

# (Fluoren-9-ylidene)methanedithiolato Complexes of Platinum: Synthesis, Reactivity, and Luminescence<sup>1</sup>

José Vicente,<sup>†,‡</sup> Pablo González-Herrero,<sup>\*,†</sup> María Pérez-Cadenas,<sup>†</sup> Peter G. Jones,<sup>‡,⊥</sup> and Delia Bautista<sup>§,¶</sup>

Grupo de Química Organometálica, Departamento de Química Inorgánica, Facultad de Química, Universidad de Murcia, Apdo. 4021, 30071 Murcia, Spain, Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany, and SACE, Universidad de Murcia, Apdo. 4021, 30071 Murcia, Spain

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Platinum(II) complexes with (fluoren-9-ylidene)methanedithiolato and its 2,7-di-*tert*-butyl- and 2,7-dimethoxy-substituted analogues were obtained by reacting different chloroplatinum(II) precursors with the piperidinium dithioates (pipH)-[(2,7-R<sub>2</sub>C<sub>12</sub>H<sub>6</sub>)CHCS<sub>2</sub>] [R = H (**1a**), *t*-Bu (**1b**), or OMe (**1c**)] in the presence of piperidine. The anionic complexes Q<sub>2</sub>[Pt{S<sub>2</sub>C=C(C<sub>12</sub>H<sub>6</sub>R<sub>2-2,7</sub>)}<sub>2</sub>] [R = H, (Pr<sub>4</sub>N)<sub>2</sub>**2a**; R = *t*-Bu, (Pr<sub>4</sub>N)<sub>2</sub>**2b**, (Et<sub>4</sub>N)<sub>2</sub>**2b**; R = OMe, (Pr<sub>4</sub>N)<sub>2</sub>**2c**] were prepared from PtCl<sub>2</sub>, piperidine, the corresponding QCl salt, and **1a–c** in molar ratio 1:2:2:2. In the absence of QCl, the complexes (pipH)<sub>2</sub>**2b** and [Pt(pip)<sub>4</sub>]**2b** were isolated depending on the PtCl<sub>2</sub>:pip molar ratio. The neutral complexes [Pt{S<sub>2</sub>C=C(C<sub>12</sub>H<sub>6</sub>R<sub>2-2,7</sub>)L<sub>2</sub>] [L = PPh<sub>3</sub>, R = H (**3a**), *t*-Bu (**3b**), OMe (**3c**); L = PEt<sub>3</sub>, R = H (**4a**), *t*-Bu (**4b**), OMe (**4c**); L<sub>2</sub> = dbbpy, R = H (**5a**), *t*-Bu (**5b**), OMe (**5c**) (dbbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridyl)] were similarly prepared from the corresponding precursors [PtCl<sub>2</sub>L<sub>2</sub>] and **1a–c** in the presence of piperidine. Oxidation of Q<sub>2</sub>**2b** with [FeCp<sub>2</sub>]PF<sub>6</sub> afforded the mixed Pt(II)–Pt(IV) complex Q<sub>2</sub>[Pt<sub>2</sub>{S<sub>2</sub>C=C[C<sub>12</sub>H<sub>6</sub>(*t*-Bu)<sub>2-2,7</sub>]}<sub>4</sub>] (Q<sub>2</sub>**6**, Q = Et<sub>4</sub>N<sup>+</sup>, Pr<sub>4</sub>N<sup>+</sup>). The protonation of (Pr<sub>4</sub>N)<sub>2</sub>**2b** with 2 equiv of triflic acid gave the neutral dithioato complex [Pt<sub>2</sub>{S<sub>2</sub>C=C[C<sub>12</sub>H<sub>6</sub>(*t*-Bu)<sub>2-2,7</sub>]}<sub>4</sub>] (**7**). The same reaction in 1:1 molar ratio gave the mixed dithiolato/dithioato complex Pr<sub>4</sub>N[Pt{S<sub>2</sub>C=C[C<sub>12</sub>H<sub>6</sub>(*t*-Bu)<sub>2-2,7</sub>]}{S<sub>2</sub>CCH[C<sub>12</sub>H<sub>6</sub>(*t*-Bu)<sub>2-2,7</sub>]}] (Pr<sub>4</sub>**8**) while the corresponding DMANH<sup>+</sup> salt was obtained by treating **7** with 2 equiv of 1,8-bis(dimethylamino)naphthalene (DMAN). The crystal structures of **3b** and **5c**·CH<sub>2</sub>Cl<sub>2</sub> have been solved by X-ray crystallography. All the platinum complexes are photoluminescent at 77 K in CH<sub>2</sub>Cl<sub>2</sub> or KBr matrix, except for Q<sub>2</sub>**6**. Compounds **5a–c** and Q<sub>2</sub>**8** show room-temperature luminescence in fluid solution. The electronic absorption and emission spectra of the dithiolato complexes reveal charge-transfer absorption and emission energies which are significantly lower than those of analogous platinum complexes with previously described 1,1-ethylenedithiolato ligands and in most cases compare well to those of 1,2-dithiolene complexes.

## Introduction

Transition metal complexes with unsaturated dithiolato ligands are currently the subject of intensive research because of their outstanding electronic, spectral, magnetic, and redox

properties, which make them interesting candidates for numerous technological applications.<sup>2</sup> The majority of investigations concentrate on 1,2-dithiolene complexes, i.e., those containing the parent ligands 1,2-ethylenedithiolate and 1,2-benzenedithiolate or their derivatives. The chemistry of complexes with the 1,1-ethylenedithiolate structural isomers has developed in parallel<sup>3</sup> but has been studied to a lesser extent, mostly because of the reduced degree of metal–ligand

\* To whom correspondence should be addressed. E-mail: pgh@um.es. WWW: <http://www.um.es/gqo/>.

<sup>†</sup> Grupo de Química Organometálica, Departamento de Química Inorgánica, Facultad de Química, Universidad de Murcia, Apdo. 4021, 30071 Murcia, Spain.

<sup>‡</sup> Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany.

<sup>§</sup> SACE, Universidad de Murcia, Apdo. 4021, 30071 Murcia, Spain.

<sup>||</sup> E-mail: jvs1@um.es. WWW: <http://www.um.es/gqo/>.

<sup>⊥</sup> E-mail: p.jones@tu-bs.de.

<sup>¶</sup> E-mail: dbc@um.es.

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delocalization and subsequently diminished ability to undergo facile redox changes. However, there has been considerable interest in 1,1-ethylenedithiolates in connection with their ability to form clusters<sup>4</sup> and heteropolynuclear complexes,<sup>5</sup> stabilize high oxidation states,<sup>6</sup> or make use of multiple donor atoms to form coordination polymers.<sup>7</sup>

Platinum complexes with 1,1-ethylenedithiolates have been the subject of intensive research because of their interesting excited-state properties. Dianionic complexes of the type [Pt(1,1-ethylenedithiolato)<sub>2</sub>]<sup>2-</sup><sup>8</sup> and neutral complexes [Pt(1,1-ethylenedithiolato)L<sub>2</sub>] with phosphines, diphosphines, phosphates,<sup>9,10</sup> and 1,5-cyclooctadiene<sup>11</sup> are luminescent, and their emissions have been assigned to a charge-transfer excited-state involving a HOMO that is a mixture of dithiolate and metal orbital character and a LUMO that is a dithiolate-based  $\pi^*$  orbital. Special attention has been devoted to platinum diimine complexes containing 1,1-ethylenedithiolato or 1,2-dithiolene ligands, which display solvatochromic behavior and room-temperature luminescence in solution<sup>12–14</sup> and have been considered suitable candidates for applications as photocatalysts in light-to-chemical energy conversion processes.<sup>15–17</sup> In these systems, the observed luminescence has

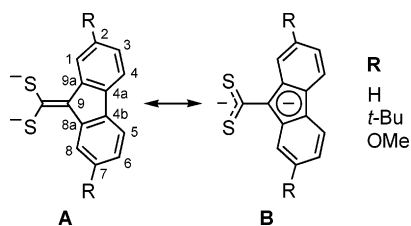
been ascribed to a charge-transfer transition involving a HOMO of mixed metal/dithiolato character and a LUMO which is a diimine-based  $\pi^*$  orbital. This transition has been referred to as mixed-metal/ligand-to-ligand charge-transfer (MMLLCT) or, more generally, charge-transfer-to-diimine.

The presence of strongly electron-withdrawing functional groups is a common feature of the majority of 1,1-ethylenedithiolato ligands described to date. In the case of platinum, the most widely used ligands of this kind are *i*-mnt (XYC=CS<sub>2</sub><sup>2-</sup> with X = Y = CN) and ecda (X = CN, Y = CO<sub>2</sub>Et),<sup>8–13,18,19</sup> and all other ligands contain at least one CN, C(O)R, or CO<sub>2</sub>R function,<sup>14,20–22</sup> with the exception of (cyclopentadienylidene)methanedithiolate, which was employed by Bereman for the preparation of anionic Ni, Pd, and Pt complexes.<sup>23</sup> Probably as a result of this, the exhaustive studies based on systematic ligand variation, which have been carried out to understand the influence of dithiolato and diimine ligands in the photoluminescence of their platinum complexes, have not found appreciable differences among the 1,1-ethylenedithiolato complexes and have attributed little or no influence to the substituents on these ligands.<sup>15,16,18</sup> Usually, the greatest differences are found between 1,2-dithiolenes and 1,1-ethylenedithiolates, the former showing much lower charge-transfer absorption and emission energies.<sup>2</sup>

Following our work on the synthesis and study of the reactivity and properties of gold, palladium, and platinum complexes containing the 2,2-diacetyl-1,1-ethylenedithiolato ligand,<sup>24,25</sup> we recently started to investigate the reactivity and emission properties of transition metal complexes containing the (fluoren-9-ylidene)methanedithiolato ligand and its 2,7-di-*tert*-butyl- and 2,7-bis(octyloxy)-substituted derivatives with the preparation of the first series of gold complexes.<sup>26</sup> These ligands show remarkable differences with respect to the previously used 1,1-ethylenedithiolates, which are mainly due to the absence of strongly electron-withdrawing substituents. Thus, the very low energies of the LMCT emissions of the gold(I) complexes with (fluoren-9-ylidene)-

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Chart 1



methanedithiolate and its substituted derivatives, as well as their facile oxidation to gold(III) under atmospheric conditions, revealed a marked influence of the strongly electron-donating character of the new ligands on the emission properties and redox behavior of their complexes.

In this paper, we describe the preparation and characterization of the first series of platinum(II) complexes with (fluorene-9-ylidene)methanedithiolate and its 2,7-di-*tert*-butyl- and 2,7-dimethoxy-substituted derivatives (Chart 1) and report on the effect of the electron-donating character of the dithiolato ligands on their photoluminescence and reactivity. The complexes studied are of the basic types  $[\text{Pt}(\text{dithiolate})_2]^{2-}$  and  $[\text{Pt}(\text{dithiolate})\text{L}_2]$ , with  $\text{L} = \text{PPh}_3$ ,  $\text{PEt}_3$  or  $\text{L}_2 = 4,4'$ -di-*tert*-butyl-2,2'-bipyridyl (dbbpy). We also present the oxidation and protonation reactions of the anionic complex with (2,7-di-*tert*-butylfluorene-9-ylidene)methanedithiolate, which lead to the formation of an unprecedented Pt(II)–Pt(IV) dithiolato complex or dithioato complexes, respectively.

