup>40</sup> bpy = 2,2'-bipyridyl) and related complexes.<sup>2,45</sup> The appreciably longer Pt-S1 bond distance of 2.3781(8) Å is attributable to the trans influence of the arylic donor atom C21. The Au atom is in an almost linear environment, and the Au-S1 bond distance of 2.3621(8) Å is only slightly longer than those found in  $[{Au(PPh_3)}_2(bdt)]$  and  $[{Au(PPh_3)}_2(tdt)]$ (range 2.316-2.325 Å; <sup>46</sup> tdt = 2,3-toluenedithiolate). The arrangement of the Au atom with respect to the platinum coordination mean plane is defined by the torsion angle Au-S1-Pt-S2 of 95.78° and the angle Au-S1-Pt of 76.34(2)°. The latter is appreciably narrower than that found for the cationic complex  $[Pt{S_2C=(t-Bu-fy)}(dbbpy){Au(PCy_3)}]^+$  $[91.93(2)^{\circ};^{33}$  t-Bu-fy = 2,7-di-tert-butylfluoren-9-ylidene] and thus leads to a significantly shorter Au---Pt contact in 3b [2.92940(17) vs 3.3108(2) Å]. This difference is attributable to the anionic character of the platinum precursor 2b, which allows stronger interaction with the [Au(PCy<sub>3</sub>)]<sup>+</sup> unit. Complexes with weak Au---Pt contacts shorter than 3.0 Å are scarce and usually contain bridging diphosphines, as in  $[{Pt(CN)_2}Au(\mu-dcpm)_2]PF_6$  [2.953 Å; dcpm = 1,1-bis-dicyclohexylphosphino)methane],<sup>47</sup> [ ${PtCl(Ph)}Au(\mu-dcpm)_2$ ] dppm)<sub>2</sub>]PF<sub>6</sub> (2.965 Å),<sup>48</sup> and [{Pt(CCPh)}Au( $\mu$ -dppm)<sub>2</sub>]X [X = PF<sub>6</sub> (2.910 Å),<sup>49</sup> SbF<sub>6</sub> (2.927 Å)<sup>30</sup>], while Au····Pt contacts supported by bridging sulfido or thiolato ligands lie in the range  $3.053-3.730\,$  Å.  $^{31,33,50}$ 

Complex 4b crystallized with one molecule of  $CH_2Cl_2$  in the asymmetric unit. The molecular structure of the cation is shown in Figure 2, and selected bond distances and angles are given in Table 3. The structure is composed of one  $[Pt(tbpiq)(bdt)]^-$  unit, with two  $[Au(PCy_3)]^+$  units bonded to the S atoms of the



**Figure 2.** Thermal ellipsoid representation (50% probability) of the cation of complex **4b**. H atoms have been omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for 4b·CH<sub>2</sub>Cl<sub>2</sub>

Pt-C11	2.016(2)	Au2-P2	2.2633(7)
Pt-N21	2.052(3)	Au1-S1	2.3388(6)
Pt-S1	2.2734(6)	Au2-S2	2.3586(6)
Pt-S2	2.37815(6)	S1-C31	1.790(3)
Pt-Au1	3.14862(15)	S2-C32	1.780(3)
Pt-Au2	3.01407(14)	N21-C22	1.353(3)
Au1-P1	2.2586(6)	N31-C40	1.371(3)
C11-Pt-N21	80.35(9)	C31-S1-Au1	102.35(8)
C11-Pt-S1	94.98(7)	C31-S1-Pt	105.57(8)
N21-Pt-S2	96.16(6)	Au1-S1-Pt	86.10(2)
S2-Pt-S1	88.64(2)	C32-S2-Au2	99.36(8)
P1-Au1-S1	175.21(2)	C32-S2-Pt	102.97(9)
P2-Au2-S2	177.18(2)	Au2-S2-Pt	79.027(19)
Au1-Pt-Au2	134.697(4)		

dithiolate. The coordination environment and bond distances around the Pt atom are very similar to those found for **3b**. The  $[Au(PCy_3)]^+$  units lie on opposite sides of the platinum coordination mean plane and form torsion angles Au1-S1-Pt-S2 and Au2-S2-Pt-S1 of  $104.45^\circ$  and  $95.10^\circ$ , respectively. The Au2-S2 bond distance (unit trans to C11) of 2.3586(6) Å is very similar to the corresponding distance found for **3b**, while the Au1-S1 distance (unit trans to N) of 2.3388(6) Å is somewhat shorter. The angles Au1-S1-Pt of  $86.10(2)^\circ$  and Au2-S2-Pt of  $79.027(19)^\circ$  are wider than those found in **3b** and lead to longer  $Au\cdots Pt$  contacts in **4b**  $[Pt\cdots Au2, 3.01407(14); Pt\cdots Au1, 3.14862(15) Å], which is$ 

attributable to a diminished electrostatic contribution to these interactions because of the cationic character of the complex. The arrangement of the tbpiq ligand is similar to that observed for **3b**, with the phenyl ring mean plane subtending an angle of  $27.4^{\circ}$  with the isoquinoline ring. The conformation adopted by this ligand is also the one in which the *tert*-butylphenyl group bends away from the  $[Au(PCv_3)]^+$  unit trans to it.

