

This document is the Accepted Manuscript version of a Published Work that appeared in final form in *Inorganic Chemistry*, copyright © American Chemical Society, after peer review and technical editing by the publisher. To access the final edited and published work see <https://doi.org/10.1021/ic202465k>

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

Fabio Juliá,[†] Peter G. Jones,[‡] and Pablo González-Herrero^{*,†}

*[†]Grupo de Química Organometálica, Departamento de Química Inorgánica, Facultad de Química, Universidad de Murcia, Apdo. 4021, 30071 Murcia, Spain
E-mail: pgh@um.es. Phone: +34 868887097. Fax. +34 868884148*

*[‡]Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany
E-mail: p.jones@tu-bs.de*

The cyclometallated compounds $[\text{Pt}(\text{C}^{\wedge}\text{N})(\text{HC}^{\wedge}\text{N})\text{Cl}]$ [$\text{HC}^{\wedge}\text{N}$ = 2-phenylpyridine (Hppy) (**1a**) or 1-(4-*tert*-butylphenyl)isoquinoline (Htbpiq) (**1b**)] react with 1,2-benzenedithiol, *t*-BuOK and Bu_4NCl in 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 (**Bu₄N2a**) or tbbpiq (**Bu₄N2b**)]. 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**), tbbpiq (**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**), tbbpiq (**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 sulfur atoms of the dithiolate. Complexes **Bu₄N2a** 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 ($\text{L} = \text{bdt}$, $\text{L}' = \text{C}^{\wedge}\text{N}$), 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 HOMO 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 L'C and ML'CT contributions.

Introduction

Square planar Pt(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. Pt(II) complexes with di- and trimine 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 Pt(II) systems with cyclometallated aromatic ligands, such as 2-arylpdridines 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 devices⁵⁻⁷ and molecular sensors.⁸ One of the keys to the success of these compounds lies in the beneficial effects that cyclometallation 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, result in a strong ligand field that ensures a higher energy for the non-emitting MC (d-d) states, which would otherwise provide thermally accessible pathways for the radiationless deactivation of emitting LC/MLCT excited states.^{5,6,9} Homoleptic complexes of the type $[\text{Pt}(\text{C}^{\wedge}\text{N})_2]$ were among the first reported Pt(II) complexes to display luminescence at room temperature in fluid solution.¹⁰ However, heteroleptic derivatives of the types $[\text{Pt}(\text{C}^{\wedge}\text{N})(\text{L}^{\wedge}\text{X})]$, $[\text{Pt}(\text{C}^{\wedge}\text{N})(\text{L}^{\wedge}\text{L})]^+$ or $[\text{Pt}(\text{C}^{\wedge}\text{N})\text{X}_2]^-$ have important advantages because the variation of the ancillary ligands allows 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 Pt(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 Pt(II) diimine dithiolates $[\text{Pt}(\text{N}^{\wedge}\text{N})(\text{S}^{\wedge}\text{S})]$.^{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 the modification of emission properties. Notably, a variety of Pt(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 Pd(II) and Pt(II) complexes of the type $[\text{M}'\{\text{S}_2\text{C}=\text{C}(\text{COMe})_2\}\text{L}_2]$ with $\text{M}' = \text{Pd}, \text{Pt}$ and $\text{L} = \text{PPh}_3$, *t*-BuCN or $\text{L}_2 = 1,5\text{-cyclooctadiene (cod)}$.^{31,32} More recently, we employed complexes of the types $[\text{M}\{\text{S}_2\text{C}=(\textit{t}\text{-Bu-fy})\}_2]^{2-}$ and $[\text{M}\{\text{S}_2\text{C}=(\textit{t}\text{-Bu-fy})\}(\text{dbbpy})]$ ($\text{M} = \text{Pd}, \text{Pt}$; *t*-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 Pt(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 article, we report the synthesis and photophysical characterization of $[\text{Pt}(\text{C}^{\wedge}\text{N})(\text{bdt})]^-$ [$\text{C}^{\wedge}\text{N}$ = 2-phenylpyridine, 1-(4-*tert*-butylphenyl)isoquinoline]; bdt = 1,2-benzenedithiolate], and di- and trinuclear Pt(II)/Au(I) derivatives resulting from the coordination of $[\text{Au}(\text{PCy}_3)]^+$ units, and analyze the modifications of the excited-state properties as a consequence of the successive addition of gold 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 THF were degassed and dried using a Pure Solv MD-5 solvent purification system from Innovative Technologies, Inc. The compounds $[\text{AuCl}(\text{PCy}_3)]^{34}$ and $[\text{Pt}(\text{ppy})(\text{Hppy})\text{Cl}]^{35}$ 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 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 tbpiq ligands. The atoms of the non-metallated 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% MeOH in CD_3OD . The 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. Infrared spectra were recorded in the range $4000\text{-}200\text{ cm}^{-1}$ on a Perkin-Elmer Spectrum 100 spectrophotometer using Nujol mulls between polyethylene sheets. High-resolution ESI mass spectra were recorded on an Agilent 6220 Accurate-Mass 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 which are emissive in solution

at room temperature, using [Ru(bpy)₃](PF₆)₂ in 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**·CH₂Cl₂ suitable for X-ray diffraction studies were obtained by the liquid-liquid diffusion method from CH₂Cl₂/MeOH or CH₂Cl₂/pentane, respectively. Numerical details are presented in Table 1. The data were collected on an Oxford Diffraction Xcalibur S diffractometer using monochromated Mo-*K* α radiation in ω -scan mode. The structures were refined anisotropically on F^2 using the program SHELXL-97 (G. M. Sheldrick, University of Göttingen).³⁸ Methyl hydrogens were included as part of rigid idealised methyl groups allowed to rotate but not tip; other hydrogens were included using a riding model. *Special features of refinement:* The dichloromethane molecule in **4b**·CH₂Cl₂ is disordered over two sites with relative occupation 0.65/0.35. Appropriate similarity restraints were used to improve stability of refinement.

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.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 (BHT) (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 an 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 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(tbpiq)(Htbpiq)Cl] (1b). The following procedure is based on the method described for [Pt(ppy)(Hppy)Cl] (**1a**).³⁵ K₂[PtCl₄] (450 mg, 1.08 mmol), Htbpiq (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 an N₂ atmosphere and the resulting solution was stirred at 80 °C for 4 d. 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 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, $^3J_{\text{HH}} = 8.2$ Hz, 1 H, Iq5), 7.74 (d, $^3J_{\text{HH}} = 6.8$ Hz, 1 H, Iq4'), 7.67 (t, $^3J_{\text{HH}} = 7.2$ Hz, 1 H, Iq6), 7.53-7.63 (m, 2 H, Iq7', Iq7), 7.50 (dd, $^3J_{\text{HH}} = 8.2$ Hz, $^4J_{\text{HH}} = 1.8$ Hz, 1 H, Ph3'/Ph5'), 7.30-7.38 (m, 2 H, Ph2'/Ph6', Iq4), 7.22 (dd, $^3J_{\text{HH}} = 8.2$ Hz, $^4J_{\text{HH}} = 1.7$ Hz, 1 H, Ph3'/Ph5'), 7.09 (dd, $^3J_{\text{HH}} = 8.4$ Hz, $^4J_{\text{HH}} = 2.0$ Hz, 1 H, Ph5), 6.28 (d with satellites, $^4J_{\text{HH}} = 2$ Hz, $^3J_{\text{HPt}} = 25$ Hz, 1 H, Ph3), 1.21 (s, 1 H, *t*-Bu'), 1.05 (s, 1 H, *t*-Bu). $^{13}\text{C}\{^1\text{H}\}$ APT NMR (100.81 MHz, CDCl_3): 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 (CMe_3), 34.4 (CMe_3), 31.1 (CMe_3), 30.9 (CMe_3).

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 [Pt(ppy)(Hppy)Cl] (**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 slow addition of Et₂O (20 mL) led to the precipitation of a red solid which was filtered off, washed with Et₂O (2 \times 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 $^\circ\text{C}$. ^1H NMR (300.1 MHz, CDCl_3): δ 9.22 (dd, $^3J_{\text{HH}} = 5.4$ Hz, $^3J_{\text{HPt}} = 24$ Hz, 1 H, py6), 7.93 (dd, $^3J_{\text{HH}} = 6.6$ Hz, $^3J_{\text{HPt}} = 29.4$ Hz, 1 H, Ph3), 7.69 (t, $^3J_{\text{HH}} = 7.5$ Hz, 1 H, py4), 7.61 (d, $^3J_{\text{HH}} = 8.1$ Hz, 1 H, py3), 7.46 (d, $^3J_{\text{HH}} = 6.9$ 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(tbpiq)(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 the 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 [Pt(ppy)(Hppy)Cl] (150 mg, 0.20 mmol) in CH₂Cl₂ (25 mL). After stirring for 60 min, a red solution was obtained. [AuCl(PCy₃)] (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 C₃₅H₄₅AuNPtS₂: 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). $^{31}\text{P}\{^1\text{H}\}$ NMR (162.3 MHz, CDCl_3): δ 52.84 (s).