## Experimental Section

**General Considerations, Materials, and Instrumentation.** All preparations were carried out at room temperature unless otherwise stated. Solvents were dried by standard methods. The ligand precursors piperidinium 9*H*-fluorene-9-carbodithioate and its 2,7-di-*tert*-butyl- and 2,7-dimethoxy-substituted analogues (**1a–c**) were prepared by following the published procedure.<sup>27</sup> The platinum compounds *cis*- $[\text{PtCl}_2\text{L}_2]$  with  $\text{L} = \text{PPh}_3$  or  $\text{PEt}_3$  were prepared from commercial  $\text{PtCl}_2$  and the corresponding phosphine (1:2) in  $\text{CH}_2\text{Cl}_2$ . The complex  $[\text{PtCl}_2(\text{dbbpy})]$  was prepared by refluxing  $\text{PtCl}_2$  with dbbpy in  $\text{Me}_2\text{CO}$  for 3 h and purified by recrystallization from hot  $\text{CHCl}_3$ . All other reagents were obtained from commercial sources and used without further purification. NMR spectra were recorded on Bruker Avance 200, 300, 400, or 600 spectrometers usually at 298 K, unless otherwise indicated. Chemical shifts are referred to internal TMS ( $^1\text{H}$  and  $^{13}\text{C}\{\text{H}\}$ ), external 85%  $\text{H}_3\text{PO}_4$  ( $^31\text{P}\{\text{H}\}$ ), or external  $\text{Na}_2\text{PtCl}_6$  ( $^{195}\text{Pt}\{\text{H}\}$ ). The  $^{13}\text{C}\{\text{H}\}$  NMR resonances arising from the cations are not given. The assignments of the  $^1\text{H}$  and  $^{13}\text{C}\{\text{H}\}$  NMR spectra were made with the help of HMBC and HSQC experiments. Chart 1 shows the atom numbering of the dithiolato ligands. Solution conductivities were measured in  $\text{Me}_2\text{CO}$  or  $\text{MeNO}_2$  with a Crison microCM 2200 conductimeter. 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 4000–200  $\text{cm}^{-1}$  on a Perkin-Elmer 16F PC FT-IR spectrophotometer using Nujol mulls between polyethylene sheets or KBr pellets. FAB mass spectra were recorded on a VG Autospec 5000 mass spectrometer using 3-nitrobenzyl alcohol as matrix. ESI mass spectra were recorded on an Agilent 1100 LC/MSD VL. UV–

Table 1. Crystallographic Data for **3b** and **5c**· $\text{CH}_2\text{Cl}_2$ 

param	<b>3b</b>	<b>5c</b> · $\text{CH}_2\text{Cl}_2$
formula	$\text{C}_{58}\text{H}_{54}\text{P}_2\text{PtS}_2$	$\text{C}_{35}\text{H}_{38}\text{Cl}_2\text{N}_2\text{O}_2\text{PtS}_2$
fw	1072.16	848.78
$T$ (K)	133(2)	100(2)
$\lambda$ (Å)	0.710 73	0.710 73
cryst syst	orthorhombic	orthorhombic
space group	$P2_12_12_1$	$P2_12_12_1$
$a$ (Å)	13.1260(8)	8.1462(4)
$b$ (Å)	14.7812(8)	17.0641(9)
$c$ (Å)	24.6345(14)	24.0539(13)
$V$ (Å <sup>3</sup> )	4779.5(5)	3343.7(3)
$Z$	4	4
$\rho_{\text{calc}}$ ( $\text{Mg m}^{-3}$ )	1.490	1.686
$\mu$ ( $\text{mm}^{-1}$ )	3.129	4.516
$R1^a$	0.0193	0.0279
$wR2^b$	0.0405	0.0670

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

visible absorption spectra were recorded on Unicam UV500 (range 190–900 nm) or Hitachi U-2000 (range 190–1100 nm) spectrophotometers. 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 Hamamatsu R-928P photomultiplier. The solid-state measurements were made in front-face configuration using finely pulverized KBr dispersions of the samples in 5 mm quartz NMR tubes; the solution measurements were carried out in right angle configuration using degassed solutions of the samples in 10 mm quartz fluorescence cells (298 K) or 5 mm quartz NMR tubes (77 K). The solvents used were  $\text{CH}_2\text{Cl}_2$  at 298 K and  $\text{CH}_2\text{Cl}_2$ , DMF/ $\text{CH}_2\text{Cl}_2$ /MeOH (1:1:1), or PrCN at 77 K, as specified. For the low-temperature measurements a liquid-nitrogen dewar with quartz windows was employed. Emission quantum yields were calculated relative to  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$  in MeCN ( $\Phi = 0.062$ )<sup>28</sup> at 298 K for those compounds which are emissive at room temperature, using the method described by Demas and Crosby.<sup>29</sup>

**X-ray Structure Determinations.** Crystals of **3b** and **5c**· $\text{CH}_2\text{Cl}_2$  suitable for X-ray diffraction studies were obtained by slow diffusion of  $\text{Et}_2\text{O}$  into solutions of the compounds in  $\text{CH}_2\text{Cl}_2$ . Numerical details are presented in Table 1. Data for **3b** were recorded on a Bruker SMART 1000 CCD diffractometer to  $2\theta_{\text{max}} 60^\circ$ ; data for **5c**· $\text{CH}_2\text{Cl}_2$  on a Bruker SMART APEX diffractometer to  $2\theta_{\text{max}} 56^\circ$ . Multiscan absorption corrections were performed (program SADABS). The structures were refined on  $F^2$  using the program SHELXL-97 (G. M. Sheldrick, University of Göttingen). Hydrogen atoms were included using rigid methyl groups or a riding model. The Flack parameters refined to  $-0.014(2)$  and  $0.039(6)$ , although the concept of absolute configuration is not applicable to the bulk materials. Some restraints to local aromatic ring symmetry or light atom displacement factor components were applied. One methoxy group of **5c**· $\text{CH}_2\text{Cl}_2$  is disordered over two sites.

**General Procedure for the Preparation of  $\text{Q}_2[\text{Pt}\{\text{S}_2\text{C}=\text{C}(\text{C}_{12}\text{H}_6\text{R}_2-2,7)\}_2]$  (**Q2a–c**).** To a suspension of  $\text{PtCl}_2$  (1.30 mmol) in  $\text{CH}_2\text{Cl}_2$  (40 mL) were added piperidine (300  $\mu\text{L}$ , 3.03 mmol) and the corresponding QCl salt (2.66 mmol). A pale yellow solution formed, which was filtered through Celite to remove a small amount of colloidal Pt. Addition of dithioate **1a**, **1b**, or **1c** (2.62 mmol) led to immediate reaction with formation of an orange precipitate. After the mixture was stirred for 1 h, the solvent was partially evaporated

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(15 mL) and the solid was filtered off, washed with  $\text{CH}_2\text{Cl}_2$  (2  $\times$  5 mL) and MeOH (2  $\times$  5 mL), and vacuum-dried to give **Q<sub>2</sub>a-c**.

**Data for (Pr<sub>4</sub>N)<sub>2</sub>2a.** Yield: 41%. Anal. Calcd for  $\text{C}_{52.5}\text{H}_{73}\text{ClN}_2\text{PtS}_4$ : C, 59.57; H, 6.92; N, 2.67; S, 12.23. Found: C, 59.48; H, 7.09; N, 2.83; S, 12.04. Mp: 237 °C.  $\Lambda_M$  ( $\text{MeNO}_2$ ,  $1.2 \times 10^{-4}$  M):  $130 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu(\text{C}=\text{CS}_2)$ , 1500;  $\nu(\text{Pt}-\text{S})$ , 341.  $^1\text{H}$  NMR [400.9 MHz,  $(\text{CD}_3)_2\text{SO}$ ]:  $\delta$  8.65 (d,  $^3J_{\text{HH}} = 7.8$  Hz, 4 H, H1, H8), 7.81 (d,  $^3J_{\text{HH}} = 7.6$  Hz, 4 H, H4, H5), 7.18 (t,  $^3J_{\text{HH}} = 7.6$  Hz, 4 H, H2, H7), 7.04 (t,  $^3J_{\text{HH}} = 7.6$  Hz, 4 H, H3, H6), 3.10 (m, 16 H,  $\text{NCH}_2$ ), 1.58 (m, 16 H,  $\text{CH}_2$ ), 0.86 (t,  $^3J_{\text{HH}} = 7.3$  Hz, 24 H, Me).  $^{13}\text{C}\{^1\text{H}\}$  NMR [100.8 MHz,  $(\text{CD}_3)_2\text{SO}$ ]:  $\delta$  187.1 ( $\text{CS}_2$ ), 137.8 (C8a, C9a), 134.0 (C4a, C4b), 125.3 (C9), 125.0 (C2, C7), 122.5 (C1, C8), 121.1 (C3, C6), 118.3 (C4, C5).

**Data for (Et<sub>4</sub>N)<sub>2</sub>2b.** Yield: 43%. Anal. Calcd for  $\text{C}_{60}\text{H}_{88}\text{N}_2\text{PtS}_4$ : C, 62.09; H, 7.64; N, 2.41; S, 11.05. Found: C, 61.73; H, 7.70; N, 2.51; S, 11.05. Mp: 242 °C.  $\Lambda_M$  ( $\text{MeNO}_2$ ,  $1.2 \times 10^{-4}$  M):  $128 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu(\text{C}=\text{CS}_2)$ , 1500;  $\nu(\text{Pt}-\text{S})$ , 342.  $^1\text{H}$  NMR [400.9 MHz,  $(\text{CD}_3)_2\text{SO}$ ]:  $\delta$  8.78 (d,  $^4J_{\text{HH}} = 1.6$  Hz, 4 H, H1, H8), 7.63 (d,  $^3J_{\text{HH}} = 8.0$  Hz, 4 H, H4, H5), 7.07 (dd,  $^3J_{\text{HH}} = 8.0$  Hz,  $^4J_{\text{HH}} = 1.6$  Hz, 4 H, H3, H6), 3.15 (q,  $^3J_{\text{HH}} = 7.2$  Hz,  $\text{NCH}_2$ , 16 H), 1.35 (s, 36 H, *t*-Bu), 1.11 (tt,  $^3J_{\text{HH}} = 7.2$  Hz,  $^3J_{\text{HN}} = 1.7$  Hz, 24 H, Me,  $\text{Et}_4\text{N}^+$ ).

**Data for (Pr<sub>4</sub>N)<sub>2</sub>2b.** Yield: 51%. Anal. Calcd for  $\text{C}_{68}\text{H}_{104}\text{N}_2\text{PtS}_4$ : C, 64.16; H, 8.24; N, 2.20; S, 10.08. Found: C, 64.42; H, 8.30; N, 2.38; S, 9.80. Mp: 230 °C.  $\Lambda_M$  ( $\text{MeNO}_2$ ,  $1.0 \times 10^{-4}$  M):  $134 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu(\text{C}=\text{CS}_2)$ , 1500;  $\nu(\text{Pt}-\text{S})$ , 338.  $^1\text{H}$  NMR [400.9 MHz,  $(\text{CD}_3)_2\text{SO}$ ]:  $\delta$  8.78 (d,  $^4J_{\text{HH}} = 1.6$  Hz, 4 H, H1, H8), 7.62 (d,  $^3J_{\text{HH}} = 8.0$  Hz, 4 H, H4, H5), 7.07 (dd,  $^3J_{\text{HH}} = 8.0$  Hz,  $^4J_{\text{HH}} = 1.6$  Hz, 4 H, H3, H6), 3.11 (m,  $\text{NCH}_2$ , 16 H), 1.59 (m,  $\text{CH}_2$ , 16 H), 1.34 (s, 36 H, *t*-Bu), 0.87 (t,  $^3J_{\text{HH}} = 7.2$  Hz, 24 H, Me,  $\text{Pr}_4\text{N}^+$ ).