NMR Spectra and Dynamic Behavior. The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of the platinum(II) complexes Bu<sub>4</sub>N2a and Bu<sub>4</sub>N2b show the expected chemical inequivalence of all of the H and C atoms of the bdt ligand, with atoms H3, H6, C1, and C2 being the most affected by the different electronic properties of the phenyl and pyridine or isoquinoline groups.

The heterometallic derivatives **3a**, **3b**, **4a**, and **4b** were expected to undergo dynamic processes in solution involving migration of the  $[Au(PCy_3)]^+$  units between the S atoms of the dithiolato ligand. We have previously shown that such processes take place in the related complexes  $[M\{S_2C=(t-Bu-fy)\}\{dbbpy\}\{Au(PCy_3)\}]^+$  and  $[M\{S_2C=(t-Bu-fy)\}_2\{Au(PCy_3)\}_2]$  (M=Pd,Pt). In that study, we also proved that stronger metallophilic contacts lead to higher rate constants for the migration process and concluded that they facilitate the migration by lowering the energy of the transition state. The possible dynamic processes in the present heterometallic derivatives were investigated by means of variable-temperature  $^{31}P\{^1H\}$  NMR studies.

The cases of the trinuclear derivatives  $\bf 4a$  and  $\bf 4b$  allow a more detailed analysis and are presented first. These complexes give a very broad resonance in the  $^{31}P\{^1H\}$  NMR spectra at room temperature, which splits into two sharp resonances that appear at 53.4 and 54.8 ppm  $\bf (4a)$  or 53.2 and 54.9 ppm  $\bf (4b)$  at 202 K in CDCl<sub>3</sub> (Figure 3 and the Supporting Information) and coalesce at 271  $\bf (4a)$  or 296 K  $\bf (4b)$ . The two distinct

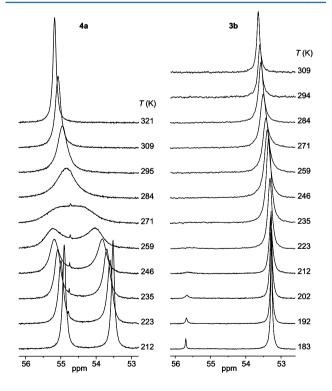


Figure 3.  $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$  NMR spectra of 4a in CDCl $_{3}$  and 3b in CD $_{2}\mathrm{Cl}_{2}$  at various temperatures.

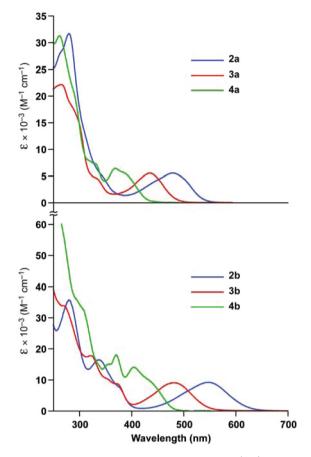


Figure 4. Electronic absorption spectra of 2–4a (top) and 2–4b (bottom) in a  $CH_2Cl_2$  solution (ca.  $5 \times 10^{-5}$  M) at 298 K.

resonances arise because the [Au(PCy<sub>3</sub>)]<sup>+</sup> units are bonded to inequivalent S atoms, one of them trans to the arylic C atom and the other trans to the N atom. The exchange between the environments of the P atoms can only be achieved via the concerted migration of the [Au(PCy<sub>3</sub>)]<sup>+</sup> units to the opposite S atom (Scheme 2). In the case of the ppy derivative 4a, this process leads to the interconversion of two enantiomeric forms. In the case of 4b, there are two possible enantiomeric pairs of diastereomers that differ in the conformation of the tbpiq ligand and could give rise to four resonances at low temperatures, as both migration of the [Au(PCy<sub>3</sub>)]<sup>+</sup> units and interconversion between the tbpiq conformations slow down. In order to check this possibility, we registered the <sup>31</sup>P{<sup>1</sup>H} NMR spectra of **4b** in CD<sub>2</sub>Cl<sub>2</sub> between 202 and 183 K, but only a further sharpening of the two resonances was observed (see the Supporting Information). This means either

that the conformational change of the tbpiq ligand does not have an observable effect on the chemical shifts of the phosphorus resonances or that only the most stable enantiomeric pair is observed.

