

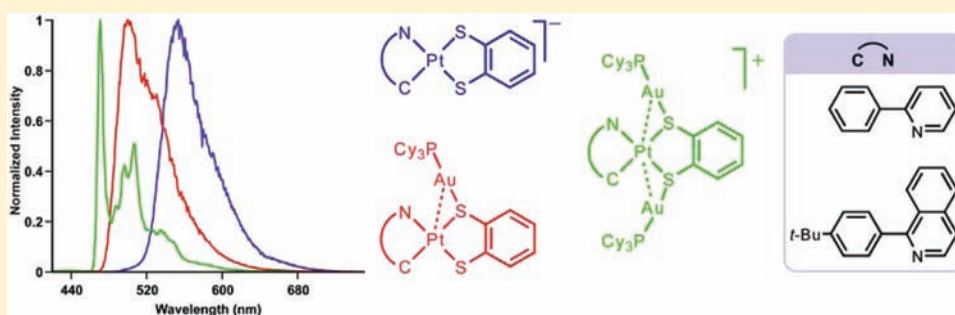
Synthesis and Photophysical Properties of Cyclometalated Platinum(II) 1,2-Benzenedithiolate Complexes and Heterometallic Derivatives Obtained from the Addition of $[\text{Au}(\text{PCy}_3)]^+$ Units

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S Supporting Information



ABSTRACT: The cyclometalated compounds $[\text{Pt}(\text{C}^{\wedge}\text{N})(\text{HC}^{\wedge}\text{N})\text{Cl}]$ [$\text{HC}^{\wedge}\text{N}$ = 2-phenylpyridine (Hppy; **1a**), 1-(4-*tert*-butylphenyl)isoquinoline (Htbpqi; **1b**)] react with 1,2-benzenedithiol, *t*-BuOK, and Bu_4NCl in a 1:1:2:1 molar ratio in $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to give the complexes $\text{Bu}_4\text{N}[\text{Pt}(\text{C}^{\wedge}\text{N})(\text{bdt})]$ [bdt = 1,2-benzenedithiolate; $\text{C}^{\wedge}\text{N}$ = ppy ($\text{Bu}_4\text{N2a}$), tbpqi ($\text{Bu}_4\text{N2b}$)]. In the absence of Bu_4NCl , the same reactions afford solutions of **K2a** and **K2b**, which react with $[\text{AuCl}(\text{PCy}_3)]$ to give the neutral heterometallic derivatives $[\text{Pt}(\text{C}^{\wedge}\text{N})(\text{bdt})\{\text{Au}(\text{PCy}_3)\}]$ [$\text{C}^{\wedge}\text{N}$ = ppy (**3a**), tbpqi (**3b**)]. The cationic derivatives $[\text{Pt}(\text{C}^{\wedge}\text{N})(\text{bdt})\{\text{Au}(\text{PCy}_3)\}_2]\text{ClO}_4$ [$\text{C}^{\wedge}\text{N}$ = ppy (**4a**), tbpqi (**4b**)] are obtained by reacting **3a** and **3b** with acetone solutions of $[\text{Au}(\text{OCIO}_3)(\text{PCy}_3)]$. The crystal structures of **3b** and **4b** reveal the formation of short $\text{Pt}\cdots\text{Au}$ 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 $[\text{Au}(\text{PCy}_3)]^+$ units between the S atoms of the dithiolate. Complexes $\text{Bu}_4\text{N2a}$ and **2b** display a moderately solvatochromic band in their electronic absorption spectra that can be ascribed to a transition of mixed $\text{ML}'\text{CT}/\text{LL}'\text{CT}$ character (M = metal; L = bdt; L' = $\text{C}^{\wedge}\text{N}$; CT = charge transfer), while their emissions are assignable to transitions of the same orbital parentage but from triplet excited states. The successive addition of $[\text{Au}(\text{PCy}_3)]^+$ 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 $\text{LL}'\text{CT}$ character in the involved electronic transitions, with a concomitant increase of the $L'\text{C}$ and $\text{ML}'\text{CT}$ 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 trisimine ligands, i.e., bi- and terpyridyls, have gained importance associated with their possible use as sensitizers for the photocatalyzed generation of hydrogen from water,¹ systems for photoinduced charge separation,^{2,3} and chemosensors.⁴ 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^{5–7} and molecular sensors.⁸

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 σ -donor ability of the aromatic C-donor atom, combined with π -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 $[\text{Pt}(\text{C}^{\wedge}\text{N})_2]$ were among the first reported platinum(II) complexes to display luminescence.

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cence at room temperature in a fluid solution.¹⁰ However, heteroleptic derivatives of the types $[\text{Pt}(\text{C}^{\wedge}\text{N})(\text{L}^{\wedge}\text{X})]$, $[\text{Pt}(\text{C}^{\wedge}\text{N})(\text{L}^{\wedge}\text{L})]^+$, and $[\text{Pt}(\text{C}^{\wedge}\text{N})\text{X}_2]^-$ have important advantages because variation of the ancillary ligands allows one to control the charge, solubility, and emission properties.⁶ The most frequently employed ancillary ligands are β -diketonates,^{11,12} although other monoanionic chelating $\text{O}^{\wedge}\text{O}$ ¹³ and $\text{O}^{\wedge}\text{N}$ ¹⁴ 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,^{17,18} xanthates, dithiophosphates,¹⁹ and monofunctional thiolates.^{14,19,20} Only four anionic complexes of the type $[\text{Pt}(\text{C}^{\wedge}\text{N})(\text{S}^{\wedge}\text{S})]^-$, containing maleonitriledithiolate¹⁵ or sulfur-rich 1,2-dithiolates,²¹ 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 $[\text{Pt}(\text{N}^{\wedge}\text{N})(\text{S}^{\wedge}\text{S})]$.^{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^{10} , d^8 , s^2)²⁴ and their impact on the structures and photophysical properties.²⁵ 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,²⁶ thiolato,²⁷ thione,²⁸ and alkynyl^{29,30} 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^+ , $[\text{M}(\text{PPh}_3)]^+$ ($\text{M} = \text{Ag}, \text{Au}$), or $[\text{Ag}(\text{PPh}_3)_2]^+$ ions to palladium(II) and platinum(II) complexes of the type $[\text{M}\{\text{S}_2\text{C}=\text{C}(\text{OMe})_2\}\text{L}_2]$ with $\text{M} = \text{Pd}, \text{Pt}$ and $\text{L} = \text{PPh}_3$, t -BuCN or $\text{L}_2 = 1,5$ -cyclooctadiene (cod).^{31,32} More recently, we employed complexes of the types $[\text{M}\{\text{S}_2\text{C}=(t\text{-Bu-fy})\}_2]^{2-}$ and $[\text{M}\{\text{S}_2\text{C}=(t\text{-Bu-fy})\}(\text{dbbpy})]$ ($\text{M} = \text{Pd}, \text{Pt}$; $t\text{-Bu-fy} = 2,7$ -di-*tert*-butylfluoren-9-ylidene; dbbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridyl) as metalloligands toward $[\text{Au}(\text{PCy}_3)]^+$ units to obtain heteronuclear complexes of the types $[\text{M}\{\text{S}_2\text{C}=(t\text{-Bu-fy})\}_2\{\text{Au}(\text{PCy}_3)\}_2]$, $[\text{M}\{\text{S}_2\text{C}=(t\text{-Bu-fy})\}(\text{dbbpy})\{\text{Au}(\text{PCy}_3)\}]^+$, and $[\text{M}\{\text{S}_2\text{C}=(t\text{-Bu-fy})\}(\text{dbbpy})\{\text{Au}(\text{PCy}_3)\}_2]^{2+}$, with the main objective of evaluating the modification of their emission properties.³³ 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 $[\text{Au}(\text{PCy}_3)]^+$ 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 $[\text{Pt}(\text{C}^{\wedge}\text{N})(\text{bdt})]^-$ [$\text{C}^{\wedge}\text{N} = 2$ -phenylpyridine (Hppy), 1-(4-*tert*-butylphenyl)-