**Data for (Pr<sub>4</sub>N)<sub>2</sub>2c.** Yield: 60%. Anal. Calcd for  $\text{C}_{56}\text{H}_{80}\text{N}_2\text{O}_4\text{PtS}_4$ : C, 57.56; H, 6.90; N, 2.40; S, 10.98. Found: C, 57.79; H, 6.54; N, 2.29; S, 11.00. Mp: 229 °C.  $\Lambda_M$  ( $\text{Me}_2\text{CO}$ ,  $2.3 \times 10^{-4}$  M):  $94 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu(\text{C}=\text{CS}_2)$ , 1500;  $\nu(\text{Pt}-\text{S})$ , 340.  $^1\text{H}$  NMR [300.1 MHz,  $(\text{CD}_3)_2\text{SO}$ ]:  $\delta$  8.24 (d,  $^4J_{\text{HH}} = 2.2$  Hz, 4 H, H1, H8), 7.55 (d,  $^3J_{\text{HH}} = 8.2$  Hz, 4 H, H4, H5), 6.60 (dd, 4 H, H3, H6), 3.76 (s, 12 H, OMe), 3.10 (m, 16 H,  $\text{NCH}_2$ ), 1.58 (m, 16 H,  $\text{CH}_2$ ), 0.87 (t,  $^3J_{\text{HH}} = 7.2$  Hz, 24 H, Me,  $\text{Pr}_4\text{N}^+$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR [75.5 MHz,  $(\text{CD}_3)_2\text{SO}$ ]:  $\delta$  186.5 ( $\text{CS}_2$ ), 157.2 (C2, C7), 139.1 (C8a, C9a), 128.0 (C4a, C4b), 125.4 (C9), 117.9 (C4, C5), 108.6 (C3, C6), 106.9 (C1, C8), 54.9 (OMe).

**(pipH)<sub>2</sub>[Pt{S<sub>2</sub>C=C(C<sub>12</sub>H<sub>6</sub>R<sub>2</sub>-2,7)}<sub>2</sub>]} (pipH)<sub>2</sub>2b.** To a suspension of  $\text{PtCl}_2$  (272 mg, 1.02 mmol) in  $\text{CH}_2\text{Cl}_2$  (50 mL) was added piperidine (250  $\mu\text{L}$ , 2.53 mmol), and the resulting pale yellow solution was filtered through Celite to remove a small amount of colloidal Pt. Addition of **1b** (973 mg, 2.04 mmol) led to immediate reaction with formation of an orange precipitate, which was filtered off, washed with  $\text{CH}_2\text{Cl}_2$  (2  $\times$  5 mL), and vacuum-dried to give (pipH)<sub>2</sub>2b. Yield: 810 mg, 74%. Anal. Calcd for  $\text{C}_{54}\text{H}_{72}\text{N}_2\text{PtS}_4$ : C, 60.47; H, 6.77; N, 2.61; S, 11.96. Found: C, 60.39; H, 6.89; N, 2.72; S, 11.63. Mp: 239 °C.  $\Lambda_M$  ( $\text{Me}_2\text{CO}$ ,  $4.7 \times 10^{-4}$  M):  $83 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu(\text{NH})$ , 3168;  $\nu(\text{C}=\text{CS}_2)$ , 1506;  $\nu(\text{Pt}-\text{S})$ , 348.  $^1\text{H}$  NMR [300.1 MHz,  $(\text{CD}_3)_2\text{SO}$ ]:  $\delta$  8.78 (d,  $^4J_{\text{HH}} = 1.5$  Hz, 4 H, H1, H8), 7.63 (d,  $^3J_{\text{HH}} = 7.8$  Hz, 4 H, H4, H5), 7.07 (dd,  $^3J_{\text{HH}} = 8.1$  Hz,  $^4J_{\text{HH}} = 1.6$  Hz, 4 H, H3, H6), 3.36 (br, 4 H,  $\text{NH}_2$ ), 2.99 (m,  $\text{NCH}_2$ , 8 H), 1.60 (m,  $\text{CH}_2$ , 8 H), 1.53 (m,  $\text{CH}_2$ , 4 H), 1.35 (s, 36 H, *t*-Bu).  $^{13}\text{C}\{^1\text{H}\}$  NMR [100.8 MHz,  $(\text{CD}_3)_2\text{SO}$ ]:  $\delta$  183.6 ( $\text{CS}_2$ ), 147.3 (C2, C7), 138.5 (C8a, C9a), 132.1 (C4a, C4b), 126.3 (C9), 119.7 (C1, C8), 118.9 (C3, C6), 117.6 (C4, C5), 34.8 ( $\text{CMe}_3$ ), 32.0 ( $\text{CMe}_3$ ).

**[Pt(pip)<sub>4</sub>][Pt{S<sub>2</sub>C=C(C<sub>12</sub>H<sub>6</sub>(*t*-Bu)<sub>2</sub>-2,7)}<sub>2</sub>]} ([Pt(pip)<sub>4</sub>]2b).** This orange microcrystalline compound was obtained by following the

procedure described for (pipH)<sub>2</sub>2b but using equimolar amounts of  $\text{PtCl}_2$  (372 mg, 1.40 mmol) and **1b** (668 mg, 1.40 mmol) and 3 equiv of piperidine (420  $\mu\text{L}$ , 4.25 mmol). Yield: 830 mg, 83%. Anal. Calcd for  $\text{C}_{64}\text{H}_{92}\text{N}_4\text{Pt}_2\text{S}_4$ : C, 53.54; H, 6.46; N, 3.90; S, 8.93. Found: C, 53.62; H, 6.65; N, 3.97; S, 8.66. Mp: 207 °C (dec).  $\Lambda_M$  ( $\text{Me}_2\text{CO}$ ,  $4.2 \times 10^{-4}$  M):  $74 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu(\text{NH})$ , 3280, 3165;  $\nu(\text{C}=\text{CS}_2)$ , 1503;  $\nu(\text{Pt}-\text{S})$ , 348.  $^1\text{H}$  NMR [300 MHz,  $(\text{CD}_3)_2\text{SO}$ ]:  $\delta$  8.79 (d,  $^4J_{\text{HH}} = 1.8$  Hz, 2 H, H1, H8), 7.63 (d,  $^3J_{\text{HH}} = 8.1$  Hz, 2 H, H4, H5), 7.22 (dd,  $^3J_{\text{HH}} = 8.1$  Hz,  $^4J_{\text{HH}} = 1.8$  Hz, 2 H, H3, H6), 2.88 (m, 8 H,  $\text{NCH}_2$ ), 1.55 (m, 12 H,  $\text{CH}_2$ ), 1.36 (s, 18 H, *t*-Bu).  $^{13}\text{C}\{^1\text{H}\}$  NMR [75.5 MHz,  $(\text{CD}_3)_2\text{SO}$ ]:  $\delta$  183.8 ( $\text{CS}_2$ ), 147.0 (C2, C7), 138.3 (C8a, C9a), 131.9 (C4a, C4b), 126.0 (C9), 119.5 (C1, C8), 118.7 (C3, C6), 117.4 (C4, C5), 44.7 ( $\text{NCH}_2$ ), 34.6 ( $\text{CMe}_3$ ), 31.8 ( $\text{CMe}_3$ ), 23.6 ( $\text{CH}_2$ ), 22.6 ( $\text{CH}_2$ ).

**[Pt{S<sub>2</sub>C=C(C<sub>12</sub>H<sub>6</sub>)}(PPh<sub>3</sub>)<sub>2</sub>] (3a).** To a solution of **1a** (80 mg, 0.25 mmol) and piperidine (26  $\mu\text{L}$ , 0.26 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) was added *cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (153 mg, 0.20 mmol), and the mixture was stirred for 15 min. Partial evaporation of the clear orange solution (2 mL) and addition of Et<sub>2</sub>O (15 mL) led to the precipitation of a yellow microcrystalline solid, which was filtered off, washed with MeOH (2  $\times$  3 mL) and Et<sub>2</sub>O (2  $\times$  3 mL), and vacuum-dried to give **3a**·0.5Et<sub>2</sub>O. Yield: 120 mg, 60%. Anal. Calcd for  $\text{C}_{52}\text{H}_{43}\text{O}_{0.5}\text{P}_2\text{PtS}_2$ : C, 62.64; H, 4.35; S, 6.43. Found: C, 62.56; H, 4.63; S, 6.32. Mp: 130 °C (dec). IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu(\text{C}=\text{CS}_2)$ , 1530.  $^1\text{H}$  NMR (400.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.26 (m, 2 H, H1, H8), 7.69 (m, 2 H, H4, H5), 7.52 (m, 12 H, *o*-H, Ph), 7.34 (m, 6 H, *p*-H, Ph), 7.23 (m, 12 H, *m*-H, Ph), 7.09 (m, 4 H, H2, H3, H6, H7), 3.47 (q,  $^3J_{\text{HH}} = 7.0$  Hz, 2 H,  $\text{CH}_2$ , Et<sub>2</sub>O), 1.21 (t, 3 H, Me, Et<sub>2</sub>O).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  162.5 ( $\text{CS}_2$ ), 138.6 (C8a, C9a), 137.2 (C4a, C4b), 134.6 (m, *o*-C, Ph), 130.7 (m, *p*-C, Ph), 129.4 (m, *i*-C, Ph), 127.9 (m, *m*-C, Ph), 125.9 (C2, C7), 124.4 (C1, C8), 123.6 (C3, C6), 118.4 (C4, C5) (C9 not observed).  $^{31}\text{P}\{^1\text{H}\}$  NMR (121.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.8 ( $^1J_{\text{PP}} = 3031$  Hz).

**[Pt{S<sub>2</sub>C=C(C<sub>12</sub>H<sub>6</sub>(*t*-Bu)<sub>2</sub>-2,7)}(PPh<sub>3</sub>)<sub>2</sub>] (3b).** This yellow complex was prepared as described for **3a**, from *cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (143 mg, 0.19 mmol) and **1b** (100 mg, 0.21 mmol). Yield: 151 mg, 76%. Anal. Calcd for  $\text{C}_{58}\text{H}_{54}\text{P}_2\text{PtS}_2$ : C, 64.97; H, 5.08; S, 5.98. Found: C, 64.65; H, 5.25; S, 5.61. Mp: 120 °C (dec). IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu(\text{C}=\text{CS}_2)$ , 1538.  $^1\text{H}$  NMR (400.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.33 (d,  $^4J_{\text{HH}} = 1.7$  Hz, 2 H, H1, H8), 7.53 (d,  $^3J_{\text{HH}} = 8.0$  Hz, 2 H, H4, H5), 7.49 (m, 12 H, *o*-H, Ph), 7.32 (m, 6 H, *p*-H, Ph), 7.22 (m, 12 H, *m*-H, Ph), 7.10 (dd,  $^3J_{\text{HH}} = 8.0$  Hz,  $^4J_{\text{HH}} = 1.7$  Hz, 2 H, H3, H6), 1.21 (s, 18 H, *t*-Bu).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.8 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.5 ( $\text{CS}_2$ ), 148.2 (C2, C7), 139.0 (C8a, C9a), 134.9 (C4a, C4b), 134.6 (m, *o*-C, Ph), 130.6 (m, *p*-C, Ph), 129.4 (m, *i*-C, Ph), 127.9 (m, *m*-C, Ph), 121.7 (C1, C8), 120.8 (C3, C6), 117.5 (C4, C5), 34.6 [ $\text{C}(\text{CH}_3)_3$ ], 31.7 [ $\text{C}(\text{CH}_3)_3$ ] (C9 not observed).  $^{31}\text{P}\{^1\text{H}\}$  NMR (162.3 MHz,  $\text{CDCl}_3$ ):  $\delta$  19.6 ( $^1J_{\text{PP}} = 3018$  Hz).