[Pt(tbpq)(bdt){Au(PCy₃)}] (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 $[\text{AuCl}(\text{PCy}_3)]$ (103 mg, 0.20 mmol). Yield: 178 mg, 83%. Anal. Calcd for $\text{C}_{43}\text{H}_{55}\text{AuNPPtS}_2$: 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, CD_2Cl_2): δ 8.88 (d, $^3J_{\text{HH}} = 8.7$ Hz, 1 H, Iq8), 8.85 (dd, $^3J_{\text{HH}} = 6.4$ Hz, $^3J_{\text{HPt}} = 28.8$ Hz, 1 H, Iq3), 8.12 (dd, $^4J_{\text{HH}} = 1.9$ Hz, $^3J_{\text{HPt}} = 55.4$ Hz, 1 H, Ph3), 8.06 (d, $^3J_{\text{HH}} = 8.4$ Hz, 1 H, Ph6), 7.83 (d, $^3J_{\text{HH}} = 8.0$ Hz, 1 H, Iq5), 7.76 (t, $^3J_{\text{HH}} = 7.2$ Hz, 1 H, Iq6), 7.66 (t, $^3J_{\text{HH}} = 7.6$ Hz, 1 H, Iq7), 7.61 (d, $^3J_{\text{HH}} = 8.0$ Hz, 1 H, bdt), 7.57 (d, $^3J_{\text{HH}} = 8.0$ Hz, 1 H, bdt), 7.34 (d, $^3J_{\text{HH}} = 6.4$ Hz, 1 H, Iq4), 7.23 (dd, $^3J_{\text{HH}} = 8.4$ Hz, $^4J_{\text{HH}} = 1.8$ Hz, Ph5), 6.90 (t, $^3J_{\text{HH}} = 7.2$ Hz, 1 H, bdt), 6.80 (t, $^3J_{\text{HH}} = 7.2$ 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). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.8 MHz, CDCl_3): 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 (CMe_3), 33.2 (d, $^1J_{\text{PC}} = 28$ Hz, C1, Cy), 31.5 (CMe_3), 30.4 (C2, C6, Cy), 27.0 (d, $^3J_{\text{PC}} = 12$ Hz, C3, C5, Cy), 25.7 (C4, Cy). $^{31}\text{P}\{^1\text{H}\}$ NMR (162.3 MHz, CD_2Cl_2): δ 53.08 (br).

[Pt(ppy)(bdt){Au(PCy₃)₂]ClO₄ (4a). To a solution of $[\text{AuCl}(\text{PCy}_3)]$ (117 mg, 0.23 mmol) in acetone (25 mL) was added AgClO_4 (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 the 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(tbpq)(bdt){Au(PCy₃)₂]ClO₄ (4b). This yellow complex was obtained as described for **4a**, from [AuCl(PCy₃)] (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, 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). 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).

Table 1. Crystallographic Data for **3b** and **4b**·CH₂Cl₂.

	3b	4b ·CH ₂ Cl ₂
formula	C ₄₃ H ₅₅ AuNPtS ₂	C ₆₂ H ₉₀ Au ₂ Cl ₃ NO ₄ P ₂ PtS ₂
fw	1073.03	1734.78
<i>T</i> (K)	100.2(2)	100.2(2)
<i>λ</i> (Å)	0.71073	0.71073
cryst syst	triclinic	monoclinic
space group	<i>P</i> □	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	11.9157(2)	24.0411(4)
<i>b</i> (Å)	12.0728(2)	11.0278(2)
<i>c</i> (Å)	14.8775(2)	24.6578(4)
<i>α</i> (deg)	79.1084(11)	90
<i>β</i> (deg)	85.5256(11)	90.042(3)
<i>γ</i> (deg)	70.3669(12)	90
<i>V</i> (Å ³)	1979.23(5)	6537.28(19)
<i>Z</i>	2	4
<i>ρ</i> _{calcd} (Mg m ⁻³)	1.801	1.763
<i>μ</i> (mm ⁻¹)	7.409	6.892

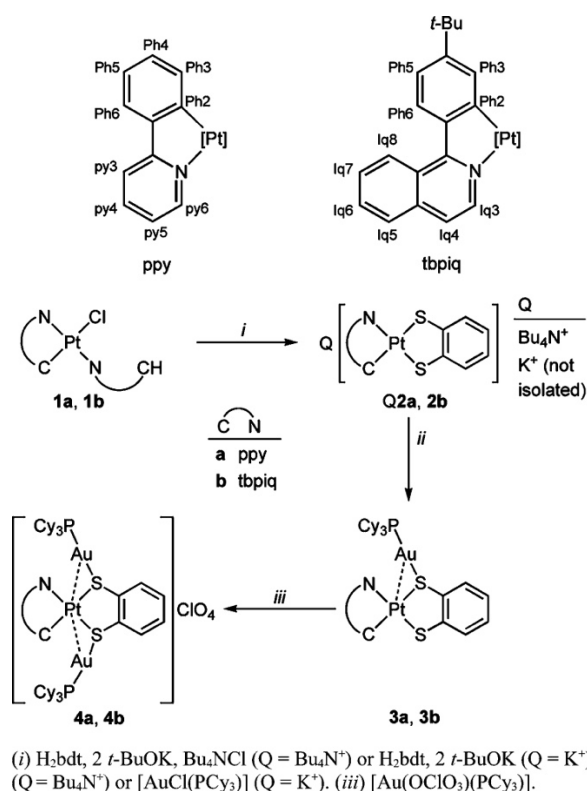
R1 ^a	0.0231	0.0236
wR2 ^b	0.0521	0.0434

^a $R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$ for reflections with $I > 2\sigma(I)$. ^b $wR2 = \frac{[\sum [w(F_o^2 - F_c^2)^2]]}{\sum [w(F_o^2)^2]}^{0.5}$ 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.

Results and Discussion

Syntheses. The cyclometallated compounds [Pt(C[^]N)(HC[^]N)Cl] [HC[^]N = 2-phenylpyridine (Hppy) (**1a**) or 1-(4-*tert*-butylphenyl)isoquinoline (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 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 of color. This decomposition is probably caused by a photooxidation process, which is common for Pt(II) diimine dithiolate complexes that display low energy charge-transfer absorptions.⁴⁰⁻⁴²

Scheme 1



We initially attempted the coordination of $[\text{Au}(\text{PCy}_3)]^+$ units to the anionic complexes $\text{Bu}_4\text{N2a}$ and $\text{Bu}_4\text{N2b}$ by reacting them with acetone solutions of $[\text{Au}(\text{OCIO}_3)(\text{PCy}_3)]$, which in turn were generated from $[\text{AuCl}(\text{PCy}_3)]$ and AgClO_4 .³³ Thus, the reaction of $\text{Bu}_4\text{N2a}$ with 1 equiv of $[\text{Au}(\text{OCIO}_3)(\text{PCy}_3)]$ in acetone gave the neutral complex $[\text{Pt}(\text{ppy})(\text{bdt})\{\text{Au}(\text{PCy}_3)\}]$ (**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 $\text{Bu}_4\text{N2b}$, this method afforded the analogous complex $[\text{Pt}(\text{tbpiq})(\text{bdt})\{\text{Au}(\text{PCy}_3)\}]$ (**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 [AuCl(PCy₃)]. Given the anionic nature of the dithiolato complexes, we expected that the sulfur atoms would have sufficient coordinating ability to displace the chloro ligand from the Au precursor. This procedure allowed the preparation of both **3a** and **3b** in good yields. The cationic trinuclear derivatives [Pt(C[^]N)(bdt){Au(PCy₃)₂}ClO₄] [C[^]N = ppy (**4a**), tbpiq (**4b**)] were prepared by reacting **3a** or **3b** with 1 equiv of [Au(OCIO₃)(PCy₃)] 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(PCy₃)]⁺ unit bonded to the sulfur atom *trans* to the aryl carbon. The other possible structural isomer, with the [Au(PCy₃)]⁺ unit bonded to the sulfur *trans* to the nitrogen, was not present in the crystal. The Pt atom is in a slightly distorted square planar environment [the mean deviation from plane C(21)-N(31)-Pt-S(1)-S(2) 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 C(21)-Pt-N(31) 79.80(12)°. The tbpiq ligand is not planar, because of the steric repulsion between the hydrogen 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 ligand (piq) in [Pt(piq)(Hpiq)Cl].⁴³ Of the two possible conformations, the tbpiq ligand adopts the one in which the *tert*-butylphenyl group bends away from the [Au(PCy₃)]⁺ unit, reasonably to minimize the steric repulsions between the *tert*-butyl substituent and the phosphine. The bond distances Pt-C(21) and Pt-N(31) are similar to those found for cyclometallated complexes containing ppy and derivatives.⁴⁴ The Pt-S(2) bond distance (*trans* to N) of 2.2653(8) Å is similar to those

found in [Pt(bdt)(bpy)] (2.250, 2.244 Å;⁴⁰ bpy = 2,2'-bipyridyl) and related complexes.^{2,45} The appreciably longer Pt-S(1) 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-S(1) bond distance of 2.3621(8) Å is only slightly longer than those found in [Au(PPh₃)₂(bdt)] and [Au(PPh₃)₂(tdt)] (range 2.316-2.325 Å;⁴⁶ tdt = 2,3-toluenedithiolate). The arrangement of the Au atom with respect to the Pt coordination mean plane is defined by the torsion angle Au-S(1)-Pt-S(2) of 95.78° and the angle Au-S(1)-Pt of 76.34(2)°. The latter is appreciably narrower than that found for the cationic complex [Pt{S₂C=(*t*-Bu-fy)}(dbbpy){Au(PCy₃)}]⁺ [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 Pt precursor **2b**, which allows a stronger interaction with the [Au(PCy₃)]⁺ 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(μ-dcpm)₂}PF₆ [2.953 Å; dcpm = 1,1-bis(dicyclohexylphosphino)methane],⁴⁷ [PtCl(Ph)}Au(μ-dppm)₂}PF₆ (2.965 Å),⁴⁸ and [Pt(CPh)}Au(μ-dppm)₂}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}