isoquinoline] (Htbpq); bdt = 1,2-benzenedithiolate], and di- and trinuclear platinum(II)/gold(I) derivatives resulting from coordination of the $[\text{Au}(\text{PCy}_3)]^+$ 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. CH_2Cl_2 , Et_2O , and tetrahydrofuran (THF) were degassed and dried using a Pure Solv MD-5 solvent purification system from Innovative Technologies, Inc. The compounds $[\text{AuCl}(\text{PCy}_3)]^+$ and $[\text{Pt}(\text{ppy})(\text{Hppy})\text{Cl}]$ (**1a**)³⁵ 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; ^1H and $^{13}\text{C}\{^1\text{H}\}$) or external 85% H_3PO_4 ($^{31}\text{P}\{^1\text{H}\}$). The assignments of the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were made with the help of HMBC and HMQC experiments. Scheme 1 shows the atom numbering for the ppy and tbpq ligands. The atoms of the nonmetalated Htbpq 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_3OD . Line-shape analyses of the temperature-dependent $^{31}\text{P}\{^1\text{H}\}$ 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^{-1} 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, double-grating monochromators, and a TBX-04 photomultiplier. The solid-state 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 method³⁶ for those compounds that are emissive in solution at room temperature, using $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ in a deaerated MeCN solution as the standard, for which the recently reevaluated absolute quantum yield is $\Phi = 0.095$.³⁷ The estimated uncertainty in the quoted Φ values is $\pm 20\%$ or better.

X-ray Structure Determinations. Crystals of **3b** and **4b**· CH_2Cl_2 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 ω -scan mode. The structures were refined anisotropically on F^2 using the program SHELXL-97 (Sheldrick, G. M. University of Göttingen, Göttingen, Germany).³⁸ 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_2Cl_2 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·CH₂Cl₂

	3b	4b·CH ₂ Cl ₂
formula	C ₄₃ H ₅₀ AuNPtS ₂	C ₆₂ H ₉₀ Au ₂ Cl ₃ NO ₄ P ₂ PtS 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	$P\bar{1}$	$P2_1/n$
a (Å)	11.9157(2)	24.0411(4)
b (Å)	12.0728(2)	11.0278(2)
c (Å)	14.8775(2)	24.6578(4)
α (deg)	79.1084(11)	90
β (deg)	85.5256(11)	90.042(3)
γ (deg)	70.3669(12)	90
V (Å ³)	1979.23(5)	6537.28(19)
Z	2	4
ρ _{calcd} (Mg m ⁻³)	1.801	1.763
μ (mm ⁻¹)	7.409	6.892
R1 ^a	0.0231	0.0236
wR2 ^b	0.0521	0.0434

^aR1 = $\sum ||F_o| - |F_c|| / \sum |F_o|$ for reflections with $I > 2\sigma(I)$. ^bwR2 = $[\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{0.5}$ 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 (Htbpq). The following procedure is based on the method described for some quinoline derivatives.³⁹ A mixture of 1-chloroisoquinoline (850 mg, 5.20 mmol), 4-tert-butylphenylboronic acid (930 mg, 5.22 mmol), Ba(OH)₂·8H₂O (3.3 g, 10.5 mmol), 2,6-di-tert-butyl-4-methylphenol (30 mg, 0.14 mmol), Pd(PPh₃)₄ (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 N₂ atmosphere. The solvent was removed under a vacuum, and the residue was extracted using a 1:1 mixture of CH₂Cl₂ and H₂O (140 mL). The organic phase was decanted and dried over anhydrous MgSO₄. 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 C₁₉H₁₉N [M + H]⁺: 262.1590. Found: 262.1595. Error: 1.88 ppm. IR (Nujol, cm⁻¹): 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). ¹H NMR (400.9 MHz, CDCl₃): δ 8.60 (d, ³J_{HH} = 5.6 Hz, 1 H, Iq3), 8.18 (d, ³J_{HH} = 8.4 Hz, 1 H, Iq8), 7.87 (d, ³J_{HH} = 8.6 Hz, 1 H, Iq5), 7.64–7.72 (m, 3 H, Iq6, Ph2), 7.62 (d, ³J_{HH} = 5.6 Hz, 1 H, Iq4), 7.49–7.59 (m, 3 H, Ph3, Iq7), 1.41 (s, 9 H, *t*-Bu). ¹³C{¹H} APT NMR (100.8 MHz, CDCl₃): δ 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 (CMe₃), 31.3 (CMe₃).

[Pt(tbpq)(Htbpq)Cl] (1b). The following procedure is based on the method described for 1a.³⁵ K₂[PtCl₄] (450 mg, 1.08 mmol), Htbpq (580 mg, 2.22 mmol), and a previously degassed 3:1 (v/v) mixture of 2-ethoxyethanol and H₂O (40 mL) were placed in a Carius tube under a N₂ 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 CH₂Cl₂ as the eluent. Crystallization from CH₂Cl₂/*n*-pentane afforded orange crystals of 1b·¹/₃CH₂Cl₂·²/₃H₂O. Yield: 565 mg, 69%. Mp: 177 °C. Anal. Calcd for C_{38.3}H₃₉Cl_{1.67}N₂O_{0.67}Pt: C, 58.10; H, 4.96; N, 3.54. Found: C, 58.12; H, 4.96; N, 3.75. IR (Nujol, cm⁻¹): 1620 (w), 1581 (w), 1265 (w), 1020 (m), 828 (m), 466 (w), 451 (w). ¹H NMR (400.91 MHz, CDCl₃): δ 9.51 (d with satellites, ³J_{HH} = 6.4 Hz, ³J_{Hpt} =

~13 Hz, 1 H, Iq3), 9.08 (d with satellites, ³J_{HH} = 6.7 Hz, ³J_{Hpt} = ~16 Hz, 1 H, Iq3'), 8.68 (d, ³J_{HH} = 8.6 Hz, 1 H, Iq8), 8.20 (dd, ³J_{HH} = 8.2 Hz, ⁴J_{HH} = 1.6 Hz, 1 H, Ph2'/Ph6'), 7.97 (d, ³J_{HH} = 8.2 Hz, 1 H, Iq5'), 7.80–7.91 (m, 3 H, Iq6', Iq8', Ph6), 7.76 (d, ³J_{HH} = 8.2 Hz, 1 H, Iq5), 7.74 (d, ³J_{HH} = 6.8 Hz, 1 H, Iq4'), 7.67 (t, ³J_{HH} = 7.2 Hz, 1 H, Iq6), 7.53–7.63 (m, 2 H, Iq7', Iq7), 7.50 (dd, ³J_{HH} = 8.2 Hz, ⁴J_{HH} = 1.8 Hz, 1 H, Ph3'/Ph5'), 7.30–7.38 (m, 2 H, Ph2'/Ph6', Iq4), 7.22 (dd, ³J_{HH} = 8.2 Hz, ⁴J_{HH} = 1.7 Hz, 1 H, Ph3'/Ph5'), 7.09 (dd, ³J_{HH} = 8.4 Hz, ⁴J_{HH} = 2.0 Hz, 1 H, Ph5), 6.28 (d with satellites, ⁴J_{HH} = 2 Hz, ³J_{Hpt} = 25 Hz, 1 H, Ph3), 1.21 (s, 1 H, *t*-Bu'), 1.05 (s, 1 H, *t*-Bu). ¹³C{¹H} APT NMR (100.81 MHz, CDCl₃): δ 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 (CMe₃), 34.4 (CMe₃), 31.1 (CMe₃), 30.9 (CMe₃).