**[Pt{S<sub>2</sub>C=C(C<sub>12</sub>H<sub>6</sub>(OMe)<sub>2</sub>-2,7)}(PPh<sub>3</sub>)<sub>2</sub>] (3c).** This yellow complex was prepared as described for **3a**, from *cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (159 mg, 0.21 mmol) and **1c** (86 mg, 0.22 mmol). Yield: 83 mg, 40%. Anal. Calcd for  $\text{C}_{52}\text{H}_{42}\text{O}_2\text{P}_2\text{PtS}_2$ : C, 61.23; H, 4.15; S, 6.29. Found: C, 61.40; H, 4.24; S, 6.07. Mp: 125 °C (dec). IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu(\text{C}=\text{CS}_2)$ , 1537.  $^1\text{H}$  NMR (400.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.86 (d,  $^4J_{\text{HH}} = 2.2$  Hz, 2 H, H1, H8), 7.51 (m, 12 H, *o*-H, Ph), 7.44 (d,  $^3J_{\text{HH}} = 8.3$  Hz, 2 H, H4, H5), 7.32 (m, 6 H, *p*-H, Ph), 7.23 (m, 12 H, *m*-H, Ph), 6.65 (dd, 2 H, H3, H6), 3.63 (s, 6 H, OMe).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.8 MHz,  $\text{CDCl}_3$ ):  $\delta$  162.3 ( $\text{CS}_2$ ), 157.7 (C2, C7), 139.6 (C8a, C9a), 134.6 (m, *o*-C, Ph), 130.8 (C4a, C4b), 130.6 (m, *p*-C, Ph), 129.4 (m, *i*-C, Ph), 128.8 (C9), 127.9 (m, *m*-C, Ph), 118.2 (C4, C5), 111.5 (C3, C6), 108.3 (C1, C8), 55.2 (OMe).  $^{31}\text{P}\{^1\text{H}\}$  NMR (162.3 MHz,  $\text{CDCl}_3$ ):  $\delta$  19.3 ( $^1J_{\text{PP}} = 3030$  Hz).

**[Pt{S<sub>2</sub>C=C(C<sub>12</sub>H<sub>8</sub>)}(PEt<sub>3</sub>)<sub>2</sub>] (4a).** This yellow complex was prepared as described for **3a**, from *cis*-[PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] (126 mg, 0.25 mmol) and **1a** (93 mg, 0.28 mmol). Yield: 109 mg, 65%. Anal. Calcd for C<sub>26</sub>H<sub>38</sub>P<sub>2</sub>PtS<sub>2</sub>: C, 46.49; H, 5.70; S, 9.55. Found: C, 46.48; H, 5.84; S, 9.42. Mp: 228 °C. IR (Nujol, cm<sup>-1</sup>): ν(C=CS<sub>2</sub>), 1527. <sup>1</sup>H NMR (400.9 MHz, CDCl<sub>3</sub>): δ 8.73 (d, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, 2 H, H1, H8), 7.75 (d, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, 2 H, H4, H5), 7.26 (t, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, 2 H, H2, H7), 7.17 (t, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, 2 H, H3, H6), 1.83 (m, 12 H, CH<sub>2</sub>), 1.16 (m, 18 H, Me, PEt<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, CDCl<sub>3</sub>): δ 165.2 (CS<sub>2</sub>), 138.7 (C8a, C9a), 137.2 (C4a, C4b), 129.9 (C9), 126.0 (C2, C7), 124.7 (C1, C8), 123.7 (C3, C6), 118.5 (C4, C5), 15.9 (m, CH<sub>2</sub>), 8.1 (<sup>3</sup>J<sub>PC</sub> = 23 Hz, Me, PEt<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (81.0 MHz, CDCl<sub>3</sub>): δ 4.0 (<sup>1</sup>J<sub>PP</sub> = 2902 Hz).

**[Pt{S<sub>2</sub>C=C[C<sub>12</sub>H<sub>6</sub>(*t*-Bu)-2,7]}(PEt<sub>3</sub>)<sub>2</sub>] (4b).** This yellow complex was prepared as described for **3a**, from *cis*-[PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] (137 mg, 0.27 mmol) and **1b** (132 mg, 0.28 mmol). Yield: 114 mg, 53%. Anal. Calcd for C<sub>34</sub>H<sub>54</sub>P<sub>2</sub>PtS<sub>2</sub>: C, 52.09; H, 6.94; S, 8.18. Found: C, 51.72; H, 7.19; S, 8.02. Mp: 246 °C (dec). IR (Nujol, cm<sup>-1</sup>): ν(C=CS<sub>2</sub>), 1536. <sup>1</sup>H NMR (400.9 MHz, CDCl<sub>3</sub>): δ 8.78 (d, <sup>4</sup>J<sub>HH</sub> = 1.7 Hz, 2 H, H1, H8), 7.60 (d, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, 2 H, H4, H5), 7.19 (dd, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, <sup>4</sup>J<sub>HH</sub> = 1.7 Hz, 2 H, H3, H6), 1.90 (m, 12 H, CH<sub>2</sub>), 1.39 (s, 18 H, *t*-Bu), 1.20 (m, 18 H, Me, PEt<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (50.3 MHz, CDCl<sub>3</sub>): δ 162.7 (t, <sup>3</sup>J<sub>PC</sub> = 79 Hz, CS<sub>2</sub>), 148.4 (C2, C7), 139.1 (C8a, C9a), 134.9 (C4a, C4b), 130.4 (t, <sup>4</sup>J<sub>PC</sub> = 3 Hz, C9), 121.8 (C1, C8), 121.1 (C3, C6), 117.6 (C4, C5), 34.9 (CMe<sub>3</sub>), 31.8 (CMe<sub>3</sub>), 15.8 (m, CH<sub>2</sub>), 8.2 (<sup>3</sup>J<sub>PC</sub> = 22 Hz, Me, PEt<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (162.3 MHz, CDCl<sub>3</sub>): δ 3.28 (<sup>1</sup>J<sub>PP</sub> = 2894 Hz).

**[Pt{S<sub>2</sub>C=C[C<sub>12</sub>H<sub>6</sub>(OMe)-2,7]}(PEt<sub>3</sub>)<sub>2</sub>] (4c).** This yellow complex was prepared as described for **3a**, from *cis*-[PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] (69 mg, 0.14 mmol) and **1c** (71 mg, 0.18 mmol). Yield: 72 mg, 73%. Anal. Calcd for C<sub>28</sub>H<sub>42</sub>O<sub>2</sub>P<sub>2</sub>PtS<sub>2</sub>: C, 45.96; H, 5.79; S, 8.76. Found: C, 46.15; H, 5.99; S, 8.78. Mp: 240 °C (dec). IR (Nujol, cm<sup>-1</sup>): ν(C=CS<sub>2</sub>), 1532. <sup>1</sup>H NMR (400.9 MHz, CDCl<sub>3</sub>): δ 8.31 (d, <sup>4</sup>J<sub>HH</sub> = 2.2 Hz, 2 H, H1, H8), 7.53 (d, <sup>3</sup>J<sub>HH</sub> = 8.2 Hz, 2 H, H4, H5), 6.73 (dd, 2 H, H3, H6), 3.88 (s, 6 H, OMe), 1.90 (m, 12 H, CH<sub>2</sub>), 1.19 (m, 18 H, Me, PEt<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100.8 MHz, CDCl<sub>3</sub>): δ 158.0 (C2, C7), 140.0 (C8a, C9a), 131.2 (C4a, C4b), 118.1 (C4, C5), 111.0 (C3, C6), 109.4 (C1, C8), 55.6 (OMe), 15.9 (m, CH<sub>2</sub>), 8.2 (<sup>3</sup>J<sub>PC</sub> = 22 Hz, Me, PEt<sub>3</sub>) (CS<sub>2</sub> and C9 not observed). <sup>31</sup>P{<sup>1</sup>H} NMR (121.5 MHz, CDCl<sub>3</sub>): δ 4.19 (<sup>1</sup>J<sub>PP</sub> = 2903 Hz).

**[Pt{S<sub>2</sub>C=C(C<sub>12</sub>H<sub>8</sub>)}(dbbpy)] (5a).** To a solution of **1a** (237 mg, 0.72 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (25 mL) were added piperidine (100 μL, 1.01 mmol) and [PtCl<sub>2</sub>(dbbpy)] (361 mg, 0.68 mmol). A dark purple solution formed immediately, which was stirred for 10 min and evaporated to dryness. Treatment of the residue with MeOH (12 mL) led to the formation of a purple precipitate, which was filtered off, washed with MeOH (3 × 5 mL), and vacuum-dried to give **5a**. Yield: 345 mg, 72%. Anal. Calcd for C<sub>32</sub>H<sub>32</sub>N<sub>2</sub>PtS<sub>2</sub>: C, 54.61; H, 4.58; N, 3.98; S, 9.11. Found: C, 54.34; H, 4.73; N, 4.08; S, 8.99. Mp: 200 °C (dec). IR (Nujol, cm<sup>-1</sup>): ν(C=CS<sub>2</sub>), 1522. <sup>1</sup>H NMR (400.9 MHz, CDCl<sub>3</sub>): δ 8.71 (d, <sup>4</sup>J<sub>HH</sub> = 7.7 Hz, 2 H, H1, H8), 8.56 (d, <sup>3</sup>J<sub>HH</sub> = 5.9 Hz, 2 H, H6, dbbpy), 7.92 (d, <sup>4</sup>J<sub>HH</sub> = 1.8 Hz, 2 H, H3, dbbpy), 7.80 (d, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, 2 H, H4, H5), 7.44 (dd, 2 H, H5, dbbpy), 7.32 (td, <sup>4</sup>J<sub>HH</sub> = 1.0 Hz, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, 2 H, H2, H7), 7.22 (td, <sup>4</sup>J<sub>HH</sub> = 1.0 Hz, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 2 H, H3, H6), 1.39 (s, 18 H, *t*-Bu). <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, CDCl<sub>3</sub>): δ 163.0 (C4, dbbpy), 162.2 (CS<sub>2</sub>), 155.1 (C2, dbbpy), 147.6 (C6, dbbpy), 138.3 (C8a, C9a), 137.0 (C4a, C4b), 129.2 (C9), 126.0 (C2, C7), 124.6 (C5, dbbpy), 123.9 (C3, C6), 122.8 (C1, C8), 119.6 (C3, dbbpy), 118.8 (C4, C5), 35.8 (CMe<sub>3</sub>), 30.2 (CMe<sub>3</sub>).