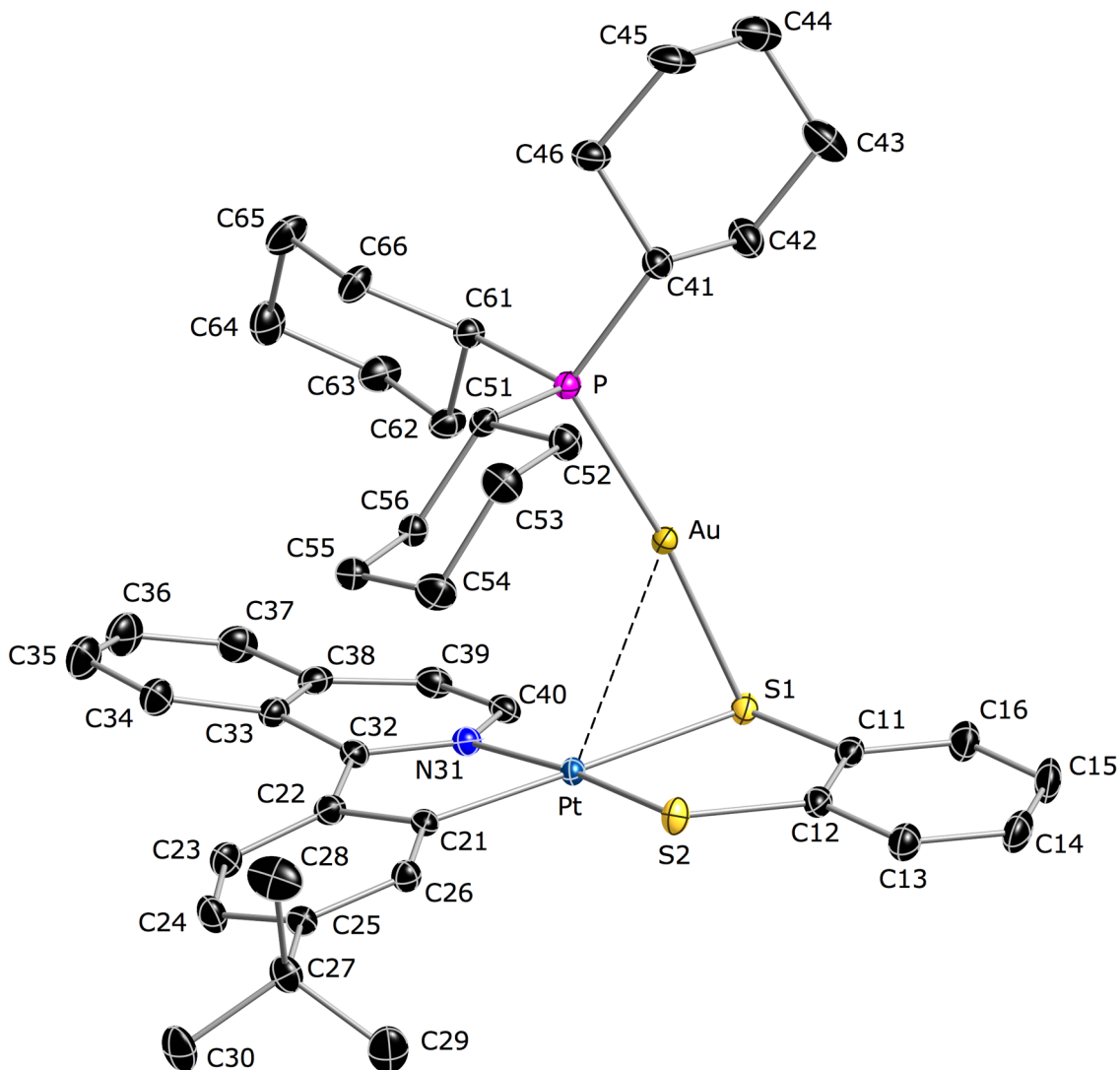


Figure 1. Thermal ellipsoid representation (50% probability) of the structure of complex **3b**. H atoms have been omitted for clarity.

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

Pt-C(21)	2.001(3)	Au-S(1)	2.3621(8)
Pt-N(31)	2.051(3)	S(1)-C(11)	1.774(3)
Pt-S(2)	2.2653(8)	S(2)-C(12)	1.752(3)
Pt-S(1)	2.3781(8)	N(31)-C(32)	1.346(4)
Pt-Au	2.92940(17)	N(31)-C(40)	1.363(4)
Au-P	2.2698(8)		

C(21)-Pt-N(31)	79.80(12)	C(11)-S(1)-Au	105.91(11)
C(21)-Pt-S(2)	94.42(10)	C(11)-S(1)-Pt	102.73(12)
N(31)-Pt-S(1)	97.54(8)	Au-S(1)-Pt	76.34(2)
S(2)-Pt-S(1)	88.23(3)	C(12)-S(2)-Pt	105.22(12)
P-Au-S(1)	172.68(3)		

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 [Pt(tbpiq)(bdt)]⁻ unit with two [Au(PCy₃)]⁺ units bonded to the sulfur atoms of the 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 Pt coordination mean plane and form torsion angles Au(1)-S(1)-Pt-S(2) and Au(2)-S(2)-Pt-S(1) of 104.45° and 95.10°, respectively. The Au(2)-S(2) bond distance (unit *trans* to C11) of 2.3586(6) Å is very similar to the corresponding distance found for **3b**, while the Au(1)-S(1) distance (unit *trans* to N) of 2.3388(6) Å is somewhat shorter. The angles Au(1)-S(1)-Pt of 86.10(2)° and Au(2)-S(2)-Pt of 79.027(19)° are wider than that found in **3b** and lead to longer Au⋯Pt contacts in **4b** [Pt⋯Au(2), 3.01407(14); Pt⋯Au(1), 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 in *trans* to it.

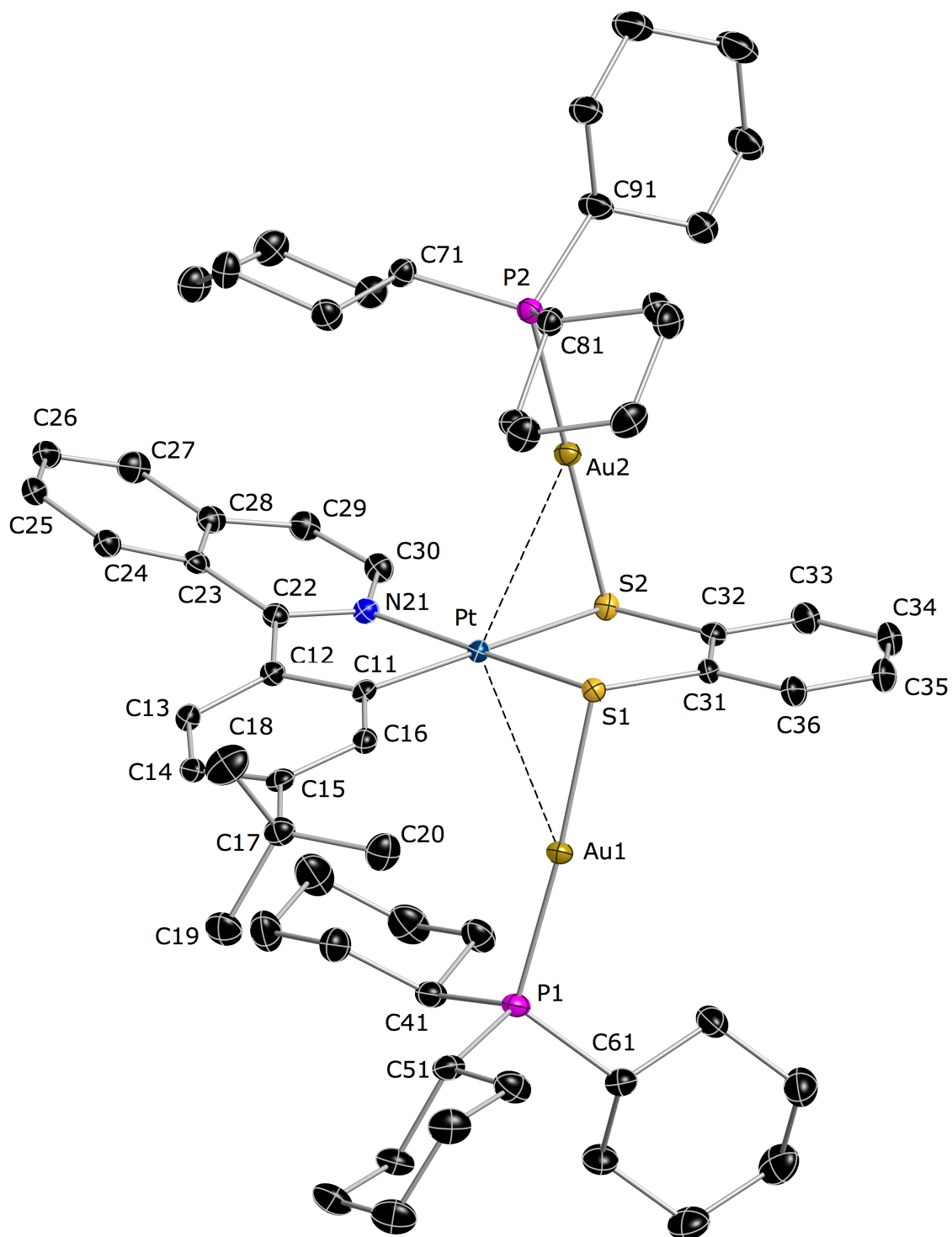


Figure 2. Thermal ellipsoid representation (50% probability) of the cation of complex **4b**. H atoms have been omitted for clarity.