The Arrhenius and Eyring activation parameters corresponding to the exchange process in 4a and 4b were obtained by means of line-shape analysis of the temperature-dependent <sup>31</sup>P{<sup>1</sup>H} NMR resonances <sup>52</sup> and are listed in Table 4. The negative values of the activation entropies are compatible with the unimolecular nature of migration and indicate that the transition state is more symmetrical than the ground state. It is therefore reasonable to propose a transition state containing equivalent [Au(PCy<sub>3</sub>)]<sup>+</sup> units and strengthened Pt···Au metallophilic interactions, which is depicted in Scheme 2 for 4b. The activation enthalpy is significantly higher for the tbpiq derivative 4b than for its ppy homologue 4a. Because Au-S bond and Pt...Au interaction energies are expected to be very similar for both complexes, a reasonable explanation for this is that migration of the [Au(PCy<sub>3</sub>)]<sup>+</sup> units in 4b requires the concomitant conformational change of the tbpiq ligand (Scheme 2). This would allow interconversion between two enantiomeric forms, reasonably the pair found in the crystal structure, in which the steric repulsions between the phosphines and the tert-butylphenyl group are minimal.

In the cases of the monoaurated derivatives 3a and 3b, two structural variations are possible because the [Au(PCy<sub>3</sub>)]<sup>+</sup> unit can be attached to either the S atom trans to the arvlic C atom or the S atom trans to the N atom. For each of these possibilities, there are two possible enantiomers in the case of 3a and two diastereomeric pairs of enantiomers in the case of 3b. If all of the possible isomers were present, one should observe two (3a) or four (3b) resonances of unequal intensity in the <sup>31</sup>P{<sup>1</sup>H} NMR spectra at low temperatures. Complex 3a gives a sharp resonance at 53.4 ppm in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum at room temperature in CD<sub>2</sub>Cl<sub>2</sub>, which does not split upon cooling to 183 K, suggesting that migration of the [Au(PCy<sub>3</sub>)]<sup>+</sup> unit between the S atoms does not take place, one of the expected structural isomers is present in undetectable concentrations, or the splitting takes place at lower temperatures. The room-temperature 31P{1H} NMR spectrum of the tbpiq derivative 3b in CD<sub>2</sub>Cl<sub>2</sub> displays a relatively broad resonance at 53.6 ppm, which splits at 183 K into two sharp resonances of highly unequal intensity at 53.3 and 55.7 ppm (Figure 3), which correspond to different species in relative proportions of 0.95 and 0.05, respectively, as calculated from the integration values. The difference in the chemical shift between the two resonances (2.4 ppm) is even greater than that found for the inequivalent  $[Au(PCy_3)]^+$  units in 4a and 4b (1.4) and 1.7 ppm, respectively), which suggests that they correspond to different structural isomers. On the basis of the method

### Scheme 2

Table 4. Arrhenius and Eyring Activation Parameters for the Exchange Processes in 4a and 4b

compd	$E_{\rm A}$ (kcal mol <sup>-1</sup> )	$\Delta H^{\ddagger}$ (kcal mol <sup>-1</sup> )	$\Delta S^{\ddagger}$ (cal mol <sup>-1</sup> K <sup>-1</sup> )	$T_{\rm coal}$ (K)	$\Delta G_{\rm coal}^{\dagger}$ (kcal mol <sup>-1</sup> )
4a	$8.0 \pm 0.4$	$7.5 \pm 0.4$	$-18 \pm 1$	271	$12.4 \pm 0.1$
4b	$11.9 \pm 0.4$	$11.3 \pm 0.4$	$-7 \pm 1$	296	$13.5 \pm 0.1$

reported by Shanan-Atidi and Bar-Eli,<sup>51</sup> the NMR data allowed an estimation of the free energies of activation  $\Delta G^{\ddagger} = 13.8$  and 12.2 kcal mol<sup>-1</sup> for the major and minor species, respectively, at the coalescence temperature,  $T_{\rm coal}$  = 271 K. The difference in the free energy between the two species can be obtained from the equation  $\Delta G_0 = -RT \ln K$ , which yields the value  $\Delta G_0 =$ 1.6 kcal mol<sup>-1</sup> at 271 K. The values of the free energies of activation are consistent with an exchange process involving migration of the [Au(PCy<sub>3</sub>)]<sup>+</sup> unit between the S atoms and probably also the concomitant conformational change of the tbpiq ligand. It is reasonable that the most intense resonance corresponds to the enantiomeric pair found in the crystal structure (see above), with the [Au(PCy<sub>3</sub>)]<sup>+</sup> unit attached to the S atom trans to the arylic C atom and the phenyl ring of the tbpiq ligand bent away from this unit. The other resonance should correspond to the isomers with the [Au(PCy<sub>3</sub>)]<sup>+</sup> unit bonded to the S atom trans to the N atom and, possibly, the opposite tbpiq conformation. The strong trans influence of the arylic C atom explains the different stabilities of the structural isomers because it causes a weakening of the corresponding Pt-S bond, and this S atom must therefore have a higher coordinating ability toward the Au<sup>I</sup> center than the other S atom. On the basis of this reasoning, we assume that the only resonance observed for 3a corresponds to the enantiomeric pair with the [Au(PCy<sub>3</sub>)]<sup>+</sup> unit attached to the S atom trans to the arylic C atom.