**[Pt{S<sub>2</sub>C=C[C<sub>12</sub>H<sub>6</sub>(*t*-Bu)-2,7]}(dbbpy)] (5b).** This dark blue complex was prepared as described for **5a**, from [PtCl<sub>2</sub>(dbbpy)]

(324 mg, 0.61 mmol) and **1b** (296 mg, 0.62 mmol). Yield: 428 mg, 86%. Anal. Calcd for C<sub>40</sub>H<sub>48</sub>N<sub>2</sub>PtS<sub>2</sub>: C, 58.87; H, 5.93; N, 3.43; S, 7.86. Found: C, 58.85; H, 6.14; N, 3.41; S, 7.56. Mp: 180 °C (dec). IR (Nujol, cm<sup>-1</sup>): ν(C=CS<sub>2</sub>), 1538, 1520. <sup>1</sup>H NMR (400.9 MHz, CDCl<sub>3</sub>): δ 8.82 (d, <sup>4</sup>J<sub>HH</sub> = 1.4 Hz, 2 H, H1, H8), 8.50 (d, <sup>3</sup>J<sub>HH</sub> = 5.9 Hz, 2 H, H6, dbbpy), 8.04 (d, <sup>4</sup>J<sub>HH</sub> = 1.7 Hz, 2 H, H3, dbbpy), 7.67 (d, <sup>3</sup>J<sub>HH</sub> = 7.9 Hz, 2 H, H4, H5), 7.48 (dd, 2 H, H5, dbbpy), 7.25 (dd, 2 H, H3, H6), 1.47, 1.42 (both s, 18 H each, *t*-Bu). <sup>13</sup>C{<sup>1</sup>H} NMR (100.8 MHz, CDCl<sub>3</sub>): δ 162.8 (C4, dbbpy), 159.1 (CS<sub>2</sub>), 155.0 (C2, dbbpy), 148.6 (C2, C7), 147.3 (C6, dbbpy), 138.8 (C8a, C9a), 134.9 (C4a, C4b), 130.0 (C9), 124.7 (C5, dbbpy), 121.4 (C3, C6), 119.9 (C1, C8), 119.8 (C3, dbbpy), 117.9 (C4, C5), 35.9, 35.0 (CMe<sub>3</sub>), 31.9, 30.2 (CMe<sub>3</sub>).

**[Pt{S<sub>2</sub>C=C[C<sub>12</sub>H<sub>6</sub>(OMe)-2,7]}(dbbpy)] (5c).** This purple complex was prepared as described for **5a**, from [PtCl<sub>2</sub>(dbbpy)] (359 mg, 0.93 mmol) and **1c** (393 mg, 0.74 mmol). Yield: 444 mg, 79%. Anal. Calcd for C<sub>34</sub>H<sub>36</sub>N<sub>2</sub>O<sub>2</sub>PtS<sub>2</sub>: C, 53.46; H, 4.75; N, 3.67; S, 8.40. Found: C, 53.31; H, 4.88; N, 3.78; S, 8.24. Mp: 190 °C (dec). IR (Nujol, cm<sup>-1</sup>): ν(C=CS<sub>2</sub>), 1537. <sup>1</sup>H NMR (400.9 MHz, CDCl<sub>3</sub>): δ 8.61 (d, <sup>3</sup>J<sub>HH</sub> = 5.9 Hz, 2 H, H6, dbbpy), 8.33 (d, <sup>4</sup>J<sub>HH</sub> = 2.2 Hz, 2 H, H1, H8), 7.95 (d, <sup>4</sup>J<sub>HH</sub> = 1.8 Hz, 2 H, H3, dbbpy), 7.57 (d, <sup>3</sup>J<sub>HH</sub> = 8.1 Hz, 2 H, H4, H5), 7.48 (dd, 2 H, H5, dbbpy), 6.77 (dd, 2 H, H3, H6), 3.94 (s, 6 H, OMe), 1.42 (s, 18 H, *t*-Bu). <sup>13</sup>C{<sup>1</sup>H} NMR (100.8 MHz, CDCl<sub>3</sub>): δ 163.0 (C4, dbbpy), 158.2 (C2, C7), 155.0 (C2, dbbpy), 147.7 (C6, dbbpy), 139.6 (C8a, C9a), 130.8 (C4a, C4b), 124.7 (C5, dbbpy), 119.5 (C3, dbbpy), 118.4 (C4, C5), 110.7 (C3, C6), 108.2 (C1, C8), 55.7 (OMe), 35.9 (CMe<sub>3</sub>), 30.2 (CMe<sub>3</sub>) (CS<sub>2</sub>, C9 not observed).

**(Pr<sub>4</sub>N)<sub>2</sub>[Pt<sub>2</sub>{S<sub>2</sub>C=C[C<sub>12</sub>H<sub>6</sub>(*t*-Bu)-2,7]}<sub>4</sub>] [(Pr<sub>4</sub>N)<sub>2</sub>6].** To a suspension of (Pr<sub>4</sub>N)<sub>2</sub>**2b** (553 mg, 0.43 mmol) in THF (25 mL) was added [FeCp<sub>2</sub>]PF<sub>6</sub> (151 mg, 0.46 mmol), and the mixture was stirred for 1.5 h. Partial evaporation of the resulting dark brown solution (10 mL) and addition of Et<sub>2</sub>O (25 mL) caused the precipitation of a reddish brown solid, which was filtered off, washed with MeOH (2 × 5 mL), and vacuum-dried to give (Pr<sub>4</sub>N)<sub>2</sub>**6**. Yield: 231 mg, 49%. Anal. Calcd for C<sub>112</sub>H<sub>152</sub>N<sub>2</sub>Pt<sub>2</sub>S<sub>8</sub>: C, 61.90; H, 7.05; N, 1.29; S, 11.80. Found: C, 61.70; H, 7.27; N, 1.30; S, 11.70. Mp: 211 °C (dec). Λ<sub>M</sub> (Me<sub>2</sub>CO, 3.6 × 10<sup>-4</sup> M): 121 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. IR (Nujol, cm<sup>-1</sup>): ν(C=CS<sub>2</sub>), 1510. <sup>1</sup>H NMR [400.9 MHz, (CD<sub>3</sub>)<sub>2</sub>CO]: δ 8.90, 8.88, 8.52, 8.14 (all d, <sup>4</sup>J<sub>HH</sub> = 1.5 Hz, 2 H each, H1, H8), 7.70, 7.67, 7.62, 7.47 (all d, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, 2 H each, H4, H5), 7.30 (app td, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, <sup>4</sup>J<sub>HH</sub> = 1.5 Hz, 4 H, H3, H6), 7.16, 7.01 (both dd, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, <sup>4</sup>J<sub>HH</sub> = 1.5 Hz, 2 H each, H3, H6), 3.11 (m, 16 H, NCH<sub>2</sub>), 1.52 (m, CH<sub>2</sub>, 16 H), 1.47, 1.40, 1.29, 1.13 (all s, 18 H each, *t*-Bu), 0.79 (t, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 24 H, Me, Pr<sub>4</sub>N<sup>+</sup>).

**(Et<sub>4</sub>N)<sub>2</sub>[Pt<sub>2</sub>{S<sub>2</sub>C=C[C<sub>12</sub>H<sub>6</sub>(*t*-Bu)-2,7]}<sub>4</sub>] [(Et<sub>4</sub>N)<sub>2</sub>6].** This compound was prepared as described for (Pr<sub>4</sub>N)<sub>2</sub>**6**, from (Et<sub>4</sub>N)<sub>2</sub>**2b** (93 mg, 0.08 mmol) and [FeCp<sub>2</sub>]PF<sub>6</sub> (29 mg, 0.09 mmol). Yield: 73 mg, 89%. Anal. Calcd for C<sub>104</sub>H<sub>136</sub>N<sub>2</sub>Pt<sub>2</sub>S<sub>8</sub>: C, 60.61; H, 6.65; N, 1.36; S, 12.45. Found: C, 60.09; H, 6.46; N, 1.47; S, 12.19. Mp: 240 °C (dec). Λ<sub>M</sub> (Me<sub>2</sub>CO, 1.6 × 10<sup>-4</sup> M): 149 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. IR (Nujol, cm<sup>-1</sup>): ν(C=CS<sub>2</sub>), 1514. <sup>1</sup>H NMR [400.9 MHz, (CD<sub>3</sub>)<sub>2</sub>CO]: δ 8.94, 8.86, 8.55, 8.04 (all d, <sup>4</sup>J<sub>HH</sub> = 1.5 Hz, 2 H each, H1, H8), 7.70, 7.66, 7.63, 7.49 (all d, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, 2 H each, H4, H5), 7.31, 7.29, 7.17, 7.03 (all dd, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, <sup>4</sup>J<sub>HH</sub> = 1.5 Hz, 2 H each, H3, H6), 3.24 (q, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, 16 H, NCH<sub>2</sub>), 1.45, 1.41, 1.31, (all s, 18 H each, *t*-Bu), 1.13 (tt, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, <sup>3</sup>J<sub>NH</sub> = 1.5 Hz, 24 H, Me, Et<sub>4</sub>N<sup>+</sup>), 1.12 (s, 18 H, *t*-Bu).

**(PPN)<sub>2</sub>[Pt<sub>2</sub>{S<sub>2</sub>C=C[C<sub>12</sub>H<sub>6</sub>(*t*-Bu)-2,7]}<sub>4</sub>] [(PPN)<sub>2</sub>6].** To a suspension of (Pr<sub>4</sub>N)<sub>2</sub>**6** (249 mg, 0.12 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) were added (PPN)Cl (330 mg, 0.57 mmol) and water (8 mL), and the mixture was vigorously stirred for 15 min. The dark brown organic

layer was decanted, filtered through anhydrous  $\text{MgSO}_4$ , and concentrated (2 mL). Addition of MeOH (8 mL) led to the formation of a dark brown solid, which was filtered off, washed with MeOH (2 × 3 mL) and  $\text{Et}_2\text{O}$  (2 × 3 mL), and vacuum-dried to give (PPN)<sub>2</sub>**6**. Yield: 298 mg, 86%. Anal. Calcd for  $\text{C}_{160}\text{H}_{156}\text{N}_2\text{Pt}_2\text{S}_8$ : C, 66.78; H, 5.46; N, 0.97; S, 8.91. Found: C, 66.59; H, 5.64; N, 1.05; S, 8.69. Mp: 200 °C (dec).  $\Lambda_M$  ( $\text{Me}_2\text{CO}$ ,  $4.4 \times 10^{-4}$  M):  $144 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu(\text{C}=\text{CS}_2)$ , 1520.  $^1\text{H}$  NMR [400.9 MHz,  $(\text{CD}_3)_2\text{CO}$ ]:  $\delta$  8.94, 8.83, 8.56, 8.12 (all d,  $^4J_{\text{HH}} = 1.7$  Hz, 2 H each, H1, H8), 7.73–7.49 (m, 66 H, PPN<sup>+</sup> + H4, H5), 7.41 (d,  $^3J_{\text{HH}} = 8.0$  Hz, 2 H, H4, H5), 7.25–7.22 (m, 4 H, H3, H6), 7.12, 6.94 (both dd,  $^3J_{\text{HH}} = 8.0$  Hz,  $^4J_{\text{HH}} = 1.7$  Hz, 2 H each, H3, H6), 1.37, 1.33, 1.25, 1.07 (all s, 18 H each, *t*-Bu).  $^{13}\text{C}$ - $\{^1\text{H}\}$  NMR [100.8 MHz,  $(\text{CD}_3)_2\text{CO}$ ]:  $\delta$  174.9, 165.5, 152.5 ( $\text{CS}_2$ ), 149.4, 148.93, 148.88, 148.4 (C2, C7), 139.6, 139.5, 139.4 (C8a, C9a, two signals clearly overlapped), 136.5, 135.6, 134.3, 134.0 (C4a, C4b), 128.7, 128.6 (C9, expected third signal probably overlapped by PPN<sup>+</sup> resonances), 123.3, 123.1 (C3, C6), 121.9, 121.6 (C1, C8), 121.4, 120.5 (C3, C6), 120.3, 119.5 (C1, C8) 118.7, 118.6, 118.0 (C4, C5, two signals clearly overlapped), 35.7, 35.5, 35.3 ( $\text{CMe}_3$ , two signals clearly overlapped), 32.6, 32.5, 32.21, 32.18 ( $\text{CMe}_3$ ).