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

Pt-C(11)	2.016(2)	Au(2)-P(2)	2.2633(7)
Pt-N(21)	2.052(3)	Au(1)-S(1)	2.3388(6)
Pt-S(1)	2.2734(6)	Au(2)-S(2)	2.3586(6)
Pt-S(2)	2.37815(6)	S(1)-C(31)	1.790(3)
Pt-Au(1)	3.14862(15)	S(2)-C(32)	1.780(3)
Pt-Au(2)	3.01407(14)	N(21)-C(22)	1.353(3)
Au(1)-P(1)	2.2586(6)	N(31)-C(40)	1.371(3)
C(11)-Pt-N(21)	80.35(9)	C(31)-S(1)-Au(1)	102.35(8)
C(11)-Pt-S(1)	94.98(7)	C(31)-S(1)-Pt	105.57(8)
N(21)-Pt-S(2)	96.16(6)	Au(1)-S(1)-Pt	86.10(2)
S(2)-Pt-S(1)	88.64(2)	C(32)-S(2)-Au(2)	99.36(8)
P(1)-Au(1)-S(1)	175.21(2)	C(32)-S(2)-Pt	102.97(9)
P(2)-Au(2)-S(2)	177.18(2)	Au(2)-S(2)-Pt	79.027(19)
Au(1)-Pt-Au(2)	134.697(4)		

NMR Spectra and Dynamic Behavior. The ¹H and ¹³C{¹H} NMR spectra of the Pt(II) complexes **Bu₄N2a** and **Bu₄N2b** show the expected chemical inequivalence of all the protons and carbons of the bdt ligand, the 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,b** and **4a,b** were expected to undergo dynamic processes in solution involving the migration of the [Au(PCy₃)]⁺ units between the sulfur atoms of the dithiolato ligand. We have previously shown that such processes

take place in the related complexes $[M\{S_2C=(t\text{-Bu-fy})\}(dbbpy)\{Au(PCy_3)\}]^+$ and $[M\{S_2C=(t\text{-Bu-fy})\}_2\{Au(PCy_3)\}_2]$ ($M = Pd, Pt$).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 $^{31}P\{^1H\}$ 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 $^{31}P\{^1H\}$ 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 $CDCl_3$ (Figure 3 and Supporting Information) and coalesce at 271 (**4a**) or 296 K (**4b**). The two distinct resonances arise because the $[Au(PCy_3)]^+$ units are bonded to inequivalent sulfur atoms, one of them *trans* to the aryl carbon and the other *trans* to the nitrogen. The exchange between the environments of the phosphorus atoms can only be achieved via the concerted migration of the $[Au(PCy_3)]^+$ units to the opposite sulfur (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 the migration of $[Au(PCy_3)]^+$ units and the interconversion between the *tbpiq* conformations slow down. In order to check this possibility, we registered the $^{31}P\{^1H\}$ 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 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.

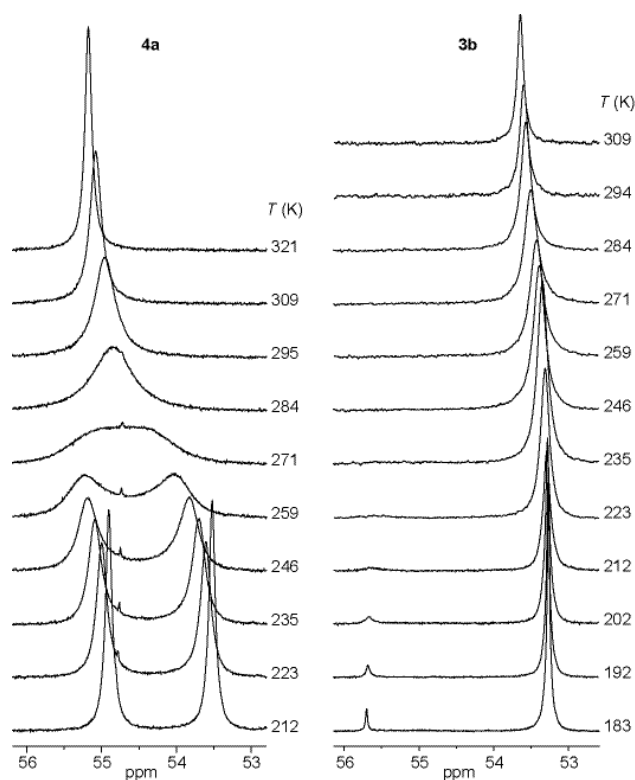
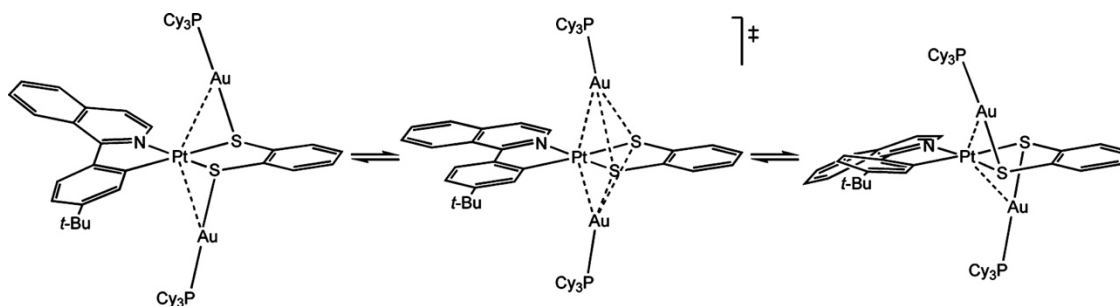


Figure 3. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **4a** in CDCl_3 and **3b** in CD_2Cl_2 at various temperatures.

Scheme 2



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 resonances and are listed in Table 4. The negative values of the activation entropies are compatible with the unimolecular nature of the 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 Pt \cdots Au metallophilic interactions, which is depicted in Scheme 2 for **4b**. The activation enthalpy is significantly higher for the tbiq derivative **4b** than for its ppy homologue **4a**. Since Au–S bond and Pt \cdots Au interaction energies are expected to be very similar for both complexes, a reasonable explanation for this is that the migration of the $[\text{Au}(\text{PCy}_3)]^+$ units in **4b** requires the concomitant conformational change of the tbiq ligand (Scheme 2). This would allow the 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.

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)	$\Delta G^\ddagger_{\text{coal}}$ (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

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 sulfur *trans* to the aryl carbon or the sulfur *trans* to the nitrogen. 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 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 the migration of the $[\text{Au}(\text{PCy}_3)]^+$ unit between the sulfur 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 tbpiq 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 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 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, $T_c = 271$ 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 the migration of the $[\text{Au}(\text{PCy}_3)]^+$ unit between the sulfur 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 $[\text{Au}(\text{PCy}_3)]^+$ unit attached to the sulfur *trans* to the aryl carbon and the phenyl ring of the tbpiq ligand bent away from this unit. The other resonance should correspond to the isomers with the $[\text{Au}(\text{PCy}_3)]^+$ unit bonded to the sulfur *trans* to the nitrogen and, possibly, the opposite tbpiq conformation. The strong *trans* influence of the aryl carbon explains the different stabilities of the structural isomers, because it causes a weakening of the corresponding

Pt-S bond, and this sulfur atom must therefore have a higher coordinating ability towards the Au(I) center than the other sulfur. 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 sulfur *trans* to the aryl carbon.

The ¹³C{¹H} NMR spectra of the heterometallic derivatives are not sensitive to the exchange processes mentioned above. The coordination of [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	δ (C1/C2)
Bu ₄ N 2a	148.8, 144.5
3a	148.6, 135.6
4a	139.3, 133.5
Bu ₄ N 2b	149.5, 145.0
3b	150.5, 134.9
4b	139.3, 134.7

^appm, CDCl₃ solution

Electronic Absorption Spectra. The UV-vis absorption spectra were measured in CH₂Cl₂ at 298 K for all the new compounds and the results are summarized in Table 6. The data for **1a**^{44,53} and the ligand precursor Htbp_{iq} are included for comparison. The tbp_{iq} 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 tbpiq 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 extinction coefficients, the corresponding electronic states are assigned as $^1\text{MLCT}$. We note, however, that the assignment to pure MLCT states is a simplification, since 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 the two overlapping MLCT absorptions observed for the ppy analogue **1a** (384 and 402 nm),^{44,53} which is indicative of a significantly lower HOMO-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, as 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 the absorptions of the other ppy and tbpiq complexes described in this work.

Table 6. Electronic Absorption Data for Compounds **1-4a,b** in CH_2Cl_2 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)

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 tbiq ligands. A very broad band is observed in the visible region, whose energy is solvent-dependent (Table 7), although the variations with 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 Pt(II) diimine dithiolates, 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 Pt(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 singlet in view of the relatively high extinction coefficients. The diminished solvatochromism of these complexes compared to Pt(II) diimine dithiolates is possibly a consequence of their anionic character, which may become the dominant factor in the solvation of the ground and excited states. Recent TD-DFT 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 sulfur orbitals.

Table 7. Lowest-Energy Absorption Band for Complexes Bu₄N**2a**, Bu₄N**2b**, **3a** and **3b** in Solvents of Differing Polarity.^a

solvent	λ_{\max} , nm			
	Bu ₄ N 2a	Bu ₄ N 2b	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

^a 5 × 10⁻⁵ M.