Bu₄N[Pt(ppy)(bdt)] (2a). 1,2-Benzenedithiol (55 μL, 0.48 mmol), *t*-BuOK (105 mg, 0.93 mmol), and Bu₄NCl (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 CH₂Cl₂ (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 CH₂Cl₂ (30 mL) and filtered through anhydrous MgSO₄. Partial evaporation of the filtrate (4 mL) and the slow addition of Et₂O (20 mL) led to the precipitation of a red solid, which was filtered off, washed with Et₂O (2 × 3 mL), and recrystallized from CH₂Cl₂/Et₂O 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. ¹H NMR (300.1 MHz, CDCl₃): δ 9.22 (dd, ³J_{HH} = 5.4 Hz, ³J_{Hpt} = 24 Hz, 1 H, py6), 7.93 (dd, ³J_{HH} = 6.6 Hz, ³J_{Hpt} = 29.4 Hz, 1 H, Ph3), 7.69 (t, ³J_{HH} = 7.5 Hz, 1 H, py4), 7.61 (d, ³J_{HH} = 8.1 Hz, 1 H, py3), 7.46 (d, ³J_{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, NCH₂), 1.10 (m, 8 H, CH₂), 0.91 (m, 8 H, CH₂), 0.62 (m, 12 H, Me, Bu₄N). ¹³C{¹H} NMR (75.45 MHz, CDCl₃): 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 (NCH₂), 23.8 (CH₂), 19.2 (CH₂), 13.6 (Me, Bu₄N).

Bu₄N[Pt(tbpq)(bdt)] (2b). This purple compound was obtained as described for 2a, from 1b (250 mg, 0.33 mmol), bdt (42 μL, 0.36 mmol), *t*-BuOK (82 mg, 0.73 mmol), and Bu₄NCl (101 mg, 0.36 mmol). Yield: 250 mg, 90%. Anal. Calcd for C₄₁H₅₈N₂PtS₂: 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. ¹H NMR (400.9 MHz, CDCl₃): δ 9.12 (dd, ³J_{HH} = 6.4 Hz, ³J_{Hpt} = 29.2 Hz, 1 H, Iq3), 8.81 (d, ³J_{HH} = 8.5 Hz, 1 H, Iq8), 8.24 (dd, ⁴J_{HH} = 2.1 Hz, ³J_{Hpt} = 47.6 Hz, 1 H, Ph3), 7.99 (d, ³J_{HH} = 8.5 Hz, 1 H, Ph6), 7.72 (dd, ³J_{HH} = 8.1 Hz, ⁴J_{HH} = 1.0 Hz, 1 H, Iq5), 7.66 (td, ³J_{HH} = 8.1 Hz, ⁴J_{HH} = 1.0 Hz, 1 H, Iq6), 7.54 (ddd, ³J_{HH} = 8.5 Hz, ³J_{HH} = 7.0 Hz, ⁴J_{HH} = 1.5 Hz, 1 H, Iq7), 7.46 (m, 1 H, bdt), 7.39 (m, 1 H, bdt), 7.16 (d, ³J_{HH} = 6.4 Hz, 1 H, Iq4), 7.11 (dd, ³J_{HH} = 8.4 Hz, ⁴J_{HH} = 2.1 Hz, 1 H, Ph5), 6.58 (m, 2 H, bdt), 2.87 (m, 8 H, NCH₂), 1.37 (s, 9 H, *t*-Bu), 1.18 (m, 8 H, CH₂), 0.97 (m, 8 H, CH₂), 0.64 (t, ³J_{HH} = 7.3 Hz, 12 H, Me, Bu₄N). ¹³C{¹H} NMR (75.45 MHz, CDCl₃): δ 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 (NCH₂), 35.0 (CMe₃), 31.5 (CMe₃), 24.0 (CH₂), 19.3 (CH₂), 13.6 (Me, Bu₄N).

[Pt(ppy)(bdt){Au(PCy₃)}] (3a). Method A. To a solution of [AuCl(PCy₃)] (85 mg, 0.16 mmol) in acetone (10 mL) was added AgClO₄ (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 × 4 mL), and vacuum-dried to give **3a**. Yield: 124 mg, 78%. **Method B.** 1,2-Benzenedithiol (28 μ 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 CH₂Cl₂ (25 mL). After stirring for 60 min, a red solution was obtained. [AuCl(PCy₃)₃] (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 CH₂Cl₂ (40 mL), and the extract was filtered through anhydrous MgSO₄. 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 C₃₃H₄₃AuNPtS₂: 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. ¹H NMR (300.1 MHz, CDCl₃): δ 9.07 (dd, ³J_{HH} = 5.9 Hz, ³J_{HPt} = 32 Hz, 1 H, py6), 7.97 (dd, ³J_{HH} = 7.4 Hz, ³J_{HPt} = 44 Hz, 1 H, Ph3), 7.80 (t, ³J_{HH} = 7.2 Hz, 1 H, py4), 7.72 (d, ³J_{HH} = 8.1 Hz, 1 H, py3), 7.63 (m, 2 H, bdt), 7.54 (d, ³J_{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). ¹³C{¹H} NMR (75.45 MHz, CDCl₃): 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, ¹J_{CP} = 28.1 Hz, C1, Cy), 30.3 (C2, Cy), 26.9 (d, ³J_{CP} = 12.1 Hz, C3, Cy), 25.62 (C4, Cy). ³¹P{¹H} NMR (162.3 MHz, CDCl₃): δ 52.84 (s).