The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of the heterometallic derivatives are not sensitive to the exchange processes mentioned above. Coordination of the  $[\text{Au}(\text{PCy}_3)]^+$  units to the dithiolates 2a and 2b affects mainly the resonances of the C1/C2 atoms of the bdt ligand. Thus, for the monoaurated derivatives 3a and 3b, one of these resonances is upfield-shifted by ca. 10 ppm relative to the corresponding resonance in the mononuclear precursors, while a comparable effect is observed for both resonances in the cases of the diaurated derivatives 4a and 4b (Table 5).

Table 5. <sup>13</sup>C{<sup>1</sup>H} NMR Resonances of the C1/C2 Atoms of the bdt Ligand for the Complexes Mentioned in This Work<sup>a</sup>

compd	$\delta$ (C1/C2)	compd	$\delta(\text{C1/C2})$	
Bu <sub>4</sub> N2a	148.8, 144.5	$Bu_4N2b$	149.5, 145.0	
3a	148.6, 135.6	3b	150.5, 134.9	
4a	139.3, 133.5	4b	139.3, 134.7	
<sup>a</sup> In ppm, CDCl <sub>3</sub> solution.				

**Electronic Absorption Spectra.** The UV-vis absorption spectra were measured in  $CH_2Cl_2$  at 298 K for all of the new compounds, and the results are summarized in Table 6. The data for  $1a^{44,53}$  and the ligand precursor Htbpiq are included for comparison. The tbpiq derivative 1b gives rise to intense absorptions between 200 and 340 nm, which match the absorption range observed for free Htbpiq, and are thus assignable to metal-perturbed  $\pi$ - $\pi$ \* LC transitions localized on the tbpiq and Htbpiq ligands. The less intense absorptions with  $\lambda_{\rm max} > 340$  nm are not observed for free Htbpiq and can be assigned to MLCT transitions. In view of their significant

Table 6. Electronic Absorption Data for Compounds 1–4a,b in CH<sub>2</sub>Cl<sub>2</sub> Solution (ca.  $5 \times 10^{-5}$  M) at 298 K

compd	$\lambda/\mathrm{nm}$ ( $\varepsilon/\mathrm{M}^{-1}$ c	$m^{-1}$ )
Htbpiq	229 (25100), 283 (8400), 324 (6400)	
1a	260 (28700), 280 (18100), 314 (7600 384 (2300), 402 (2100)	), 328 (5800), 348 (4100),
1b	276 (57900), 320 (21000), 350 (1700 382 (9300), 432 (5300), 454 (5100)	0), 365 (19900), )
2a	280 (31600), 336 (5700), 479 (5500)	
2b	280 (35500), 337 (16400), 373 (8100	), 546 (9200)
3a	265 (22100), 329 (4600), 435 (5500)	
3b	269 (33900), 323 (17700), 370 (8800	), 482 (9100)
4a	261 (31100), 330 (7200), 368 (6300)	
4b	258 (64000), 304 (33200), 370 (1790	0), 404 (13900)

extinction coefficients, the corresponding electronic states are assigned as <sup>1</sup>MLCT. We note, however, that the assignment to pure MLCT states is a simplification because these states usually mix with LC states in differing proportions. <sup>54,55</sup> The shape of the lowest-energy feature, which is centered at 454 nm, suggests that it results from two unresolved absorptions (Figure 5). Their energies are appreciably lower that those of

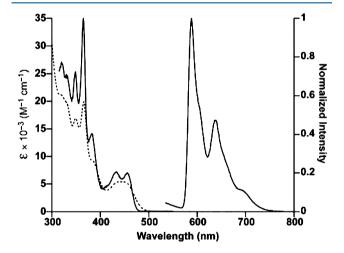


Figure 5. Excitation and emission spectra of complex 1b in PrCN glass at 77 K (—) and absorption spectrum in a  $CH_2Cl_2$  solution at 298 K (---).

the two overlapping MLCT absorptions observed for the ppy analogue 1a (384 and 402 nm), 44,53 which is indicative of a significantly lower highest occupied molecular orbital (HOMO)—lowest unoccupied molecular orbital (LUMO) energy gap in 1b. This fact can be ascribed to both a higher HOMO energy, because of the increased donor ability of the tert-butyl-substituted phenyl ring, and a lower LUMO energy, because of the extended aromatic system of the isoquinoline fragment, compared to 1a. It is also noteworthy that the absorptions of 1b exhibit considerably higher molar extinction coefficients than those of 1a, which is also observed for all of the absorptions of the other ppy and tbpiq complexes described in this work.