The absorption spectra of the heterometallic derivatives are compared with those of their mononuclear precursors in Figure 4. The introduction of [Au(PCy₃)]⁺ units results in two successive hypsochromic shifts of the lowest-energy absorption band on going from the Pt 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 Bu₄N**2a** and Bu₄N**2b**. In the cases of the diaurated derivatives **4a** and **4b**, the lowest-energy absorption is narrower and resolves into two overlapping components, the variations with solvent polarity being very small. Since 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 sulfur orbitals and hence their reduced participation in the HOMO.

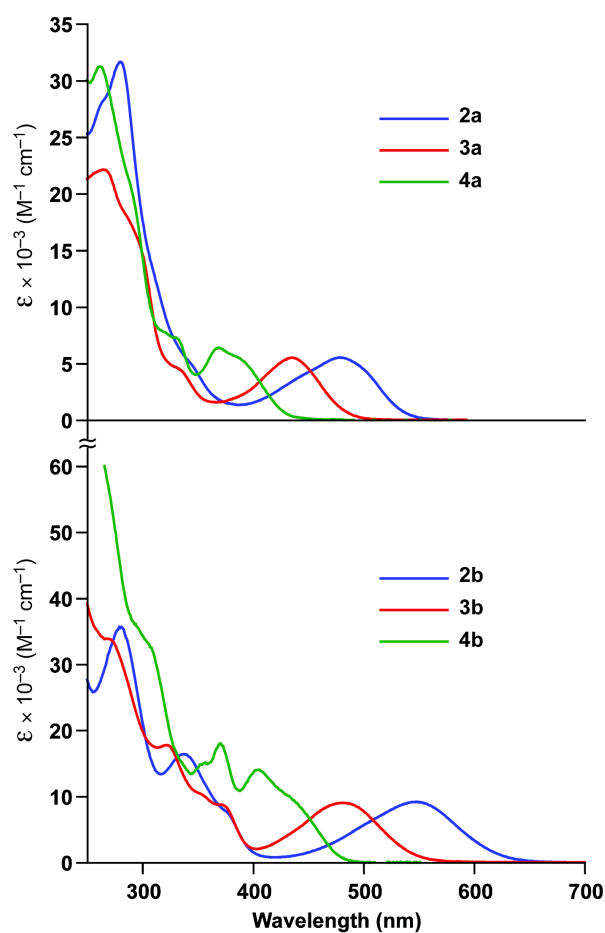


Figure 4. Electronic absorption spectra of **2-4a** (top) and **2-4b** (bottom) in CH_2Cl_2 solution (*ca.* 5×10^{-5} M) at 298 K.

Excitation and Emission Spectra. All 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 CH_2Cl_2 solution at 298 K. The excitation and emission data are summarized in Table 8.

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

Compd	medium (T/K)	$\lambda_{\text{exc}}/\text{nm}$	$\lambda_{\text{em}}/\text{nm}$	$\tau/\mu\text{s}$
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)	<i>365</i> , 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%)

^a The most intense peak is italicized. ^b Data from ref. 44.

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 μs falls in the range observed for mixed ³LC/MLCT excited states in related cyclometallated Pt(II) complexes,⁵⁵ and thus this assignment is appropriate for **1b**.

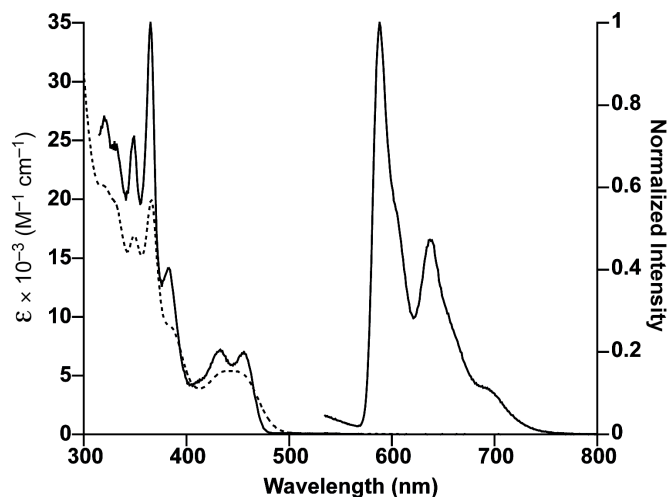


Figure 5. Excitation and emission spectra of complex **1b** in PrCN glass at 77 K (—) and absorption spectrum in CH₂Cl₂ solution at 298 K (---).

The Pt complexes Bu₄N**2a** and Bu₄N**2b** and their monoaurated derivatives **3a** and **3b** give rise to broad and nearly symmetrical emission bands in CH₂Cl₂ solution at 298 K. Notably, the emission of the ppy complex **3a** is very weak under these conditions and did not allow the measurement of lifetime and quantum yield data with acceptable accuracy. Of the diaurated complexes, only the tbpiq derivative **4b** is emissive in 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 tbpiq series). The emission spectra in the solid state at 298 K are in general very similar in shape and energy to those in fluid CH₂Cl₂ solution (see 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 Bu₄N**2a** and Bu₄N**2b** (1576 and 669 cm⁻¹, respectively) and the monoaurated derivatives **3a** and **3b** (2244 or 894 cm⁻¹, respectively), which can be

ascribed to a rigidochromic effect commonly observed for diimine^{22,33,61} and cyclometallated⁶² 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 tbpiq derivative **3b**. Complexes **4a** and **4b** display highly structured emissions at 77 K which 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 $[\text{Au}(\text{PCy}_3)]^+$ 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 the coordination of the sulfur atoms to Au(I), as has been reasoned for the absorption spectra. Secondly, as $[\text{Au}(\text{PCy}_3)]^+$ units are added, vibronic features appear or become sharper. This second effect can be attributed to a decrease in LL'CT character of the emitting excited state as a consequence of the diminishing participation of the sulfur orbitals in the HOMO, which is accompanied by an increase in 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 Based on 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 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 $^3\text{L}'\text{C}/\text{ML}'\text{CT}$ states, resulting from the loss of the $\text{LL}'\text{CT}$ contribution.

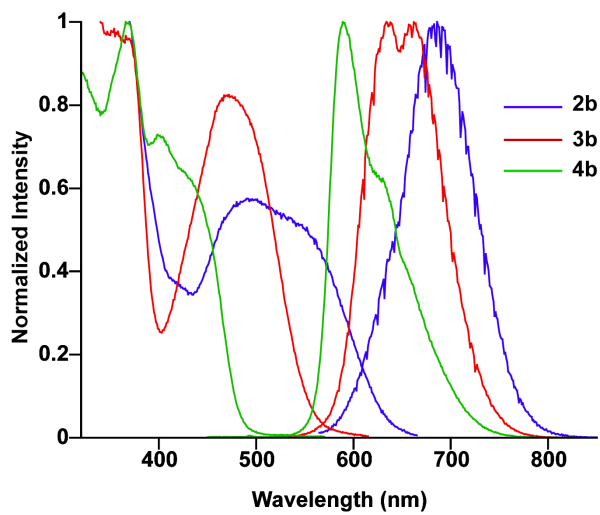


Figure 6. Excitation and emission spectra of complexes $\text{Bu}_4\text{N}2\text{b}$, **3b** and **4b** in CH_2Cl_2 solution at 298 K.

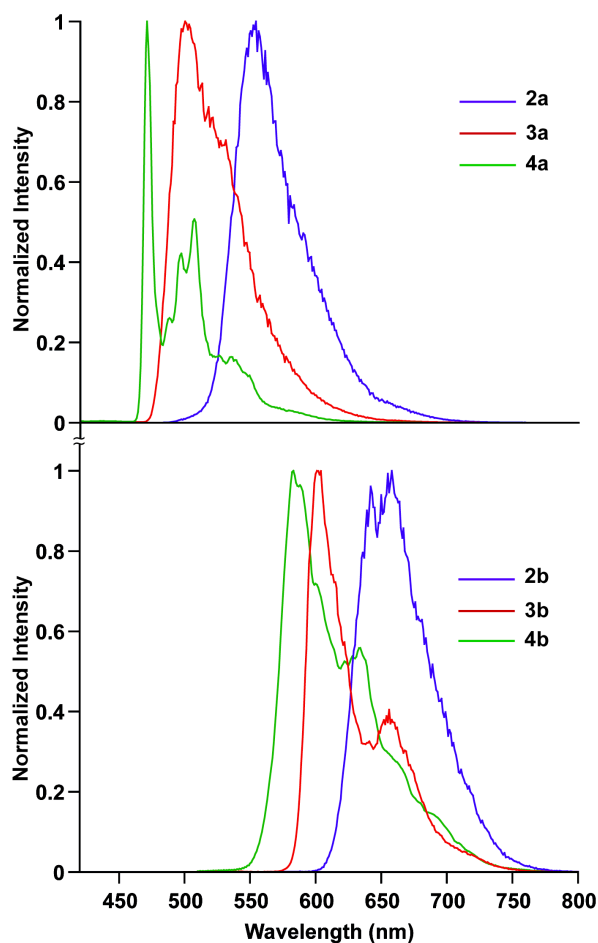


Figure 7. Emission spectra of complexes **2-4a** and **2-4b** in PrCN glass at 77 K.