[Pt<sub>2</sub>{S<sub>2</sub>CCH[C<sub>12</sub>H<sub>6</sub>(*t*-Bu)<sub>2</sub>-2,7]}<sub>4</sub>] (**7**). To a suspension of (Pr<sub>4</sub>N)<sub>2</sub>**2b** (209 mg, 0.16 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 mL) was added trifluoromethanesulfonic acid (32  $\mu\text{L}$ , 0.37 mmol). The resulting dark red solution was stirred for 5 min and evaporated to dryness. Treatment of the residue with pentane (20 mL) gave a precipitate of Pr<sub>4</sub>N(CF<sub>3</sub>SO<sub>3</sub>) and a dark red solution. The solid was removed by filtration and the clear filtrate evaporated to dryness to give **7** as a dark brown microcrystalline solid. Yield: 116 mg, 78%. Anal. Calcd for  $\text{C}_{88}\text{H}_{100}\text{Pt}_2\text{S}_8$ : C, 58.58; H, 5.59; S, 14.22. Found: C, 58.60; H, 5.93; S, 14.13. Mp: 246 °C. IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu(\text{CS}_2)$ , 1025, 998.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.57, 7.45 (both d,  $^3J_{\text{HH}} = 8.0$  Hz, 4 H each, H4, H5), 7.41, 7.40 (both br, 4 H each, H1, H8), 7.36, 7.33 (both dd,  $^3J_{\text{HH}} = 8.0$  Hz,  $^4J_{\text{HH}} = 1.6$  Hz, 4 H each, H3, H6), 5.44, 4.32 (both s, 1 H each, H9), 1.24, 1.22 (both s, 36 H each, *t*-Bu).  $^{13}\text{C}\{^1\text{H}\}$  NMR (150.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  261.5, 239.8 ( $\text{CS}_2$ ), 150.6, 150.5 (C2, C7), 144.8, 139.9 (C8a, C9a), 138.7, 138.1 (C4a, C4b), 125.7, 125.0 (C3, C6), 122.9, 121.7 (C1, C8), 119.2 (C4, C5), 71.5, 68.2 (C9), 35.0, 34.9 ( $\text{CMe}_3$ ), 31.7, 31.6 ( $\text{CMe}_3$ ).  $^{195}\text{Pt}\{^1\text{H}\}$  NMR (86.2 MHz,  $\text{CDCl}_3$ ):  $\delta$  -3176.

Pr<sub>4</sub>N[Pt{S<sub>2</sub>CCH[C<sub>12</sub>H<sub>6</sub>(*t*-Bu)<sub>2</sub>-2,7]}{S<sub>2</sub>C=C[C<sub>12</sub>H<sub>6</sub>(*t*-Bu)<sub>2</sub>-2,7]}] (Pr<sub>4</sub>N**8**). To a suspension of (Pr<sub>4</sub>N)<sub>2</sub>**2b** (112 mg, 0.09 mmol) in  $\text{CH}_2\text{Cl}_2$  (15 mL) was added trifluoromethanesulfonic acid (8  $\mu\text{L}$ , 0.09 mmol). Reaction took place immediately to give a violet solution. Partial evaporation of the solvent (4 mL) and addition of  $\text{Et}_2\text{O}$  (5 mL) led to the formation of a violet precipitate, which was filtered off, washed with a 2:3 (v/v) mixture of  $\text{CH}_2\text{Cl}_2$  and  $\text{Et}_2\text{O}$  (2 × 3 mL), and vacuum-dried to give Pr<sub>4</sub>N**8**. Yield: 81 mg, 85%. Anal. Calcd for  $\text{C}_{56}\text{H}_{77}\text{NPtS}_4$ : C, 61.85; H, 7.14; N, 1.29; S, 11.79. Found: C, 61.88; H, 7.22; N, 1.50; S, 11.83. Mp: 150 °C (dec).  $\Lambda_M$  ( $\text{Me}_2\text{CO}$ ,  $3.0 \times 10^{-4}$  M):  $97 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu(\text{C}=\text{CS}_2)$ , 1514;  $\nu(\text{Pt}-\text{S})$ , 353, 364.  $^1\text{H}$  NMR (400.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.72 (d,  $^4J_{\text{HH}} = 1.6$  Hz, 2 H, H1, H8, dithiolato), 7.81 (br s, 2 H, H1, H8, dithioato), 7.60 (app t,  $^3J_{\text{HH}} = 7.9$  Hz, 4 H, H4, H5, dithioato + dithiolato), 7.42 (dd,  $^3J_{\text{HH}} = 7.9$  Hz,  $^4J_{\text{HH}} = 1.6$  Hz, 2 H, H3, H6, dithioato), 7.14 (dd,  $^3J_{\text{HH}} = 7.9$  Hz,  $^4J_{\text{HH}} = 1.6$  Hz, 2 H, H3, H6, dithiolato), 4.85 (s, 1 H, H9, dithioato), 2.97 (m, 8 H, NCH<sub>2</sub>), 1.37 (s, 18 H, *t*-Bu), 1.35 (s, 18 H, *t*-Bu), 1.40–1.32 (m, 8H, CH<sub>2</sub>, overlapped by *t*-Bu signals), 0.70 (t,  $^3J_{\text{HH}} = 7.3$  Hz, 12 H, Me, Pr<sub>4</sub>N<sup>+</sup>).

DMANH[Pt{S<sub>2</sub>CCH[C<sub>12</sub>H<sub>6</sub>(*t*-Bu)<sub>2</sub>-2,7]}{S<sub>2</sub>C=C[C<sub>12</sub>H<sub>6</sub>(*t*-Bu)<sub>2</sub>-2,7]}] (DMANH**8**). To a solution of **7** (92 mg, 0.05 mmol) in  $\text{Et}_2\text{O}$

(10 mL) was added 1,8-bis(dimethylamino)naphthalene (22 mg, 0.10 mmol). A brownish red precipitate formed immediately, which was filtered off, washed with  $\text{Et}_2\text{O}$  (5 mL), and vacuum-dried to give DMANH**8**. Yield: 104 mg, 92%. Anal. Calcd for  $\text{C}_{58}\text{H}_{68}\text{N}_2\text{-PtS}_4$ : C, 62.39; H, 6.14; N, 2.51; S, 11.49. Found: C, 62.09; H, 6.14; N, 2.45; S, 11.32. Mp: 155 °C (dec).  $\Lambda_M$  ( $\text{Me}_2\text{CO}$ ,  $3.1 \times 10^{-4}$  M):  $95 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu(\text{C}=\text{CS}_2)$ , 1514.  $^1\text{H}$  NMR [400.9 MHz,  $(\text{CD}_3)_2\text{CO}$ ]:  $\delta$  8.80 (d,  $^4J_{\text{HH}} = 1.5$  Hz, 2 H, H1, H8, dithiolato), 8.09 (d,  $^3J_{\text{HH}} = 7.7$  Hz, 4 H, H2, H4, H5, H7, DMANH), 7.85 (br s, 2 H, H1, H8, dithioato), 7.73 (t,  $^3J_{\text{HH}} = 7.7$  Hz, 2 H, H3, H6, DMANH), 7.70, 7.60 (both d,  $^3J_{\text{HH}} = 8.0$  Hz, 2 H each, H4, H5, dithioato and dithiolato), 7.48 (dd,  $^3J_{\text{HH}} = 8.0$  Hz,  $^4J_{\text{HH}} = 1.6$  Hz, 2 H, H3, H6, dithioato), 7.12 (dd,  $^3J_{\text{HH}} = 8.0$  Hz,  $^4J_{\text{HH}} = 1.6$  Hz, 2 H, H3, H6, dithiolato), 4.87 (s, 1 H, H9, dithioato), 3.31, 3.30 (both s, 6 H each, NMe<sub>2</sub>), 1.38, 1.34 (both s, 18 H each, *t*-Bu).

## Results and Discussion

**Synthesis and Properties of Platinum(II) Complexes with (Fluoren-9-ylidene)methanedithiolato and Substituted Derivatives.** The platinum(II) complexes with (fluoren-9-ylidene)methanedithiolato ligand and its 2,7-di-*tert*-butyl- and 2,7-dimethoxy-substituted analogues were obtained by reacting different chloroplatinum(II) precursors with the dithioates (pipH)[(2,7-R<sub>2</sub>C<sub>12</sub>H<sub>6</sub>)CHCS<sub>2</sub>] [R = H (**1a**), *t*-Bu (**1b**), or OMe (**1c**)] in the presence of piperidine. As in the case of the gold(I) and gold(III) complexes, the formation of the platinum(II) complexes is straightforward, taking place by the displacement of the chloro ligands by the dithioates and the subsequent deprotonation of the C9 carbon atom of the 9-fluorenyl moiety by the base.

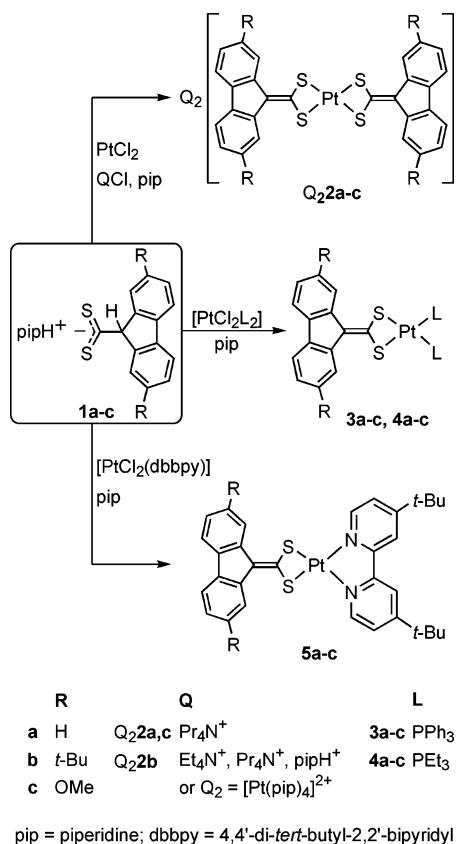
The anionic complexes Q<sub>2</sub>[Pt{S<sub>2</sub>C=C(C<sub>12</sub>H<sub>6</sub>R<sub>2</sub>-2,7)}<sub>2</sub>], where Q<sup>+</sup> = Pr<sub>4</sub>N<sup>+</sup> for R = H [(Pr<sub>4</sub>N)<sub>2</sub>**2a**], Q<sup>+</sup> = Et<sub>4</sub>N<sup>+</sup> or Pr<sub>4</sub>N<sup>+</sup> for R = *t*-Bu (Q<sub>2</sub>**2b**), or Q<sup>+</sup> = Pr<sub>4</sub>N<sup>+</sup> for R = OMe [(Pr<sub>4</sub>N)<sub>2</sub>**2c**], were prepared in moderate yields (40–60%) from the reaction of PtCl<sub>2</sub> with piperidine, the corresponding QCl salt, and the piperidinium dithioates **1a–c** in molar ratio 1:2:2:2 in  $\text{CH}_2\text{Cl}_2$  (Scheme 1). Addition of piperidine to  $\text{CH}_2\text{-Cl}_2$  suspensions of PtCl<sub>2</sub> results in the formation of clear solutions presumably containing a mixture of *cis*- and *trans*-[PtCl<sub>2</sub>(pip)<sub>2</sub>].<sup>30</sup> The dithioates **1a–c** displace the chloro and piperidine ligands and are then deprotonated by the free piperidine. In the presence of QCl salts (Q = Pr<sub>4</sub>N<sup>+</sup>, Et<sub>4</sub>N<sup>+</sup>), the poorly soluble compounds Q<sub>2</sub>**2a–c** precipitate as orange solids and can be separated from the piperidinium chloride by washing with  $\text{CH}_2\text{Cl}_2$ . Attempts to obtain more soluble salts by using bulkier cations resulted in very low yields (Bu<sub>4</sub>N<sup>+</sup>) or were unsuccessful (PPN<sup>+</sup> and Ph<sub>4</sub>P<sup>+</sup>). In absence of QCl, the piperidinium salt (pipH)<sub>2</sub>**2b** was obtained in 74% yield. In an attempt to prepare the neutral complex [Pt{S<sub>2</sub>C=C[C<sub>12</sub>H<sub>6</sub>(*t*-Bu)<sub>2</sub>-2,7]}(pip)<sub>2</sub>] from the reaction of PtCl<sub>2</sub>, **1b**, and piperidine in molar ratio 1:1:3, the Magnus-type<sup>31</sup> salt [Pt(pip)<sub>4</sub>]**2b** was obtained in 83% yield. The salts of **2a–c** are moderately stable compounds both in the solid state and in dimethyl sulfoxide solution.