The mononuclear dithiolato complexes  $Bu_4N2a$  and  $Bu_4N2b$  give intense absorptions in the UV region that are assignable to  $\pi-\pi^*$  transitions within the bdt and ppy or tbpiq ligands. A very broad band is observed in the visible region, whose energy is solvent-dependent (Table 7), although variations with the

Table 7. Lowest-Energy Absorption Band for Complexes Bu<sub>4</sub>N2a, Bu<sub>4</sub>N2b, 3a, and 3b in Solvents of Differing Polarity<sup>a</sup>

		$\lambda_{ ext{max}}$ nm			
solvent	Bu <sub>4</sub> N2a	Bu <sub>4</sub> N <b>2b</b>	3a	3b	
acetonitrile	474	540	426	470	
$CH_2Cl_2$	479	546	435	482	
acetone	496	570	440	485	
toluene	506	576	456	512	
$^{a}5 \times 10^{-5} \text{ M}.$					

solvent polarity are small and do not correlate linearly. In addition, an incipient shoulder is observed in toluene, suggesting that more than one electronic transition is involved. The characteristics of this band are similar to those of the highly solvatochromic band generally observed for platinum(II) diiminedithiolates, which has both MLCT and LLCT character and has been referred to as charge transfer to diimine. 22,56 This parallelism has also been noted for the lowest-energy absorption of previously reported complexes of the types  $[Pt(ppy)(S^S)]^{-21}$  and  $[Au(ppy)(S^S)]^{1}$ , where S^S is a sulfur-rich dithiolate, as well as [Au(ppy)(tdt)] (tdt = 2,3toluenedithiolate),58 and led to an assignment as a chargetransfer transition from a mixed metal/dithiolate HOMO and a LUMO that is a  $\pi^*$  orbital on the pyridine fragment of the ppy ligand. Analogous orbital contributions to the frontier orbitals in 2a and 2b are to be expected. The lower energy observed for this absorption in 2b relative to 2a can be explained by the lower energy of the  $\pi^*$  orbitals of the isoquinoline fragment, leading to a lower LUMO energy. On the other hand, a HOMO of mixed Pt(d)/S(p) orbital parentage is a common feature in neutral and anionic platinum(II) dithiolato complexes. 22,33,56,59 We therefore propose a mixed ML'CT/ LL'CT character (L = bdt;  $L' = C^N$ ) for the lowest-energy absorption in 2a and 2b. The multiplicity of the corresponding electronic state can be assigned as a singlet in view of the relatively high extinction coefficients. The diminished solvatochromism of these complexes compared to platinum(II) diiminedithiolates is possibly a consequence of their anionic character, which may become the dominant factor in solvation of the ground and excited states. Recent time-dependent density functional theory calculations on the related dithiocarbamate complexes  $[Pt(C^N)(S^S)]$   $(C^N = bzq =$ benzo[h]quinoline; S^S = pyrrolidinedithiocarbamate, dimethyldithiocarbamate)<sup>18</sup> have shown that the HOMO is composed of orbitals located on the phenyl ring of the bzq ligand, the dithiocarbamate, and the Pt atom. The participation of the phenyl ring orbitals in the HOMO for 2a and 2b, which would add a certain L'C character ( $L' = C^N$ ) to the lowestenergy transition, cannot be ruled out but is expected to be smaller given the dianionic character of the bdt ligand and thus the higher energy of the S orbitals.

The absorption spectra of the heterometallic derivatives are compared with those of their mononuclear precursors in Figure 4. Introduction of the  $[Au(PCy_3)]^+$  units results in two successive hypsochromic shifts of the lowest-energy absorption

band on going from the platinum complexes to the monoaurated and then to the diaurated derivatives. This effect can be associated with a decrease in the energy of both the S and Pt orbitals caused by the bonding to the Au<sup>I</sup> centers and the increasing positive charge, which result in lower HOMO energies and therefore higher HOMO-LUMO energy gaps. The metallophilic Pt...Au contacts are expected to alter the energy of the Pt orbitals, but their impact in the HOMO energies must be less important and cannot be ascertained. The monoaurated derivatives 3a and 3b display a moderate solvatochromism (Table 7), which parallels that of their parent complexes Bu<sub>4</sub>N2a and Bu<sub>4</sub>N2b. In the cases of the diaurated derivatives 4a and 4b, the lowest-energy absorption is narrower and resolves into two overlapping components, with variations with the solvent polarity being very small. Because LL'CT transitions usually lead to typically broad and highly solvatochromic bands, 41,60 the mentioned characteristics indicate that complexes 3a and 3b still retain a considerable degree of LL'CT character for the lowest-energy absorption, while it is drastically diminished for 4a and 4b as a consequence of the much lower energy of the S orbitals and, hence, their reduced participation in the HOMO.