Room-temperature quantum yields (Φ) in CH_2Cl_2 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 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 Pt(II) diimine dithiolates, the quantum yield of complex **2a** is considerably higher, while that of **2b** approaches the upper limit of the observed range.²² Since the emission of **3a** is

very weak and **4a** is not emissive under these conditions, it is clear that the successive coordination of $[\text{Au}(\text{PCy}_3)]^+$ units has an adverse effect on the emission efficiencies in 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, as 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 $[\text{Au}(\text{PCy}_3)]^+$ units arise from the increments in the radiative decay rates, as the variations in the nonradiative constants are much less marked and not regular. This effect is possibly the result of the increasing MLCT 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 $^3\text{MLCT}$ and $^1\text{MLCT}$ states.⁵⁵

Table 9. Quantum yields and radiative and nonradiative decay rate constants in CH_2Cl_2 solution at 298 K.

Compd	Φ	$k_r \times 10^{-4} (\text{s}^{-1})$	$k_{nr} \times 10^{-4} (\text{s}^{-1})$
1b	0.40	9	14
Bu₄N2a	0.030	2.2	70
Bu₄N2b	0.0018	0.16	90
3b	0.040	2.7	65
4b	0.27	34	94

Conclusions

The anionic cyclometallated Pt(II) 1,2-benzenedithiolate complexes $[\text{Pt}(\text{C}^{\wedge}\text{N})(\text{bdt})]^{-}$ [$\text{C}^{\wedge}\text{N} = \text{ppy}$ (**2a**), tbpiq (**2b**)] have been synthesized from $[\text{Pt}(\text{C}^{\wedge}\text{N})(\text{HC}^{\wedge}\text{N})\text{Cl}]$ precursors and employed as metalloligands toward $[\text{Au}(\text{PCy}_3)]^{+}$ units to obtain heterometallic derivatives of the types $[\text{Pt}(\text{C}^{\wedge}\text{N})(\text{bdt})\{\text{Au}(\text{PCy}_3)\}]$ (**3a**, **3b**) and $[\text{Pt}(\text{C}^{\wedge}\text{N})(\text{bdt})\{\text{Au}(\text{PCy}_3)\}_2]\text{ClO}_4$ (**4a**, **4b**). The crystal structures of **3b** and **4b** reveal the formation of Pt \cdots Au metallophilic contacts that are appreciably shorter than those observed for analogous heteronuclear derivatives based on Pt(II) diimine dithiolate 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 the migration of the $[\text{Au}(\text{PCy}_3)]^{+}$ units between the two inequivalent sulfur sites. Complexes **Bu**₄**N2a** and **Bu**₄**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 $[\text{Au}(\text{PCy}_3)]^{+}$ 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 fluid solution is achieved as $[\text{Au}(\text{PCy}_3)]^{+}$ units are added. In conclusion, this study has demonstrated that the orbital nature of the emitting excited states in anionic complexes of the type $[\text{Pt}(\text{C}^{\wedge}\text{N})(\text{S}^{\wedge}\text{S})]^{-}$ can be easily altered by the successive coordination to gold 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.

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. Excitation and emission spectra in the solid state at 298 K for all complexes and in 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>.

Acknowledgment

We thank Ministerio de Educación y Ciencia (Spain), FEDER (CTQ2007-60808) and Fundación Séneca (04539/GERM/06) for financial support.

References

- (1) Pevny, F.; Zabel, M.; Winter, R. F.; Rausch, A. F.; Yersin, H.; Tuczek, F.; Zalis, S. *Chem. Commun.* **2011**, *47*, 6302-6304. Du, P. W.; Knowles, K.; Eisenberg, R. *J. Am. Chem. Soc.* **2008**, *130*, 12576-12577. Du, P. W.; Schneider, J.; Jarosz, P.; Eisenberg, R. *J. Am. Chem. Soc.* **2006**, *128*, 7726-7727. Jarosz, P.; Du, P. W.; Schneider, J.; Lee, S. H.; McCamant, D.; Eisenberg, R. *Inorg. Chem.* **2009**, *48*, 9653-9663. Zhang, J.; Du, P. W.; Schneider, J.; Jarosz, P.; Eisenberg, R. *J. Am. Chem. Soc.* **2007**, *129*, 7726-7727. Wang, X.-H.; Goeb, S.; Ji, Z.-Q.; Pogulaichenko, N. A.; Castellano, F. N. *Inorg. Chem.* **2011**, *50*, 705-707.

- (2) Geary, E. A. M.; Hirata, N.; Clifford, J.; Durrant, J. R.; Parsons, S.; Dawson, A.; Yellowlees, L. J.; Robertson, N. *Dalton Trans.* **2003**, 3757-3762.
- (3) Chakraborty, S.; Wadas, T. J.; Hester, H.; Schmehl, R.; Eisenberg, R. *Inorg. Chem.* **2005**, *44*, 6865-6878.
- (4) Taylor, S. D.; Howard, W.; Kaval, N.; Hart, R.; Krause, J. A.; Connick, W. B. *Chem. Commun.* **2010**, *46*, 1070-1072. Lo, H.-S.; Yip, S.-K.; Wong, K. M.-C.; Zhu, N.; Yam, V. W.-W. *Organometallics* **2006**, *25*, 3537-3540. Ni, J.; Zhang, L.-Y.; Wen, H.-M.; Chen, Z.-N. *Chem. Commun.* **2009**, 3801-3803. Wadas, T. J.; Wang, Q. M.; Kim, Y. J.; Flaschenreim, C.; Blanton, T. N.; Eisenberg, R. *J. Am. Chem. Soc.* **2004**, *126*, 16841-16849.
- (5) Kalinowski, J.; Fattori, V.; Cocchi, M.; Williams, J. A. G. *Coord. Chem. Rev.* **2011**, *255*, 2401-2425.
- (6) Williams, J. A. G.; Develay, S.; Rochester, D. L.; Murphy, L. *Coord. Chem. Rev.* **2008**, *252*, 2596-2611.
- (7) Cocchi, M.; Virgili, D.; Sabatini, C.; Fattori, V.; Di, M. P.; Maestri, M.; Kalinowski, J. *Synth. Met.* **2004**, *147*, 253-256. Vezzu, D. A. K.; Deaton, J. C.; Jones, J. S.; Bartolotti, L.; Harris, C. F.; Marchetti, A. P.; Kondakova, M.; Pike, R. D.; Huo, S. *Inorg. Chem.* **2010**, *49*, 5107-5119. Tam, A. Y.-Y.; Tsang, D. P.-K.; Chan, M.-Y.; Zhu, N.; Yam, V. W.-W. *Chem. Commun.* **2011**, *47*, 3383-3385. Rossi, E.; Murphy, L.; Brothwood, P. L.; Colombo, A.; Dragonetti, C.; Roberto, D.; Ugo, R.; Cocchi, M.; Williams, J. A. G. *J. Mater. Chem.* **2011**, *21*, 15501-15510. Ma, B.; Djurovich, P. I.; Garon, S.; Alleyne, B.; Thompson, M. E. *Adv. Funct. Mater.* **2006**, *16*, 2438-2446. Evans, R. C.; Douglas, P.; Winscom, C. J. *Coord. Chem. Rev.* **2006**, *250*, 2093-2126. Zhou, G.; Wong, W.-Y.; Yang, X. *Chem.--Asian J.* **2011**, *6*, 1706-1727.

- (8) Guerchais, V.; Fillaut, J.-L. *Coord. Chem. Rev.* **2011**, *255*, 2448-2457. Wong, K. M.-C.; Yam, V. W.-W. *Coord. Chem. Rev.* **2007**, *251*, 2477-2488. Li, K.; Chen, Y.; Lu, W.; Zhu, N.; Che, C.-M. *Chem. Eur. J.* **2011**, *17*, 4109-4112. Yang, Q.-Z.; Wu, L.-Z.; Zhang, H.; Chen, B.; Wu, Z.-X.; Zhang, L.-P.; Tung, C.-H. *Inorg. Chem.* **2004**, *43*, 5195-5197. Che, C.-M.; Zhang, J.-L.; Lin, L.-R. *Chem. Commun.* **2002**, 2556-2557.
- (9) Chassot, L.; Von Zelewsky, A. *Inorg. Chem.* **1987**, *26*, 2814-2818. Balashev, K. P.; Puzyk, M. V.; Kotlyar, V. S.; Kulikova, M. V. *Coord. Chem. Rev.* **1997**, *159*, 109-120.
- (10) Chassot, L.; Mueller, E.; Von Zelewsky, A. *Inorg. Chem.* **1984**, *23*, 4249-4253. Maestri, M.; Sandrini, D.; Balzani, V.; Chassot, L.; Jolliet, P.; von Zelewsky, A. *Chem. Phys. Lett.* **1985**, *122*, 375-379. Chassot, L.; Von Zelewsky, A.; Sandrini, D.; Maestri, M.; Balzani, V. *J. Am. Chem. Soc.* **1986**, *108*, 6084-6085. Barigelletti, F.; Sandrini, D.; Maestri, M.; Balzani, V.; Vonzelewsky, A.; Chassot, L.; Jolliet, P.; Maeder, U. *Inorg. Chem.* **1988**, *27*, 3644-3647.
- (11) Brooks, J.; Babayan, Y.; Lamansky, S.; Djurovich, P. I.; Tsyba, I.; Bau, R.; Thompson, M. E. *Inorg. Chem.* **2002**, *41*, 3055-3066.
- (12) Ma, B.; Djurovich, P. I.; Yousufuddin, M.; Bau, R.; Thompson, M. E. *J. Phys. Chem. C* **2008**, *112*, 8022-8031. Adamovich, V.; Brooks, J.; Tamayo, A.; Alexander, A. M.; Djurovich, P. I.; D'Andrade, B. W.; Adachi, C.; Forrest, S. R.; Thompson, M. E. *New J. Chem.* **2002**, *26*, 1171-1178. Cho, J.-Y.; Domercq, B.; Barlow, S.; Suponitsky, K. Y.; Li, J.; Timofeeva, T. V.; Jones, S. C.; Hayden, L. E.; Kimyonok, A.; South, C. R.; Weck, M.; Kippelen, B.; Marder, S. R. *Organometallics* **2007**, *26*, 4816-4829. Valore, A.; Colombo, A.; Dragonetti, C.; Righetto, S.; Roberto, D.; Ugo, R.; De Angelis, F.; Fantacci, S. *Chem. Comm.* **2010**, *46*, 2414-2416.