(30) Belluco, U.; Cattalini, L.; Turco, A. *J. Am. Chem. Soc.* **1964**, *86*, 3257–3261. Kauffman, G. B.; Cowan, D. O. *Inorg. Synth.* **1965**, *7*, 249. Cattalini, L.; Guidi, F.; Tobe, M. L. *J. Chem. Soc., Dalton Trans.* **1993**, 233–236.

(31) Rodgers, M. L.; Martin, D. S. *Polyhedron* **1987**, *6*, 225–254.



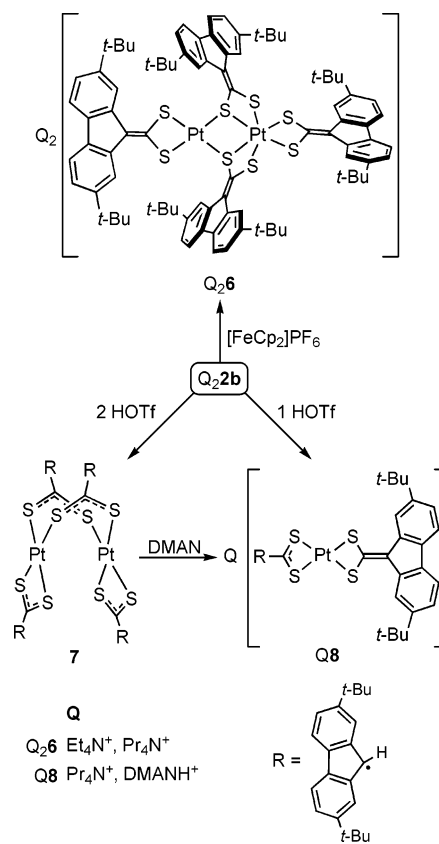
Scheme 1



The neutral complexes  $[\text{Pt}\{\text{S}_2\text{C}=\text{C}(\text{C}_{12}\text{H}_6\text{R}_{2-2,7})\text{L}_2]$ , where  $\text{L} = \text{PPh}_3$  and  $\text{R} = \text{H}$  (**3a**), *t*-Bu (**3b**), and OMe (**3c**),  $\text{L} = \text{PEt}_3$  and  $\text{R} = \text{H}$  (**4a**), *t*-Bu (**4b**), and OMe (**4c**), or  $\text{L}_2 = \text{dbbpy}$  for  $\text{R} = \text{H}$  (**5a**), *t*-Bu (**5b**), and OMe (**5c**) (dbbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridyl), were prepared in moderate to high yields by displacement of the chloro ligands in the corresponding precursors  $[\text{PtCl}_2\text{L}_2]$  with the dithioates **1a-c** in the presence of piperidine. In most cases, the piperidinium chloride can be removed easily by washing the crude products with MeOH or EtOH. The phosphine complexes **3a-c** and **4a-c** are remarkably stable yellow microcrystalline solids. In contrast, the diimine derivatives **5a-c** are very dark colored solids (purple or dark blue) and are sensitive to visible light both in the solid state and in  $\text{CHCl}_3$  or  $\text{CH}_2\text{-Cl}_2$  solutions.<sup>32</sup> Like the previously described complexes of the type  $[\text{Pt}(\text{dithiolato})(\text{diimine})]$ , compounds **5a-c** display a marked solvatochromism (see below).

**Oxidation of  $\text{Q}_{22\text{b}}$ . Formation of an Unprecedented Pt(II)–Pt(IV) Dithiolato Complex.** We have recently reported that the gold(I) complexes with (fluoren-9-ylidene)methanedithiolato ligand and its substituted analogues are readily oxidized to gold(III) complexes under atmospheric conditions or through their reactions with the organic acceptor TCNQ.<sup>26</sup> This fact was attributed to the strong electron-donating

Scheme 2



character of the ligands, which had also been revealed by the electronic absorption and emission properties of the gold(I) complexes. To investigate if the (fluoren-9-ylidene)methanedithiolato ligands would also facilitate the oxidation of the platinum(II) complexes, we carried out the reactions of  $\text{Q}_{22\text{a-c}}$  with the mild oxidant  $[\text{FeCp}_2]\text{PF}_6$ . Although the three complexes reacted at room temperature in THF, MeCN, or  $\text{Me}_2\text{CO}$ , only in the cases of the salts of **2b** was one single platinum product obtained, whose elemental analyses and negative-ion FAB mass spectra were consistent with the formulation  $\text{Q}_2[\text{Pt}_2\{\text{S}_2\text{C}=\text{C}(\text{C}_{12}\text{H}_6(\text{t-Bu})_{2-2,7})\}_4]$  ( $\text{Q}_2\text{6}$ ,  $\text{Q} = \text{Et}_4\text{N}^+$ ,  $\text{Pr}_4\text{N}^+$ ) (Scheme 2). These salts are brownish red microcrystalline solids that scarcely dissolve in  $\text{CH}_2\text{Cl}_2$  or  $\text{CHCl}_3$  and are only slightly more soluble in  $\text{Me}_2\text{CO}$  and dimethyl sulfoxide. To complete the characterization of the dianion **6** by  $^{13}\text{C}\{^1\text{H}\}$  NMR and to obtain single crystals suitable for X-ray diffraction studies, we prepared the soluble salt  $(\text{PPN})_2\text{6}$  ( $\text{PPN}^+ = [(\text{Ph}_3\text{P})_2\text{N}]^+$ ) from  $(\text{Pr}_4\text{N})_2\text{6}$  by cation metathesis with  $(\text{PPN})\text{Cl}$  in  $\text{CH}_2\text{Cl}_2/\text{water}$ . Preliminary crystallographic studies on the  $\text{Q}_2\text{6}$  salts (see below) revealed that the dianion **6** is composed of one Pt(II) center in a distorted square-planar environment and one Pt(IV) center in a distorted octahedral environment, joined together by two bridging dithiolato ligands, as depicted in Scheme 2. The compounds  $\text{Q}_2\text{6}$  ( $\text{Q} = \text{Et}_4\text{N}^+$ ,  $\text{Pr}_4\text{N}^+$ ) can also be obtained in moderate to high yields by reacting  $\text{Q}_{22\text{b}}$  with anhydrous  $\text{FeCl}_3$  or  $\text{FeCl}_2$  (1:1) in  $\text{Me}_2\text{CO}$ , MeCN, or THF. The reaction with  $\text{FeCl}_2$  succeeds only in the presence of atmospheric oxygen and is not catalytic. The dianion **6** displays a very high stability both in the solid state and in solution, and the

(32) Platinum diimine dithiolates which display low-energy charge-transfer-to-diimine absorptions have been reported to undergo photooxidation reactions. See, for example: Vogler, A.; Kunkely, H. *J. Am. Chem. Soc.* **1981**, *103*, 1559–1560. Zhang, Y.; Ley, K. D.; Schanze, K. S. *Inorg. Chem.* **1996**, *35*, 7102–7110. Connick, W. B.; Gray, H. B. *J. Am. Chem. Soc.* **1997**, *119*, 11620–11627. We are currently investigating the photoreactivity of **5a-c**.

attempts to split it into Pt(II) and Pt(IV) complexes through the reaction with excess NaCN or KSCN were unsuccessful. As far as we are aware, the previously reported 1,1-ethylenedithiolato complexes of Pt(IV) are limited to the (cyclopentadienyldiene)methanedithiolato derivative  $(Et_4N)_2$ -[Pt(S<sub>2</sub>C=C<sub>5</sub>H<sub>4</sub>)<sub>3</sub>]<sup>23</sup> and [PtBr<sub>2</sub>(tbcda)(dpphen)] (tbcda = 2-(*tert*-butoxycarbonyl)-2-cyano-1,1-ethylenedithiolate; dpphen = 4,7-diphenyl-1,10-phenanthroline).<sup>33</sup>

**Protonation of 2b.** The protonation of the anionic complexes **2a–c** was attempted to explore the basic character of the coordinated (fluoren-9-ylidene)methanedithiolato ligands and the possibility of obtaining dithioato complexes. Only in the case of complex **2b**, containing the di-*tert*-butyl-substituted dithiolato ligand, were compounds of definite compositions obtained. The reaction of (Pr<sub>4</sub>N)<sub>2</sub>**2b** with triflic acid (HO<sub>3</sub>SCF<sub>3</sub>, TfO) in molar ratio 1:2 in Et<sub>2</sub>O resulted in the protonation of both dithiolato ligands at the C9 carbon atom of the 2,7-di-*tert*-butylfluoren-9-ylidene moiety and the formation of the dinuclear dithioato complex [Pt<sub>2</sub>{S<sub>2</sub>CCH[C<sub>12</sub>H<sub>6</sub>(*t*-Bu)<sub>2</sub>-2,7]}<sub>4</sub>] (**7**). This dark brown compound is highly soluble in most organic solvents, including Et<sub>2</sub>O and hexane, and can be easily separated from the (Pr<sub>4</sub>N)TfO and isolated in almost quantitative yields. Although it was not possible to grow crystals of **7** suitable for X-ray diffraction studies, a dinuclear structure containing two bridging and two chelating dithioato ligands (Scheme 2) can be proposed on the basis of its <sup>1</sup>H and <sup>13</sup>C NMR spectra, which reveal the presence of two different dithioato ligands. This structure has been found in a dinuclear (dithiocumato)platinum(II) complex reported by Fackler and co-workers.<sup>34</sup> The positive-ion FAB mass spectrum of **7** shows the isotope distribution corresponding to a dinuclear M<sup>+</sup> ion. Compound **7** can also be obtained directly by reacting PtCl<sub>2</sub> with **1b** (1:2) in CH<sub>2</sub>Cl<sub>2</sub>. The reaction of **7** with 2 equiv of piperidine resulted in its deprotonation to give (pipH)<sub>2</sub>**2b**.