[Pt(tbpiq)(bdt){Au(PCy₃)₂}] (3b). This orange complex was prepared as described for **3a** (method B), from 1,2-benzenedithiol (24 μ L, 0.21 mmol), *t*-BuOK (48 mg, 0.43 mmol), **1b** (150 mg, 0.20 mmol), and [AuCl(PCy₃)₃] (103 mg, 0.20 mmol). Yield: 178 mg, 83%. Anal. Calcd for C₄₃H₅₅AuNPtS₂: 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. ¹H NMR (400.9 MHz, CD₂Cl₂): δ 8.88 (d, ³J_{HH} = 8.7 Hz, 1 H, Iq8), 8.85 (dd, ³J_{HH} = 6.4 Hz, ³J_{HPt} = 28.8 Hz, 1 H, Iq3), 8.12 (dd, ⁴J_{HH} = 1.9 Hz, ³J_{HPt} = 55.4 Hz, 1 H, Ph3), 8.06 (d, ³J_{HH} = 8.4 Hz, 1 H, Ph6), 7.83 (d, ³J_{HH} = 8.0 Hz, 1 H, Iq5), 7.76 (t, ³J_{HH} = 7.2 Hz, 1 H, Iq6), 7.66 (t, ³J_{HH} = 7.6 Hz, 1 H, Iq7), 7.61 (d, ³J_{HH} = 8.0 Hz, 1 H, bdt), 7.57 (d, ³J_{HH} = 8.0 Hz, 1 H, bdt), 7.34 (d, ³J_{HH} = 6.4 Hz, 1 H, Iq4), 7.23 (dd, ³J_{HH} = 8.4 Hz, ⁴J_{HH} = 1.8 Hz, Ph5), 6.90 (t, ³J_{HH} = 7.2 Hz, 1 H, bdt), 6.80 (t, ³J_{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). ¹³C{¹H} NMR (100.8 MHz, CDCl₃): δ 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 (CMe₃), 33.2 (d, ¹J_{PC} = 28 Hz, C1, Cy), 31.5 (CMe₃), 30.4 (C2, C6, Cy), 27.0 (d, ³J_{PC} = 12 Hz, C3, C5, Cy), 25.7 (C4, Cy). ³¹P{¹H} NMR (162.3 MHz, CD₂Cl₂): δ 53.08 (br).

[Pt(ppy)(bdt){Au(PCy₃)₂}]ClO₄ (4a). To a solution of [AuCl(PCy₃)₃] (117 mg, 0.23 mmol) in acetone (25 mL) was added AgClO₄ (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 MgSO₄ to remove a small amount of insoluble material. The solvent was removed under vacuum, and the residue was dissolved in CH₂Cl₂ (3 mL). The slow addition of Et₂O (30 mL) at 0 °C led to precipitation of a pale-yellow solid, which was filtered off, washed with Et₂O (2 × 3 mL), and vacuum-dried to give **4a**. Yield: 246 mg, 69%. Anal. Calcd for C₅₃H₇₈Au₂ClNO₄P₂PtS₂: 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. ¹H NMR (400.91 MHz, CDCl₃): δ 8.86 (dd, ³J_{HH} = 5.8 Hz, ³J_{HPt} = 36 Hz, 1 H, py6), 8.15 (t, ³J_{HH} = 5.8 Hz, 1 H, py4), 7.95 (d, ³J_{HH} = 6.0 Hz, 1 H, py3), 7.73–7.83 (m, 2 H, bdt), 7.64 (d, ³J_{HH} = 6.3 Hz, 2 H, Ph6), 7.61 (s with satellites, ³J_{HPt} = ~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,

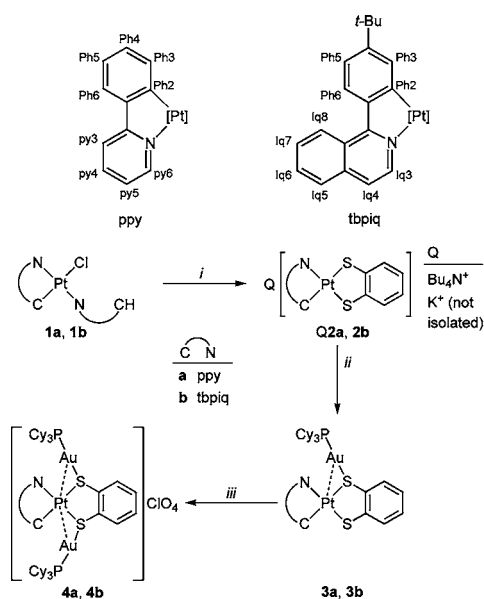
Cy), 0.88–1.24 (m, 30 H, Cy). ¹³C{¹H} NMR (75.45 MHz, CDCl₃): δ 166.7 (py2), 151.72 (Ph2), 150.1 (py6), 144.1 (Ph1), 140.1 (py4), 139.3 (C1/C2, bdt), 134.5 (C, bdt), 133.5, 132.0 (Ph3, C1/C2, C3/C6, bdt), 130.6 (Ph5), 126.3, 126.1 (C4/C5, bdt), 124.7 (Ph6), 124.5 (Ph4), 123.7 (py5), 120.0 (py2), 33.2 (d, ¹J_{CP} = 28.3 Hz, C1, Cy), 30.5 (C2, Cy), 26.7 (d, ³J_{CP} = 12.2 Hz, C3, Cy), 25.5 (C4, Cy). ³¹P{¹H} NMR (162.3 MHz, CDCl₃): δ 54.94 (br).

[Pt(tbpiq)(bdt){Au(PCy₃)₂}]ClO₄ (4b). This yellow complex was obtained as described for **4a**, from [AuCl(PCy₃)₃] (91 mg, 0.18 mmol), AgClO₄ (37 mg, 0.18 mmol), and **3b** (165 mg, 0.15 mmol). Yield: 219 mg, 86%. Anal. Calcd for C₆₁H₈₈Au₂ClNO₄P₂PtS₂: 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. ¹H NMR (400.91 MHz, CDCl₃): δ 8.86 (d, ³J_{HH} = 8.8 Hz, 1 H, Iq8), 8.70 (dd, ³J_{HH} = 6.4 Hz, ³J_{HPt} = 32 Hz, 1 H, Iq3), 8.07 (d, ³J_{HH} = 8.4 Hz, 1 H, Ph6), 8.01 (d, ³J_{HH} = 8.4 Hz, 1 H, Iq5), 7.89 (t, ³J_{HH} = 7.2 Hz, 1 H, Iq6), 7.75–7.86 (m, 4 H, Ph3, Iq7, bdt), 7.57 (d, ³J_{HH} = 6.4 Hz, 1 H, Iq4), 7.28 (dd, ³J_{HH} = 8.6 Hz, ³J_{HH} = 1.8 Hz, 1 H, Ph5), 7.15–7.20 (m, 2 H, bdt), 1.44–1.79 (m, 36 H, Cy), 1.40 (s, 9 H, *t*-Bu), 0.78–1.19 (m, 30 H, Cy). ¹³C{¹H} NMR (100.81 MHz, CDCl₃): δ 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 (CMe₃), 33.1 (d, ¹J_{CP} = 28.2 Hz, C1, Cy), 31.3 (CMe₃), 30.5 (C2, Cy), 26.7 (d, ³J_{CP} = 12.1 Hz, C3, Cy), 25.5 (C4, Cy). ³¹P{¹H} NMR (162.3 MHz, CDCl₃): δ 54.87 (br).

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.³⁵ Their reactions with 1,2-benzenedithiol, *t*-BuOK, and Bu₄NCl in a 1:1:2:1 molar ratio in CH₂Cl₂/MeOH afforded the complexes Bu₄N[Pt(C[^]N)(bdt)] [bdt = 1,2-benzenedithiolate; C[^]N = ppy (Bu₄N**2a**) or tbpiq (Bu₄N**2b**)] 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) H₂bdt, 2 *t*-BuOK, Bu₄NCl (Q = Bu₄N⁺) or H₂bdt, 2 *t*-BuOK (Q = K⁺). (ii) [Au(OClO₃)(PCy₃)₂] (Q = Bu₄N⁺) or [AuCl(PCy₃)₃] (Q = K⁺). (iii) [Au(OClO₃)(PCy₃)₂].