**Excitation and Emission Spectra.** All of the new compounds are photoluminescent in the solid state at 298 K and in PrCN glasses at 77 K. With the exception of 4a, they are also emissive in a  $CH_2Cl_2$  solution at 298 K. The excitation and emission data are summarized in Table 8.

The emission spectrum of 1b in  $CH_2Cl_2$  at 298 K is relatively narrow and shows an incipient vibronic structure, which is clearly defined at 77 K in PrCN glass (Figure 5). The corresponding excitation spectra match the room-temperature absorption, with the lowest-energy feature clearly resolved into two bands (432 and 455 nm) at low temperature. The room-temperature decay time of 4.16  $\mu$ s falls in the range observed for mixed  $^3$ LC/MLCT excited states in related cyclometalated platinum(II) complexes, and thus this assignment is appropriate for 1b.

The platinum complexes Bu<sub>4</sub>N2a and Bu<sub>4</sub>N2b and their monoaurated derivatives 3a and 3b give rise to broad and nearly symmetrical emission bands in a CH<sub>2</sub>Cl<sub>2</sub> solution at 298 K. Notably, the emission of the ppy complex 3a is very weak under these conditions and did not allow measurement of the lifetime and quantum yield data with acceptable accuracy. Of the diaurated complexes, only the tbpiq derivative 4b is emissive in a CH<sub>2</sub>Cl<sub>2</sub> solution at room temperature, giving a somewhat structured emission. In all cases, the corresponding excitation spectra closely reproduce the lowest-energy band observed in the absorption spectra (see Figure 6 for the tbpiq series). The emission spectra in the solid state at 298 K are, in general, very similar in shape and energy to those in a fluid CH<sub>2</sub>Cl<sub>2</sub> solution (see the Supporting Information). It is worth noting that both 4a and 4b are brightly emissive and give rise to structured emission bands in the solid state. The emission spectra are sharper at 77 K in PrCN glasses (Figure 7). Significant blue shifts relative to the room-temperature emissions are observed for Bu<sub>4</sub>N2a and Bu<sub>4</sub>N2b (1576 and 669 cm<sup>-1</sup>, respectively) and the monoaurated derivatives 3a and 3b (2244 and 894 cm<sup>-1</sup>, respectively), which can be ascribed to a rigidochromic effect commonly observed for diimine<sup>22,33,61</sup> and cyclometalated<sup>62</sup> complexes, and are a sign of the charge-transfer character of the emitting state.<sup>63</sup> In the cases of 3a and 3b, the low-temperature spectra also reveal some vibronic structure, which is more evident for the tbpiq

Table 8. Excitation and Emission Data for 1-4a,ba

compd	medium (T/K)	$\lambda_{ m exc}/{ m nm}$	$\lambda_{ m em}/{ m nm}$	$ au/\mu$ s
1a <sup>b</sup>	toluene	n <sub>exc</sub> / IIIII	λ <sub>em</sub> /IIII 479, 515,	11.2
	(77)		547	
	toluene (298)		489, 523, 555	0.641
	solid (298)		498, 539, 572	0.473
1b	PrCN (77)	365, 382, 432, 455	588, 637, 690	7.38
	$CH_2Cl_2$ (298)	371, 445	599, 634, 654	4.16
	solid (298)	369, 465, 539	606, 635, 656	1.05 (41%), 3.25 (26%), 0.28 (33%)
Bu <sub>4</sub> N2a	PrCN (77)	455, 481	554	19.8
	CH <sub>2</sub> Cl <sub>2</sub> (298)	476	607, 659	1.39
	solid (298)	368, 540	603, 655	1.56 (66%), 3.21 (34%)
$Bu_4N2b$	PrCN (77)	374, 458–555	655	7.40
	$ \begin{array}{c} \text{CH}_2\text{Cl}_2\\ \text{(298)} \end{array} $	493	685	1.11
	solid (298)	369, 465, 613	682	0.60 (49%), 1.22 (51%)
3a	PrCN (77)	427	503	6.78
	$CH_2Cl_2$ (298)	440	567	_
	solid (298)	365, 480	532	1.34 (73%), 4.26 (27%)
3b	PrCN (77)	373, 452, 480	600, 655	7.20
	$ \begin{array}{c} \text{CH}_2\text{Cl}_2\\ \text{(298)} \end{array} $	366, 471	634, 662	1.49
	solid (298)	368, 465, 524	640, 667	0.10 (10%), 0.24 (88%), 1.51 (2%)
<b>4</b> a	PrCN (77)	277, 314, 361	471, 488, 496, 507, 535	7.90
	solid (298)	368	480, 513, 542	0.83 (54%), 1.90 (46%)
4b	PrCN (77)	373, 400, 430	584, 633, 661, 690	11.9
	$ \begin{array}{c} \text{CH}_2\text{Cl}_2\\ (298) \end{array} $	368, 400, 430	590, 627, 652	0.78
	solid (298)	368, 465, 537, 572	593, 635, 655	3.38 (33%), 6.22 (67%)
<sup>a</sup> The most intense peak is italicized. <sup>b</sup> Data from ref 44.				

derivative **3b**. Complexes **4a** and **4b** display highly structured emissions at 77 K that are very similar in shape and energy to those of  $1a^{44}$  and 1b, respectively. Decay lifetimes in the microsecond range for all complexes are consistent with excited states of triplet parentage.