- (13) Hirani, B.; Li, J.; Djurovich, P. I.; Yousufuddin, M.; Oxgaard, J.; Persson, P.; Wilson, S. R.; Bau, R.; Goddard, W. A., III; Thompson, M. E. *Inorg. Chem.* **2007**, *46*, 3865-3875.
- (14) Shavaleev, N. M.; Adams, H.; Best, J.; Edge, R.; Navaratnam, S.; Weinstein, J. A. *Inorg. Chem.* **2006**, *45*, 9410-9415.
- (15) Kvam, P.-I.; Songstad, J. *Acta Chem. Scand.* **1995**, *49*, 313-324.
- (16) Janzen, D. E.; Mehne, L. F.; VanDerveer, D. G.; Grant, G. J. *Inorg. Chem.* **2005**, *44*, 8182-8184. Janzen, D. E.; VanDerveer, D. G.; Mehne, L. F.; da Silva Filho, D. A.; Brédas, J. L.; Grant, G. J. *Dalton Trans.* **2008**, 1872-1882.
- (17) Bevilacqua, J. M.; Eisenberg, R. *Inorg. Chem.* **1994**, *33*, 2913-2923.
- (18) Forniés, J.; Sicilia, V.; Casas, J. M.; Martín, A.; López, J. A.; Larraz, C.; Borja, P.; Ovejero, C. *Dalton Trans.* **2011**, *40*, 2898-2912.
- (19) Ghavale, N.; Jain, V. *J. Organomet. Chem.* **2010**, *695*, 1237-1245.
- (20) Weinstein, J. A.; Yurii A. Kovelonov; Blake, A. J.; George, M. W.; Matousek, P.; Mel'nikov, M. Y.; Parker, A. W.; Sun, X.-Z.; Towrie, M. *Dalton Trans.* **2005**, 2092-2097.
- (21) Suga, Y.; Nakano, M.; Tamura, H.; Matsubayashi, G.-e. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1877-1883.
- (22) Cummings, S. D.; Eisenberg, R. *J. Am. Chem. Soc.* **1996**, *118*, 1949-1960.
- (23) Adams, C. J.; Fey, N.; Parfitt, M.; Pope, S. J. A.; Weinstein, J. A. *Dalton Trans.* **2007**, 4446-4456. Lazarides, T.; McCormick, T. M.; Wilson, K. C.; Lee, S.; McCamant, D. W.; Eisenberg, R. *J. Am. Chem. Soc.* **2011**, *133*, 350-364.
- (24) Pyykkö, P. *Chem. Rev.* **1997**, *97*, 597-636. Pyykkö, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 4412-4456.

- (25) Yam, V. W. W. *Acc. Chem. Res.* **2002**, *35*, 555-563. Yam, V. W. W.; Lo, K. K. W. *Chem. Soc. Rev.* **1999**, *28*, 323-334. López-de-Luzuriaga, J. M.; Monge, M.; Olmos, M. E.; Pascual, D.; Rodríguez-Castillo, M. *Inorg. Chem.* **2011**, *50*, 6910-6921. Ríos, D.; Olmstead, M. M.; Balch, A. L. *Inorg. Chem.* **2009**, *48*, 5279-5287. Calhorda, M. J.; Ceamanos, C.; Crespo, O.; Gimeno, M. C.; Laguna, A.; Larráz, C.; Vaz, P. D.; Villacampa, M. D. *Inorg. Chem.* **2010**, *49*, 8255-8269. Fernández, E. J.; Laguna, A.; López-de-Luzuriaga, J. M.; Monge, M.; Montiel, M.; Olmos, M. E.; Pérez, J.; Puelles, R. C.; Saenz, J. C. *Dalton Trans.* **2005**, 1162-1164. Fernández, E. J.; Laguna, A.; López-de-Luzuriaga, J. M.; Monge, M.; Montiel, M.; Olmos, M. E.; Rodríguez-Castillo, M. *Dalton Trans.* **2009**, 7509-7518. Laguna, A.; Lasanta, T.; López-de-Luzuriaga, J. M.; Monge, M.; Naumov, P.; Olmos, M. E. *J. Am. Chem. Soc.* **2010**, *132*, 456-457. López-de-Luzuriaga, J. M.; Monge, M.; Olmos, M. E.; Pascual, D.; Lasanta, T. *Chem. Commun.* **2011**, *47*, 6795-6797. Stork, J. R.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **2005**, *127*, 6512-6513. Stork, J. R.; Olmstead, M. M.; Fettinger, J. C.; Balch, A. L. *Inorg. Chem.* **2006**, *45*, 849-857. Stork, J. R.; Rios, D.; Pham, D.; Bicocca, V.; Olmstead, M. M.; Balch, A. L. *Inorg. Chem.* **2005**, *44*, 3466-3472. Forniés, J.; Ibáñez, S.; Martín, A.; Sanz, M.; Berenguer, J. R.; Lalinde, E.; Torroba, J. *Organometallics* **2006**, *25*, 4331-4340. Forniés, J.; García, A.; Lalinde, E.; Moreno, M. T. *Inorg. Chem.* **2008**, *47*, 3651-3660.
- (26) Yam, V. W. W.; Yu, K. L.; Cheng, E. C. C.; Yeung, P. K. Y.; Cheung, K. K.; Zhu, N. Y. *Chem. Eur. J.* **2002**, *8*, 4121-4128.
- (27) Chen, Y. D.; Zhang, L. Y.; Shi, L. X.; Chen, Z. N. *Inorg. Chem.* **2004**, *43*, 7493-7501. Chen, Y.-D.; Qin, Y.-H.; Zhang, L.-Y.; Shi, L.-X.; Chen, Z.-N. *Inorg. Chem.* **2004**, *43*, 1197-1205.

- (28) Moussa, J.; Wong, K. M. C.; Chamoreau, L. M.; Amouri, H.; Yam, V. W. W. *Dalton Trans.* **2007**, 3526-3530.
- (29) Charmant, J. P. H.; Falvello, L. R.; Forniés, J.; Gómez, J.; Lalinde, E.; Moreno, M. T.; Orpen, A. G.; Rueda, A. *Chem. Commun.* **1999**, 2045-2046. Forniés, J.; Gómez, J.; Lalinde, E.; Moreno, M. T. *Inorg. Chem.* **2001**, *40*, 5415-5419. Gil, B.; Forniés, J.; Gómez, J.; Lalinde, E.; Martín, A.; Moreno, M. T. *Inorg. Chem.* **2006**, *45*, 7788-7798. Berenguer, J. R.; Díez, A.; Fernández, J.; Forniés, J.; García, A.; Gil, B.; Lalinde, E.; Moreno, M. T. *Inorg. Chem.* **2008**, *47*, 7703-7716. Berenguer, J. R.; Gil, B.; Fernández, J.; Forniés, J.; Lalinde, E. *Inorg. Chem.* **2009**, *48*, 5250-5262. Yip, S. K.; Chan, C. L.; Lam, W. H.; Cheung, K. K.; Yam, V. W. W. *Photochem. Photobiol. Sci.* **2007**, *6*, 365-371. Wei, Q. H.; Yin, G. Q.; Ma, Z.; Shi, L. X.; Chen, Z. N. *Chem. Commun.* **2003**, 2188-2189. Berenguer, J. R.; Forniés, J.; Gómez, J.; Lalinde, E.; Moreno, M. T. *Organometallics* **2001**, *20*, 4847-4851. Ara, I.; Berenguer, J. R.; Eguizábal, E.; Forniés, J.; Gómez, J.; Lalinde, E. *J. Organomet. Chem.* **2003**, *670*, 221-234. Fernández, J.; Forniés, J.; Gil, B.; Gómez, J.; Lalinde, E.; Moreno, M. T. *Organometallics* **2006**, *25*, 2274-2283. Forniés, J.; Fuertes, S.; Martín, A.; Sicilia, V.; Lalinde, E.; Moreno, M. T. *Chem. Eur. J.* **2006**, *12*, 8253-8266. Wong, K. M. C.; Hui, C. K.; Yu, K. L.; Yam, V. W. W. *Coord. Chem. Rev.* **2002**, *229*, 123-132. Yam, V. W. W.; Hui, C. K.; Wong, K. M. C.; Zhu, N. Y.; Cheung, K. K. *Organometallics* **2002**, *21*, 4326-4334. Yam, V. W. W.; Yu, K. L.; Wong, K. M. C.; Cheung, K. K. *Organometallics* **2001**, *20*, 721-726. Berenguer, J. R.; Forniés, J.; Gil, B.; Lalinde, E. *Chem. Eur. J.* **2006**, *12*, 785-795.
- (30) Yin, G.-Q.; Wei, Q.-H.; Zhang, L.-Y.; Chen, Z.-N. *Organometallics* **2006**, *25*, 580-587.
- (31) Vicente, J.; Chicote, M. T.; Huertas, S. *Inorg. Chem.* **2001**, *40*, 6193-6200.