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 $[\text{Au}(\text{PCy}_3)]^+$ units to the anionic complexes $\text{Bu}_4\text{N}2\text{a}$ and $\text{Bu}_4\text{N}2\text{b}$ by reacting them with acetone solutions of $[\text{Au}(\text{OClO}_3)(\text{PCy}_3)]$, which, in turn, were generated from $[\text{AuCl}(\text{PCy}_3)]$ and AgClO_4 .³³ Thus, the reaction of $\text{Bu}_4\text{N}2\text{a}$ with 1 equiv of $[\text{Au}(\text{OClO}_3)(\text{PCy}_3)]$ 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_4NClO_4 . When starting from $\text{Bu}_4\text{N}2\text{b}$, this method afforded the analogous complex **3b**, but its solubility in common solvents turned out to be very similar to that of Bu_4NClO_4 , and hence the two products could not be conveniently separated. For this reason, we devised an alternative procedure to avoid the presence of Bu_4N^+ 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 $[\text{AuCl}(\text{PCy}_3)]$. 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 $[\text{Pt}(\text{C}^{\wedge}\text{N})(\text{bdt})\{\text{Au}(\text{PCy}_3)\}_2]\text{ClO}_4$ [$\text{C}^{\wedge}\text{N} = \text{ppy}$ (**4a**), tbpiq (**4b**)] were prepared by reacting **3a** or **3b** with 1 equiv of $[\text{Au}(\text{OClO}_3)(\text{PCy}_3)]$ 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 $[\text{Pt}(\text{tbpiq})(\text{bdt})]^-$ unit with one $[\text{Au}(\text{PCy}_3)]^+$ unit bonded to the S atom trans to the aryl C atom. The other possible structural isomer, with the $[\text{Au}(\text{PCy}_3)]^+$ unit bonded to the S atom trans to the N atom, was not present in the crystal. The Pt atom is in a slightly

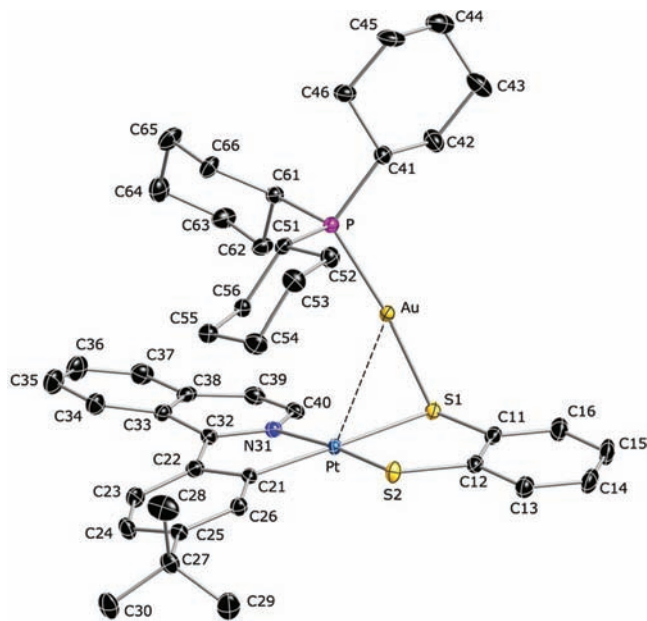


Figure 1. Thermal ellipsoid representation (50% probability) of the structure of complex **3b**. H atoms have been omitted for clarity.

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)°. The *tbpiq* 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 $[\text{Pt}(\text{piq})(\text{Hpiq})\text{Cl}]$.⁴³ Of the two possible conformations, the *tbpiq* ligand adopts the one in which the *tert*-butylphenyl group bends away from the $[\text{Au}(\text{PCy}_3)]^+$ 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 $[\text{Pt}(\text{bdt})(\text{bpy})]$ (2.250 and 2.244 Å;⁴⁰ *bpy* = 2,2'-bipyridyl) and related complexes.^{2,45} The appreciably longer Pt–S1 bond distance of 2.3781(8) Å is attributable to the trans influence of the aryl 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 $[\{\text{Au}(\text{PPh}_3)\}_2(\text{bdt})]$ and $[\{\text{Au}(\text{PPh}_3)\}_2(\text{tdt})]$ (range 2.316–2.325 Å;⁴⁶ *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 $[\text{Pt}\{\text{S}_2\text{C}=(\text{t-Bu-fy})\}(\text{dbbpy})\{\text{Au}(\text{PCy}_3)\}]^+$ [91.93(2)°;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 $[\text{Au}(\text{PCy}_3)]^+$ unit. Complexes with weak Au...Pt contacts shorter than 3.0 Å are scarce and usually contain bridging diphosphines, as in $[\{\text{Pt}(\text{CN})_2\}\text{Au}(\mu\text{-dcpm})_2]\text{PF}_6$ [2.953 Å; *dcpm* = 1,1-bis-(dicyclohexylphosphino)methane],⁴⁷ $[\{\text{PtCl}(\text{Ph})\}\text{Au}(\mu\text{-dppm})_2]\text{PF}_6$ (2.965 Å),⁴⁸ and $[\{\text{Pt}(\text{CCPh})\}\text{Au}(\mu\text{-dppm})_2]\text{X}$ [X = PF₆ (2.910 Å),⁴⁹ SbF₆ (2.927 Å)³⁰], 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 CH₂Cl₂ 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 $[\text{Pt}(\text{tbpiq})(\text{bdt})]^-$ unit, with two $[\text{Au}(\text{PCy}_3)]^+$ units bonded to the S atoms of the

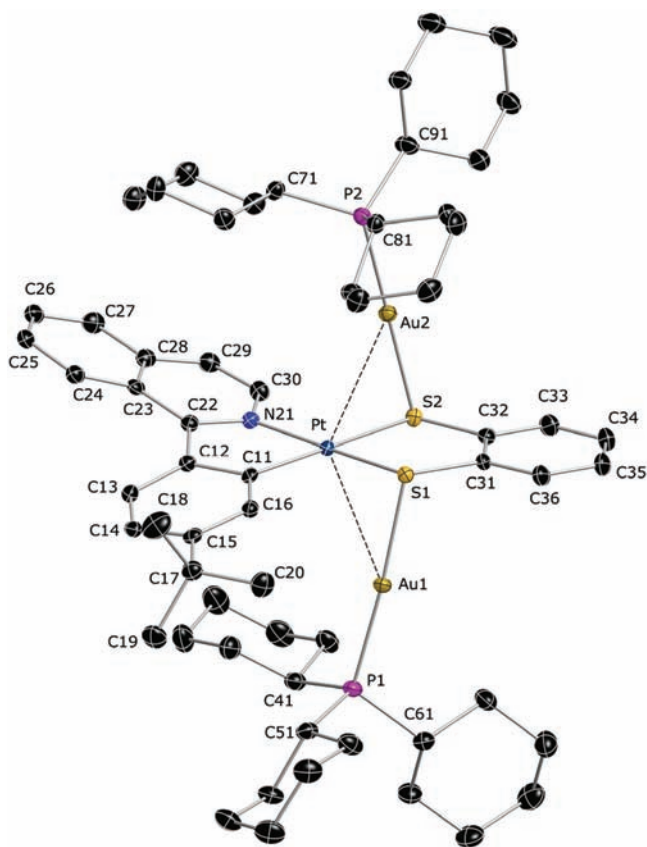


Figure 2. Thermal ellipsoid representation (50% probability) of the cation of complex **4b**. H atoms have been omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **4b**·CH₂Cl₂

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(PCy₃)]⁺ 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° and 95.10°, 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)° and Au2–S2–Pt of 79.027(19)° are wider than those found in **3b** and lead to longer Au···Pt contacts in **4b** [Pt···Au2, 3.01407(14); Pt···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° 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(PCy₃)]⁺ unit trans to it.