For both the ppy and tbpiq series of complexes, two main effects are observable as a consequence of the successive addition of [Au(PCy<sub>3</sub>)]<sup>+</sup> units to the mononuclear dithiolates Bu<sub>4</sub>N2a and Bu<sub>4</sub>N2b. First, the emission energies increase, which can be ascribed to a decrease in the HOMO energy as a result of coordination of the S atoms to Au<sup>I</sup>, as has been reasoned for the absorption spectra. Second, as [Au(PCy<sub>3</sub>)]<sup>+</sup> units are added, vibronic features appear or become sharper. This second effect can be attributed to a decrease in the LL'CT character of the emitting excited state as a consequence of the

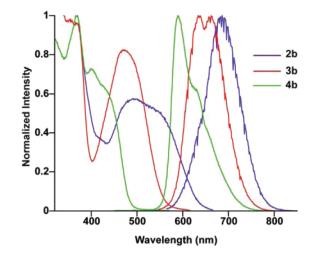


Figure 6. Excitation and emission spectra of complexes  $Bu_4N2b$ , 3b, and 4b in a  $CH_2Cl_2$  solution at 298 K.

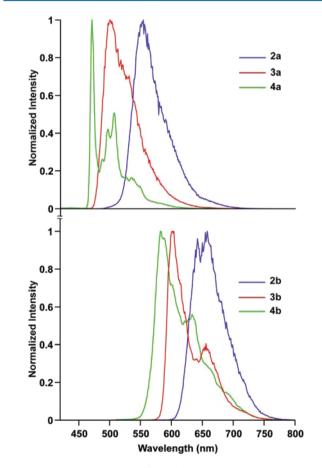


Figure 7. Emission spectra of complexes 2-4a and 2-4b in PrCN glass at 77 K.

diminishing participation of the S orbitals in the HOMO, which is accompanied by an increase in the ML'CT and L'C character. In fact, excited states of predominantly LL'CT character usually give broad and structureless emissions, <sup>41,60</sup> while mixed LC/MLCT states give structured emissions. <sup>11</sup> On the basis of these considerations, the broad and featureless emissions of the dithiolates Bu<sub>4</sub>N2a and Bu<sub>4</sub>N2b can be ascribed to <sup>3</sup>ML'CT/LL'CT excited states with predominant LL'CT character. In the cases of the monoaurated derivatives 3a and 3b, a decrease in

the LL'CT character implies a greater ML'CT contribution, while L'C states are expected to come into play as the emission energies increase and move toward those of pure L'C transitions, <sup>64</sup> which would lead to a <sup>3</sup>L'C/ML'CT/LL'CT description for their emitting states. The highly structured emissions of the diaurated complexes **4a** and **4b** suggest emitting states of the same orbital nature as those of **1a** and **1b**, respectively, that is, mixed <sup>3</sup>L'C/ML'CT states, resulting from the loss of the LL'CT contribution.

Room-temperature quantum yields  $(\Phi)$  in a CH<sub>2</sub>Cl<sub>2</sub> solution at 298 K were measured for **2a** and **1–4b**, and the corresponding radiative  $(k_{\rm r})$  and nonradiative  $(k_{\rm nr})$  rate constants were calculated according to the relationships  $k_{\rm r} = \Phi/\tau$  and  $k_{\rm nr} = (1-\Phi)/\tau$ , assuming that the emitting state is formed with unit efficiency upon excitation<sup>36</sup> (Table 9). The