- (32) Vicente, J.; Chicote, M. T.; Huertas, S.; Bautista, D. *Inorg. Chem.* **2001**, *40*, 2051-2057. Vicente, J.; Chicote, M. T.; Huertas, S.; Jones, P. G. *Inorg. Chem.* **2003**, *42*, 4268-4274.
- (33) Vicente, J.; González-Herrero, P.; Pérez-Cadenas, M.; Jones, P. G.; Bautista, D. *Inorg. Chem.* **2007**, *46*, 4718-4732.
- (34) Vicente, J.; González-Herrero, P.; García-Sánchez, Y.; Jones, P. G.; Bardají, M. *Inorg. Chem.* **2004**, *43*, 7516-7531.
- (35) Niedermair, F.; Waich, K.; Kappaun, S.; Mayr, T.; Trimmel, G.; Mereiter, K.; Slugovc, C. *Inorg. Chim. Acta* **2007**, *360*, 2767-2777.
- (36) Demas, J. N.; Crosby, G. A. *J. Am. Chem. Soc.* **1970**, *92*, 7262-7270.
- (37) Suzuki, K.; Kobayashi, A.; Kaneko, S.; Takehira, K.; Yoshihara, T.; Ishida, H.; Shiina, Y.; Oishi, S.; Tobita, S. *Phys. Chem. Chem. Phys.* **2009**, *11*, 9850-9860.
- (38) Sheldrick, G. M. *Acta Cryst., Sect. A* **2008**, *64*, 112-122.
- (39) Ciufolini, M. A.; Mitchell, J. W.; Roschangar, F. *Tetrahedron Lett.* **1996**, *37*, 8281-8284.
- (40) Connick, W. B.; Gray, H. B. *J. Am. Chem. Soc.* **1997**, *119*, 11620-11627.
- (41) Vogler, A.; Kunkely, H. *J. Am. Chem. Soc.* **1981**, *103*, 1559-60.
- (42) Zhang, Y.; Schanze, K. S.; Ley, K. D. *Inorg. Chem.* **1996**, *35*, 7102-7110.
- (43) Cho, J.-Y.; Suponitsky, K. Y.; Li, J.; Timofeeva, T. V.; Barlow, S.; Marder, S. R. *J. Organomet. Chem.* **2005**, *690*, 4090-4093.
- (44) Mdleleni, M. M.; Bridgewater, J. S.; Watts, R. J.; Ford, P. C. *Inorg. Chem.* **1995**, *34*, 2334-2342.
- (45) Pap, J. S.; Benedito, F. L.; Bothe, E.; Bill, E.; DeBeer George, S.; Weyhermüller, T.; Wieghardt, K. *Inorg. Chem.* **2007**, *46*, 4187-4196.

- (46) Gimeno, M. C.; Jones, P. G.; Laguna, A.; Laguna, M.; Terroba, R. *Inorg. Chem.* **1994**, *33*, 3932-3938. Dávila, R. M.; Elduque, A.; Grant, T.; Staples, R. J.; Fackler, J. P., Jr. *Inorg. Chem.* **1993**, *32*, 1749-1755.
- (47) Xia, B. H.; Zhang, H. X.; Che, C. M.; Leung, K. H.; Phillips, D. L.; Zhu, N. Y.; Zhou, Z. Y. *J. Am. Chem. Soc.* **2003**, *125*, 10362-10374.
- (48) Cook, T. R.; Esswein, A. J.; Nocera, D. G. *J. Am. Chem. Soc.* **2007**, *129*, 10094-10095.
- (49) Yip, H. K.; Lin, H. M.; Wang, Y.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1993**, 2939-2944.
- (50) Fong, S. W. A.; Teck Yap, W.; Vittal, J. J.; Hor, T. S. A.; Henderson, W.; Oliver, A. G.; Rickard, C. E. F. *J. Chem. Soc., Dalton Trans.* **2001**, 1986-2002. Robertson, S. D.; Slawin, A. M. Z.; Woollins, J. D. *Eur. J. Inorg. Chem.* **2007**, 247-253. Bos, W.; Bour, J. J.; Schlebos, P. P. J.; Hageman, P.; Bosman, W. P.; Smits, J. M. M.; Vanwietmarschen, J. A. C.; Beurskens, P. T. *Inorg. Chim. Acta* **1986**, *119*, 141-148. Hallam, M. F.; Luke, M. A.; Mingos, D. M. P.; Williams, I. D. *J. Organomet. Chem.* **1987**, *325*, 271-283. Fong, S. W. A.; Vittal, J. J.; Henderson, W.; Hor, T. S. A.; Oliver, A. G.; Rickard, C. E. F. *Chem. Commun.* **2001**, 421-422. Konno, T.; Yoshinari, N.; Taguchi, M.; Igashira-Kamiyama, A. *Chem. Lett.* **2009**, *38*, 526-527. Li, Z. H.; Loh, Z. H.; Mok, K. F.; Hor, T. S. A. *Inorg. Chem.* **2000**, *39*, 5299-5305. Fritsch, E.; Polborn, K.; Robl, C.; Sünkel, K.; Beck, W. Z. *Anorg. Allg. Chem.* **1993**, *619*, 2050-2060. Ruiz, J.; Rodríguez, V.; Vicente, C.; Martí, J. M.; López, G.; Pérez, J. *Inorg. Chem.* **2001**, *40*, 5354-5360. Li, Z.; Mok, K. F.; Andy Hor, T. S. *J. Organomet. Chem.* **2003**, *682*, 73-78.
- (51) Shanan-Atidi, H.; Bar-Eli, K. H. *J. Phys. Chem.* **1970**, *74*, 961-963.
- (52) Friebolin, F., *Ein- und Zweidimensionale NMR-Spektroskopie*. VCH: Weinheim, Germany, 1988.

- (53) Craig, C. A.; Garces, F. O.; Watts, R. J.; Palmans, R.; Frank, A. J. *Coord. Chem. Rev.* **1990**, *97*, 193-208.
- (54) Rausch, A. F.; Monkowius, U. V.; Zabel, M.; Yersin, H. *Inorg. Chem.* **2010**, *49*, 7818-7825.
- (55) Yersin, H.; Rausch, A. F.; Czerwieniec, R.; Hofbeck, T.; Fischer, T. *Coord. Chem. Rev.* **2011**, *255*, 2622-2652.
- (56) Cummings, S. D.; Eisenberg, R. *Inorg. Chem.* **1995**, *34*, 2007-2014.
- (57) Kubo, K.; Nakano, M.; Tamura, H.; Matsubayashi, G.-e.; Nakamoto, M. *J. Organomet. Chem.* **2003**, *669*, 141-148.
- (58) Mansour, M. A.; Lachicotte, R. J.; Gysling, H. J.; Eisenberg, R. *Inorg. Chem.* **1998**, *37*, 4625-4632.
- (59) Vicente, J.; González-Herrero, P.; Pérez-Cadenas, M.; Jones, P. G.; Bautista, D. *Inorg. Chem.* **2005**, *44*, 7200-7213.
- (60) Vogler, A.; Kunkely, H. *Comments Inorg. Chem.* **1997**, *19*, 283-306.
- (61) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85-277.
- (62) Fernández, S.; Forniés, J.; Gil, B.; Gómez, J.; Lalinde, E. *Dalton Trans.* **2003**, 822-830. Niedermair, F.; Trattinig, R.; Mereiter, K.; Schmuck, M.; Sax, S.; List, E. J. W.; Slugovc, C. *Monatsh. Chem.* **2010**, *141*, 847-858. You, Y.; Park, S. Y. *Dalton Trans.* **2009**, 1267-1282.
- (63) Chen, P.; Meyer, T. J. *Chem. Rev.* **1998**, *98*, 1439-1478.
- (64) Garg, J. A.; Blacque, O.; Fox, T.; Venkatesan, K. *Inorg. Chem.* **2010**, *49*, 11463-11472. Jenkins, D. M.; Bernhard, S. *Inorg. Chem.* **2010**, *49*, 11297-11308.
- (65) Caspar, J. V.; Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 630-632.

Table of Contents Synopsis

Anionic cyclometallated Pt(II) 1,2-benzenedithiolate complexes $[\text{Pt}(\text{C}^{\wedge}\text{N})(\text{bdt})]^{-}$ [$\text{C}^{\wedge}\text{N}$ = 2-phenylpyridine, 1-(4-*tert*-butylphenyl)isoquinoline] have been synthesized and employed as metalloligands toward $[\text{Au}(\text{PCy}_3)]^{+}$ units to obtain heterometallic derivatives of the types $[\text{Pt}(\text{C}^{\wedge}\text{N})(\text{bdt})\{\text{Au}(\text{PCy}_3)\}]$ and $[\text{Pt}(\text{C}^{\wedge}\text{N})(\text{bdt})\{\text{Au}(\text{PCy}_3)\}_2]^{+}$. The crystal structures of two of the heterometallic complexes reveal the formation of unusually short Pt...Au metallophilic contacts, favored by the anionic character of the metalloligands. The successive introduction of Au(I) centers results in substantial modifications of the electronic absorption and emission properties, associated with the gradual loss of LL'CT character in the involved electronic transitions, which vary from mixed ML'CT/LL'CT in the anionic metalloligands to L'C/ML'CT in the trinuclear derivatives (L = bdt, L' = $\text{C}^{\wedge}\text{N}$).

Synopsis Artwork