NMR Spectra and Dynamic Behavior. The ¹H and ¹³C{¹H} NMR spectra of the platinum(II) complexes Bu₄N**2a** and Bu₄N**2b** 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(PCy₃)]⁺ units between the S atoms of the dithiolato ligand. We have previously shown that such processes take place in the related complexes [M{S₂C=(*t*-Bu-fy)}(dbbpy){Au(PCy₃)}]⁺ and [M{S₂C=(*t*-Bu-fy)}₂{Au(PCy₃)}₂] (M = Pd, Pt).³³ 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 ³¹P{¹H} NMR studies.

The cases of the trinuclear derivatives **4a** and **4b** allow a more detailed analysis and are presented first. These complexes give a very broad resonance in the ³¹P{¹H} NMR spectra at room temperature, which splits into two sharp resonances that appear at 53.4 and 54.8 ppm (**4a**) or 53.2 and 54.9 ppm (**4b**) at 202 K in CDCl₃ (Figure 3 and the Supporting Information) and coalesce at 271 (**4a**) or 296 K (**4b**). The two distinct

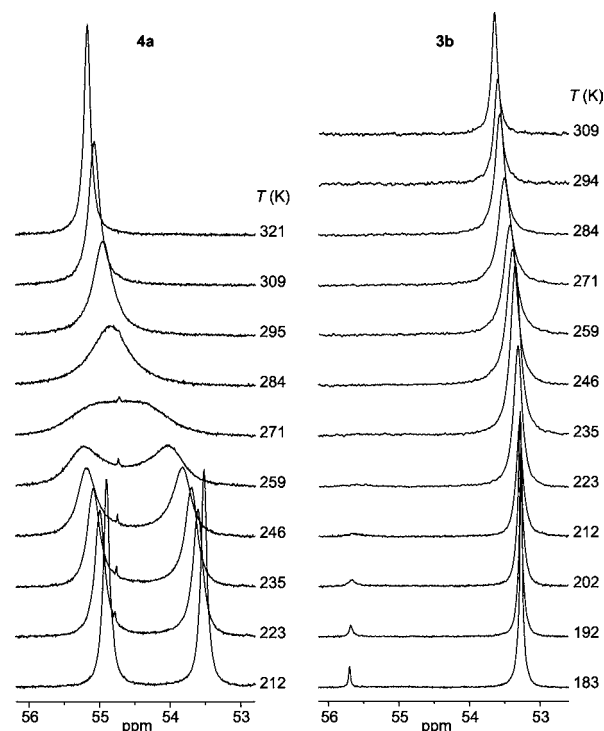


Figure 3. ³¹P{¹H} NMR spectra of **4a** in CDCl₃ and **3b** in CD₂Cl₂ at various temperatures.

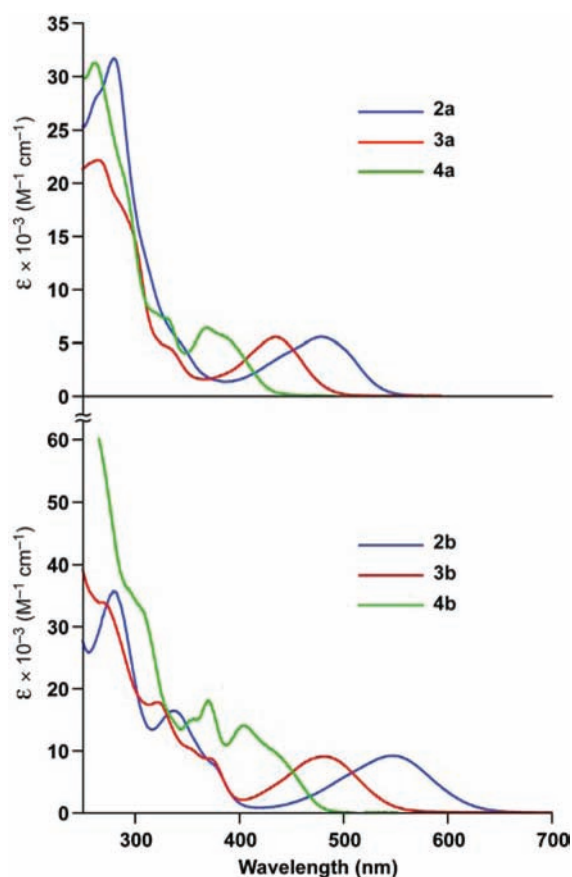


Figure 4. Electronic absorption spectra of 2–4a (top) and 2–4b (bottom) in a CH_2Cl_2 solution (ca. 5×10^{-5} M) at 298 K.

resonances arise because the $[\text{Au}(\text{PCy}_3)]^+$ units are bonded to inequivalent S atoms, one of them trans to the aryl 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 $[\text{Au}(\text{PCy}_3)]^+$ 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 tbbiq ligand and could give rise to four resonances at low temperatures, as both migration of the $[\text{Au}(\text{PCy}_3)]^+$ units and interconversion between the tbbiq conformations slow down. In order to check this possibility, we registered the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of 4b in CD_2Cl_2 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 tbbiq 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 $^{31}\text{P}\{^1\text{H}\}$ NMR resonances⁵² 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 $[\text{Au}(\text{PCy}_3)]^+$ units and strengthened $\text{Pt}\cdots\text{Au}$ metal-philic interactions, which is depicted in Scheme 2 for 4b. The activation enthalpy is significantly higher for the tbbiq derivative 4b than for its ppy homologue 4a. Because Au–S bond and $\text{Pt}\cdots\text{Au}$ interaction energies are expected to be very similar for both complexes, a reasonable explanation for this is that migration of the $[\text{Au}(\text{PCy}_3)]^+$ units in 4b requires the concomitant conformational change of the tbbiq 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 $[\text{Au}(\text{PCy}_3)]^+$ unit can be attached to either the S atom trans to the aryl 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 $^{31}\text{P}\{^1\text{H}\}$ NMR spectra at low temperatures. Complex 3a gives a sharp resonance at 53.4 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at room temperature in CD_2Cl_2 , which does not split upon cooling to 183 K, suggesting that migration of the $[\text{Au}(\text{PCy}_3)]^+$ 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 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the tbbiq derivative 3b in CD_2Cl_2 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 $[\text{Au}(\text{PCy}_3)]^+$ 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