Table 9. Quantum Yields and Radiative and Nonradiative Decay Rate Constants in a CH<sub>2</sub>Cl<sub>2</sub> Solution at 298 K

compd	Φ	$k_{\rm r} \times 10^{-4} \; ({\rm s}^{-1})$	$k_{\rm nr} \times 10^{-4} \; ({\rm s}^{-1})$
1b	0.40	9	14
$Bu_4N2a$	0.030	2.2	70
$Bu_4N2b$	0.0018	0.16	90
3b	0.040	2.7	65
4b	0.27	34	94

different  $\Phi$  values found for 2a and 2b can be related to their emission energies. Consistent with the energy gap law,<sup>65</sup> the lower emission energy of the tbpiq complex 2b leads to a lower quantum yield because it favors the nonradiative deactivation by vibrational overlap between the ground and excited states. When compared to platinum(II) diiminedithiolates, the quantum yield of complex 2a is considerably higher, while that of 2b approaches the upper limit of the observed range.<sup>2</sup> Because the emission of 3a is very weak and 4a is not emissive under these conditions, it is clear that successive coordination of the [Au(PCy<sub>3</sub>)]<sup>+</sup> units has an adverse effect on the emission efficiencies in a fluid solution along the ppy series of complexes, which contrasts with the bright emissions observed in the solid state at 298 K. However, for the tbpiq series, the emission quantum yields increase dramatically in the sequence 2b < 3b < 4b, reaching 0.27 for the diaurated derivative. This diverging behavior is apparently related to the different outcomes of two opposing effects. Thus, the low efficiencies of the ppy complexes 3a and 4a can be explained by the considerably higher energies of their emitting excited states, which make them more susceptible to radiationless deactivation via the MC states, compared to their tbpiq homologues. An inspection of the  $k_{\rm r}$  and  $k_{\rm nr}$  values along the tbpiq series reveals that the increasing emission efficiencies with the addition of [Au- $(PCy_3)$ ]<sup>+</sup> units arise from the increments in the radiative decay rates because variations in the nonradiative constants are much less marked and not regular. This effect is possibly the result of the increasing ML'CT character of the emitting excited states, which has been associated with higher radiative rate constants as a consequence of the effective spin-orbit coupling between <sup>3</sup>MLCT and <sup>1</sup>MLCT states. <sup>55</sup>

### CONCLUSIONS

The anionic cyclometalated platinum(II) 1,2-benzenedithiolate complexes  $[Pt(C^N)(bdt)]^ [C^N = ppy (2a), tbpiq (2b)]$  have been synthesized from  $[Pt(C^N)(HC^N)Cl]$  precursors and employed as metalloligands toward  $[Au(PCy_3)]^+$  units to

obtain heterometallic derivatives of the types [Pt(C^N)(bdt)- $\{Au(PCy_3)\}\]$  (3a and 3b) and  $[Pt(C^N)(bdt)\{Au(PCy_3)\}_2]$ -ClO<sub>4</sub> (4a and 4b). The crystal structures of 3b and 4b reveal the formation of Pt...Au metallophilic contacts that are appreciably shorter than those observed for analogous heteronuclear derivatives based on platinum(II) diiminedithiolate precursors; this can be attributed to the anionic nature of the metalloligands. Dynamic processes in solution are observed for complexes 3b, 4a, and 4b, which involve migration of the [Au(PCy<sub>3</sub>)]<sup>+</sup> units between the two inequivalent S sites. Complexes Bu<sub>4</sub>N2a and Bu<sub>4</sub>N2b display a moderately solvatochromic band in their electronic absorption spectra that can be ascribed to a transition of mixed ML'CT/LL'CT character (L = bdt;  $L' = C^N$ ), while their emissions are assignable to triplet excited states with the same orbital parentage. The successive addition of [Au(PCy<sub>3</sub>)]<sup>+</sup> units to the anions 2a and 2b causes an increase in the absorption and emission energies attributable to lower HOMO energies. Additionally, a gradual development of vibronic features is observed in the emission spectra, which are attributable to a decrease in the LL'CT character of the involved electronic transitions, which is accompanied by an increase of the L'C and ML'CT contributions. For the tbpiq series, a dramatic increase in the room-temperature quantum yields in a fluid solution is achieved as [Au(PCy<sub>3</sub>)]<sup>+</sup> units are added. In conclusion, this study has demonstrated that the orbital nature of the emitting excited states in anionic complexes of the type [Pt(C^N)-(S^S)] can be easily altered by the successive coordination to Au centers, resulting in substantial modifications of the absorption and emission energies and also the quantum efficiencies. The introduction of additional metal centers is thus illustrated as a method for the modification of excited-state properties that can be considered as an advantageous alternative to ligand variation or as a complementary strategy.

# ■ ASSOCIATED CONTENT

### S Supporting Information

Crystallographic data in CIF format for 3b and  $4b \cdot \text{CH}_2\text{Cl}_2$  variable-temperature  $^{31}\text{P}_1^{4}\text{H}_3$  NMR spectra of complex 4b in CDCl $_3$  (212–333 K) and CD $_2\text{Cl}_2$  (183–202 K), results of the variable-temperature  $^{31}\text{P}_1^{4}\text{H}_3$  NMR line-shape analyses for the exchange processes in 4a and 4b, including Eyring and Arrhenius plots, and excitation and emission spectra in the solid state at 298 K for all complexes and in a CH $_2\text{Cl}_2$  solution at 298 K for 1b, Bu $_4$ N2a, and 3a. 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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