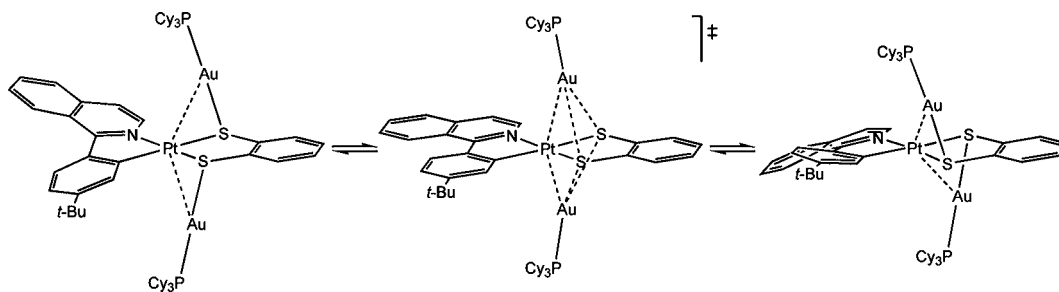


Table 4. Arrhenius and Eyring Activation Parameters for the Exchange Processes in 4a and 4b

compd	E_A (kcal mol ⁻¹)	ΔH^\ddagger (kcal mol ⁻¹)	ΔS^\ddagger (cal mol ⁻¹ K ⁻¹)	T_{coal} (K)	$\Delta G_{\text{coal}}^\ddagger$ (kcal mol ⁻¹)
4a	8.0 ± 0.4	7.5 ± 0.4	-18 ± 1	271	12.4 ± 0.1
4b	11.9 ± 0.4	11.3 ± 0.4	-7 ± 1	296	13.5 ± 0.1

reported by Shanan-Atidi and Bar-Eli,⁵¹ the NMR data allowed an estimation of the free energies of activation $\Delta G^\ddagger = 13.8$ and 12.2 kcal mol⁻¹ for the major and minor species, respectively, at the coalescence temperature, $T_{\text{coal}} = 271$ 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⁻¹ at 271 K. The values of the free energies of activation are consistent with an exchange process involving migration of the [Au(PCy₃)]⁺ unit between the S atoms and probably also the concomitant conformational change of the tbbiq ligand. It is reasonable that the most intense resonance corresponds to the enantiomeric pair found in the crystal structure (see above), with the [Au(PCy₃)]⁺ unit attached to the S atom trans to the aryl C atom and the phenyl ring of the tbbiq ligand bent away from this unit. The other resonance should correspond to the isomers with the [Au(PCy₃)]⁺ unit bonded to the S atom trans to the N atom and, possibly, the opposite tbbiq conformation. The strong trans influence of the aryl 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^I 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(PCy₃)]⁺ unit attached to the S atom trans to the aryl C atom.

The ¹³C{¹H} NMR spectra of the heterometallic derivatives are not sensitive to the exchange processes mentioned above. Coordination of the [Au(PCy₃)]⁺ 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. ¹³C{¹H} NMR Resonances of the C1/C2 Atoms of the bdt Ligand for the Complexes Mentioned in This Work^a

compd	$\delta(\text{C1/C2})$	compd	$\delta(\text{C1/C2})$
Bu ₄ N2a	148.8, 144.5	Bu ₄ N2b	149.5, 145.0
3a	148.6, 135.6	3b	150.5, 134.9
4a	139.3, 133.5	4b	139.3, 134.7

^aIn ppm, CDCl₃ solution.

Electronic Absorption Spectra. The UV–vis absorption spectra were measured in CH₂Cl₂ 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 tbbiq 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 π – π^* LC transitions localized on the tbbiq and Htbpiq ligands. The less intense absorptions with $\lambda_{\text{max}} > 340$ 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 CH₂Cl₂ Solution (ca. 5 × 10⁻⁵ M) at 298 K

compd	λ/nm ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$)
Htbpiq	229 (25100), 283 (8400), 324 (6400)
1a	260 (28700), 280 (18100), 314 (7600), 328 (5800), 348 (4100), 384 (2300), 402 (2100)
1b	276 (57900), 320 (21000), 350 (17000), 365 (19900), 382 (9300), 432 (5300), 454 (5100)
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 (17900), 404 (13900)

extinction coefficients, the corresponding electronic states are assigned as ¹MLCT. We note, however, that the assignment to pure MLCT states is a simplification because these states usually mix with LC states in differing proportions.^{54,55} 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 than those of

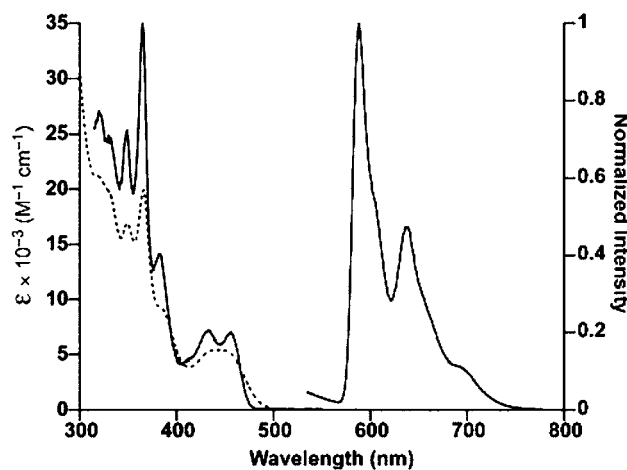


Figure 5. Excitation and emission spectra of complex 1b in PrCN glass at 77 K (—) and absorption spectrum in a CH₂Cl₂ solution at 298 K (---).

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 tbbiq complexes described in this work.

The mononuclear dithiolato complexes **Bu₄N2a** and **Bu₄N2b** give intense absorptions in the UV region that are assignable to π - π^* transitions within the bdt and ppy or tbbiq 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 **Bu₄N2a, **Bu₄N2b**, **3a**, and **3b** in Solvents of Differing Polarity^a**

solvent	λ_{max} nm			
	Bu₄N2a	Bu₄N2b	3a	3b
acetonitrile	474	540	426	470
CH ₂ Cl ₂	479	546	435	482
acetone	496	570	440	485
toluene	506	576	456	512

^a5 × 10⁻⁵ 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)],⁵⁷ where S[^]S is a sulfur-rich dithiolate, as well as [Au(ppy)(tdt)] (tdt = 2,3-toluenedithiolate),⁵⁸ and led to an assignment as a charge-transfer transition from a mixed metal/dithiolate HOMO and a LUMO that is a π^* 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 π^* 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 MLCT/LLCT 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)¹⁸ 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 lowest-energy 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(PCy₃)]⁺ 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^I 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 **Bu₄N2a** and **Bu₄N2b**. 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 LLCT 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 LLCT 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 CH₂Cl₂ solution at 298 K. The excitation and emission data are summarized in Table 8.

The emission spectrum of **1b** in CH₂Cl₂ 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 μ s falls in the range observed for mixed ³LC/MLCT excited states in related cyclometalated platinum(II) complexes,⁵⁵ and thus this assignment is appropriate for **1b**.

The platinum complexes **Bu₄N2a** and **Bu₄N2b** and their monoaurated derivatives **3a** and **3b** give rise to broad and nearly symmetrical emission bands in a CH₂Cl₂ 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 tbbiq derivative **4b** is emissive in a CH₂Cl₂ 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 tbbiq 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 CH₂Cl₂ 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 **Bu₄N2a** and **Bu₄N2b** (1576 and 669 cm⁻¹, respectively) and the monoaurated derivatives **3a** and **3b** (2244 and 894 cm⁻¹, respectively), which can be ascribed to a rigidochromic effect commonly observed for diimine^{22,33,61} and cyclometalated⁶² complexes, and are a sign of the charge-transfer character of the emitting state.⁶³ In the cases of **3a** and **3b**, the low-temperature spectra also reveal some vibronic structure, which is more evident for the tbbiq

Table 8. Excitation and Emission Data for 1–4a,b^a

compd	medium (T/K)	λ_{exc}/nm	λ_{em}/nm	$\tau/\mu\text{s}$
1a ^b	toluene (77)		479, 515, 547	11.2
	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 ₂ Cl 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 ₄ N2a	PrCN (77)	455, 481	554	19.8
	CH ₂ Cl ₂ (298)	476	607, 659	1.39
	solid (298)	368, 540	603, 655	1.56 (66%), 3.21 (34%)
Bu ₄ N2b	PrCN (77)	374, 458–555	655	7.40
	CH ₂ Cl ₂ (298)	493	685	1.11
	solid (298)	369, 465, 613	682	0.60 (49%), 1.22 (51%)
3a	PrCN (77)	427	503	6.78
	CH ₂ Cl 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
	CH ₂ Cl ₂ (298)	366, 471	634, 662	1.49
	solid (298)	368, 465, 524	640, 667	0.10 (10%), 0.24 (88%), 1.51 (2%)
4a	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
	CH ₂ Cl ₂ (298)	368, 400, 430	590, 627, 652	0.78
	solid (298)	368, 465, 537, 572	593, 635, 655	3.38 (33%), 6.22 (67%)

^aThe most intense peak is italicized. ^bData 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 tbiq series of complexes, two main effects are observable as a consequence of the successive addition of [Au(PCy₃)]⁺ units to the mononuclear dithiolates Bu₄N2a and Bu₄N2b. 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^I, as has been reasoned for the absorption spectra. Second, as [Au(PCy₃)]⁺ 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

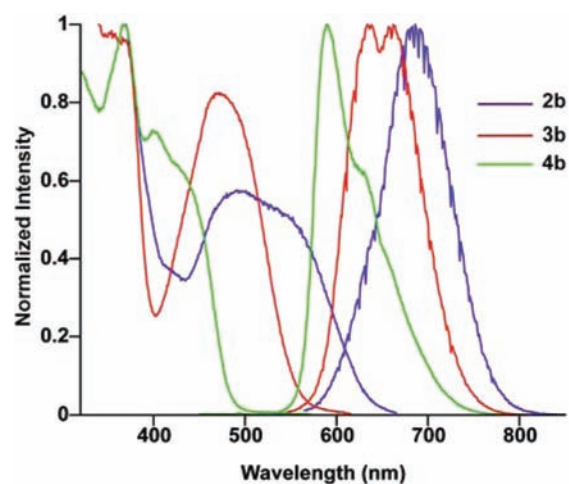


Figure 6. Excitation and emission spectra of complexes Bu₄N2b, 3b, and 4b in a CH₂Cl₂ solution at 298 K.

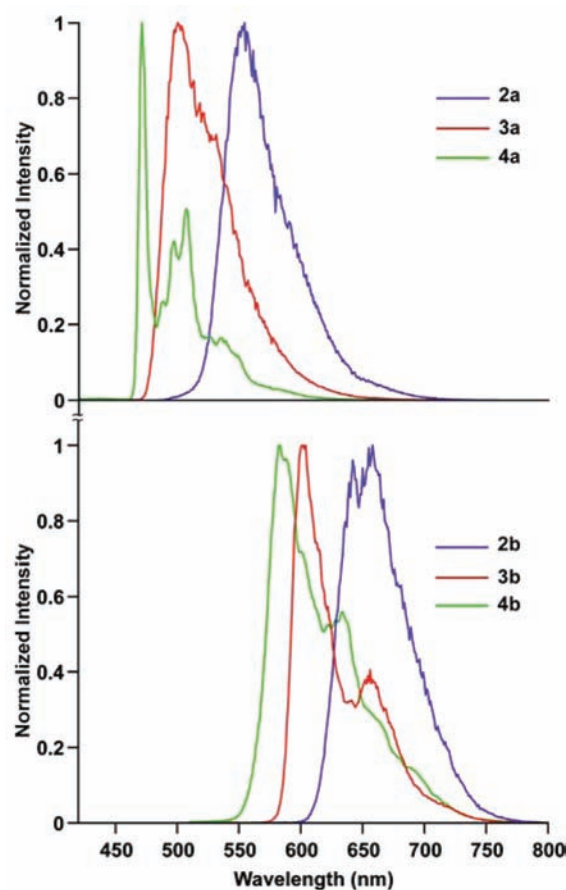


Figure 7. Emission spectra of complexes 2–4a and 2–4b in PrCN glass at 77 K.

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,^{41,60} while mixed LC/MLCT states give structured emissions.¹¹ On the basis of these considerations, the broad and featureless emissions of the dithiolates Bu₄N2a and Bu₄N2b can be ascribed to ³ML'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,⁶⁴ which would lead to a ³L'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 ³L'C/ML'CT states, resulting from the loss of the LL'CT contribution.

Room-temperature quantum yields (Φ) in a CH₂Cl₂ solution at 298 K were measured for **2a** and **1–4b**, and the corresponding radiative (k_r) and nonradiative (k_{nr}) rate constants were calculated according to the relationships $k_r = \Phi/\tau$ and $k_{nr} = (1 - \Phi)/\tau$, assuming that the emitting state is formed with unit efficiency upon excitation³⁶ (Table 9). The

Table 9. Quantum Yields and Radiative and Nonradiative Decay Rate Constants in a CH₂Cl₂ Solution at 298 K

compd	Φ	$k_r \times 10^{-4} \text{ (s}^{-1}\text{)}$	$k_{nr} \times 10^{-4} \text{ (s}^{-1}\text{)}$
1b	0.40	9	14
Bu ₄ N 2a	0.030	2.2	70
Bu ₄ N 2b	0.0018	0.16	90
3b	0.040	2.7	65
4b	0.27	34	94

different Φ values found for **2a** and **2b** can be related to their emission energies. Consistent with the energy gap law,⁶⁵ 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.²² 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(PCy₃)]⁺ 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_r and k_{nr} values along the tbpiq series reveals that the increasing emission efficiencies with the addition of [Au(PCy₃)]⁺ 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 ³MLCT and ¹MLCT states.⁵⁵

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(PCy₃)]⁺ units to

obtain heterometallic derivatives of the types [Pt(C[^]N)(bdt)-{Au(PCy₃)}] (**3a** and **3b**) and [Pt(C[^]N)(bdt){Au(PCy₃)₂}-ClO₄] (**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(PCy₃)]⁺ units between the two inequivalent S sites. Complexes Bu₄N**2a** and Bu₄N**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 (L = bdt; L' = C[^]N), while their emissions are assignable to triplet excited states with the same orbital parentage. The successive addition of [Au(PCy₃)]⁺ 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(PCy₃)]⁺ 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

Supporting Information

Crystallographic data in CIF format for **3b** and **4b**·CH₂Cl₂, variable-temperature ³¹P{¹H} NMR spectra of complex **4b** in CDCl₃ (212–333 K) and CD₂Cl₂ (183–202 K), results of the variable-temperature ³¹P{¹H} 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 CH₂Cl₂ solution at 298 K for **1b**, Bu₄N**2a**, 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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