When the protonation of (Pr<sub>4</sub>N)<sub>2</sub>**2b** was carried out with 1 equiv of triflic acid, the mixed dithiolato/dithioato complex Pr<sub>4</sub>N{Pt{S<sub>2</sub>C=C[C<sub>12</sub>H<sub>6</sub>(*t*-Bu)<sub>2</sub>-2,7]}{S<sub>2</sub>CCH[C<sub>12</sub>H<sub>6</sub>(*t*-Bu)<sub>2</sub>-2,7]}} (Pr<sub>4</sub>N**8**) was obtained (Scheme 2), which can be separated from the (Pr<sub>4</sub>N)TfO thanks to its lower solubility in CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O and isolated in high yield as a violet solid. The anion **8** can also be obtained from the reaction of **7** with 1 equiv of the proton sponge (1,8-bis(dimethylamino)naphthalene = DMAN) in Et<sub>2</sub>O, where the salt DMANH**8** precipitates as a brownish red solid. Both **Q8** salts are unstable in solution under atmospheric conditions, undergoing deprotonation and oxidation to form the Pt(II)–Pt(IV) complex **6**. The anion **8** is a rare example of mixed dithiolato/dithioato complex.

**Crystal Structures of Complexes.** The crystal structures of **3b** (Figure 1) and **5c**·CH<sub>2</sub>Cl<sub>2</sub> (Figure 2) were determined by X-ray diffraction studies. Selected bond distances and angles are listed in Tables 2 and 3. Both structures exhibit a square planar coordination around the plati-

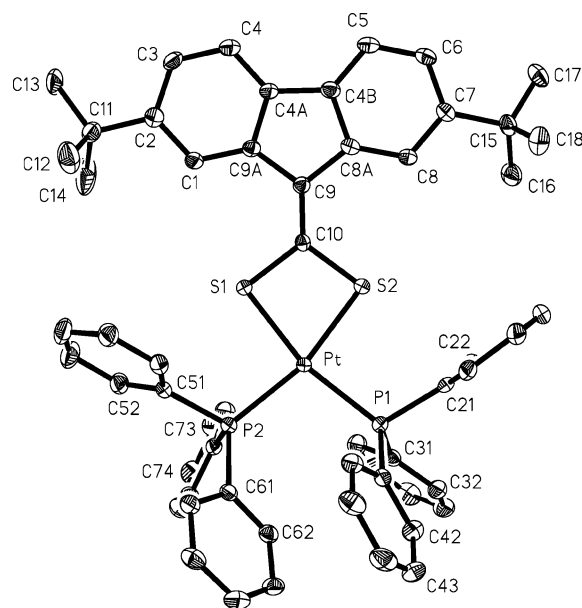


Figure 1. Structure of complex **3b**. Hydrogen atoms are omitted for clarity.

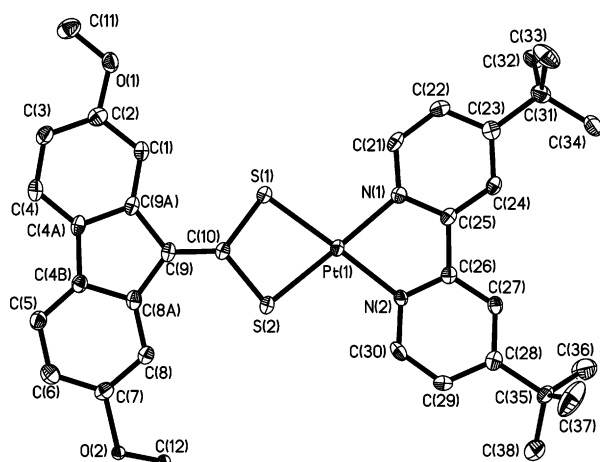


Figure 2. Structure of complex **5c**. Hydrogen atoms are omitted for clarity.

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

Pt–P(1)	2.2958(6)	S(1)–C(10)	1.756(2)
Pt–P(2)	2.2980(6)	S(2)–C(10)	1.756(2)
Pt–S(1)	2.3222(6)	C(9)–C(10)	1.362(3)
Pt–S(2)	2.3259(6)		
P(1)–Pt–P(2)	103.29(2)	S(1)–Pt–S(2)	74.33(2)
P(1)–Pt–S(1)	165.426(19)	C(10)–S(1)–Pt	89.76(7)
P(2)–Pt–S(1)	91.03(2)	C(10)–S(2)–Pt	89.64(7)
P(1)–Pt–S(2)	91.51(2)	S(2)–C(10)–S(1)	106.16(10)
P(2)–Pt–S(2)	165.00(2)		

Table 3. Selected Bond Distances (Å) and Angles (deg) for **5c**·CH<sub>2</sub>Cl<sub>2</sub>

Pt(1)–N(2)	2.035(4)	S(1)–C(10)	1.757(5)
Pt(1)–N(1)	2.048(4)	S(2)–C(10)	1.757(5)
Pt(1)–S(1)	2.2745(13)	C(9)–C(10)	1.359(7)
Pt(1)–S(2)	2.2762(13)		
N(2)–Pt(1)–N(1)	78.86(16)	S(1)–Pt(1)–S(2)	75.20(5)
N(2)–Pt(1)–S(1)	177.66(12)	C(10)–S(1)–Pt(1)	90.23(16)
N(1)–Pt(1)–S(1)	103.24(11)	C(10)–S(2)–Pt(1)	90.17(17)
N(1)–Pt(1)–S(2)	177.78(12)	S(1)–C(10)–S(2)	104.4(3)
N(2)–Pt(1)–S(2)	102.73(12)		

num atom (mean deviations from plane: S<sub>2</sub>PtP<sub>2</sub>, 0.053 Å; S<sub>2</sub>PtN<sub>2</sub>, 0.022 Å). The angles S–Pt–S of 74.33(2) (**3b**) and 75.20(5)° (**5c**) are typical of four-membered CS<sub>2</sub>M chelate rings, and the coordination geometries and Pt–S and

(33) Cummings, S. D.; Cheng, L. T.; Eisenberg, R. *Chem. Mater.* **1997**, *9*, 440–450.

(34) Fackler, J. P., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 1009–1010. Burke, J. M.; Fackler, J. P. *Inorg. Chem.* **1972**, *11*, 3000–3009.



Pt–N bond distances are very similar to those of the related complexes [Pt{S<sub>2</sub>C=C(COMe)<sub>2</sub>}(PPh<sub>3</sub>)<sub>2</sub>],<sup>25</sup> [Pt(S<sub>2</sub>C=CHCOPh)(PPh<sub>3</sub>)<sub>2</sub>]<sup>20</sup> and [Pt(S<sub>2</sub>C=CHCOFc)(PPh<sub>3</sub>)<sub>2</sub>] (Fc = ferrocenyl),<sup>22</sup> or [Pt{S<sub>2</sub>C=C(COMe)<sub>2</sub>}(dbbpy)] and [Pt{S<sub>2</sub>C=C(CN)(C<sub>6</sub>H<sub>4</sub>Br-4)}(dbbpy)].<sup>14</sup> The dithiolato ligands are essentially planar [excluding substituents of the fluoren-9-ylidene fragments; mean deviations from plane: 0.059 (**3b**) and 0.029 Å (**5c**)].

Crystals of the Et<sub>4</sub>N<sup>+</sup>, Pr<sub>4</sub>N<sup>+</sup>, and PPN<sup>+</sup> salts of dianion **6**, obtained from a variety of solvents, and also of the DMANH<sup>+</sup> salt, obtained from the aerial oxidation of DMANH**8** in Me<sub>2</sub>CO, were apparently suitable for crystallographic studies, but they either underwent rapid loss of solvent or, if stable enough to be handled, presented severe twinning or disorder problems; therefore, the structures could not be refined satisfactorily. However, in all cases the data revealed unequivocally that complex **6** has the structure depicted in Scheme 2, which can be viewed as a [Pt{S<sub>2</sub>C=C[C<sub>12</sub>H<sub>6</sub>(*t*-Bu)<sub>2</sub>-2,7]}<sub>3</sub>] unit, with a Pt(IV) in a distorted octahedral environment, attached to a [Pt{S<sub>2</sub>C=C[C<sub>12</sub>H<sub>6</sub>(*t*-Bu)<sub>2</sub>-2,7]}] fragment, containing the Pt(II) center, through two sulfur atoms of different ligands. The Ph<sub>4</sub>P<sup>+</sup> salt, obtained as described for the PPN<sup>+</sup> salt, crystallizes as a dichloromethane disolvate in the space group *P* $\bar{1}$  with *a* = 18.489(3), *b* = 18.634(3), and *c* = 19.573(3) Å and  $\alpha$  = 99.389(4),  $\beta$  = 94.922(4), and  $\gamma$  = 108.726(3)° at –140 °C. The structure was refined to wR2 0.37, R1 0.13 (anion Pt and S anisotropic, all other atoms isotropic, H atoms not included; see the CIF file in Supporting Information) and its qualitative nature established unambiguously, but large features of residual electron density (9 e Å<sup>-3</sup>) precluded satisfactory refinement. The crystal was probably twinned.

**NMR Spectra.** The <sup>1</sup>H NMR spectra of the platinum complexes with the (fluoren-9-ylidene)methanedithiolato ligand and its substituted analogues show the signals corresponding to the aromatic protons of the ligands between  $\delta$  8.94 and 6.60. The resonances of the H1 and H8 protons ( $\delta$  8.94–7.86) are significantly downfield-shifted relative to the free dithioates **1a–c** and represent a distinctive characteristic of coordinated (fluoren-9-ylidene)methanedithiolato ligands.<sup>26</sup> The <sup>13</sup>C NMR spectra show the resonance of the C9 atom within a very narrow range around  $\delta$  130, while the chemical shift of the CS<sub>2</sub> carbon atom undergoes significant variations, being much higher for the anionic derivatives Q<sub>2</sub>**2a–c** ( $\delta$  187.1–183.2) than for the neutral **3a–c**, **4a–c**, and **5a–c** ( $\delta$  165.5–159.1). These variations agree with the observations reported for the gold complexes,<sup>26</sup> for which the CS<sub>2</sub> chemical shift decreases as the negative charge on the complex decreases or as the oxidation state of the metal center or its electron-accepting character increases.

The <sup>1</sup>H NMR spectra of compounds Q<sub>2</sub>**6** (Q = Et<sub>4</sub>N<sup>+</sup>, Pr<sub>4</sub>N<sup>+</sup>, PPN<sup>+</sup>) and the <sup>13</sup>C NMR spectrum of (PPN)<sub>2</sub>**6** are fully consistent with the dinuclear structure depicted in Scheme 2. The dianion **6** is a chiral molecule with overall C<sub>2</sub> symmetry in solution, containing three types of dithiolato ligands. The two bridging dithiolates are equivalent to each other but, in contrast to the chelating dithiolates, do not lie along the C<sub>2</sub> symmetry axis and therefore do not contain

equivalent atoms. As a result, the <sup>1</sup>H NMR spectra show a total of four singlets of the same intensity for the *t*-Bu groups and four sets of signals for the aromatic protons (see Experimental Section and Supporting Information). A <sup>13</sup>C{<sup>1</sup>H} NMR spectrum could be measured only for the more soluble PPN<sup>+</sup> salt and shows four signals for each of the carbon atoms of the dithiolato ligand, except for the CS<sub>2</sub> and C9 atoms. The three expected resonances of the CS<sub>2</sub> carbon atoms appear at  $\delta$  174.9, 165.5, and 152.5, the latter displaying a higher intensity and being assignable to the bridging ligands. Only two of the three expected C9 resonances are observable (at  $\delta$  128.7 and 128.6), probably because one of them is overlapped by PPN<sup>+</sup> resonances.

The presence of the dithioato ligands in complexes **7** and **Q8** is clearly confirmed by the resonances of the H9 atoms of the 2,7-di-*tert*-butylfluoren-9-yl group, which appear in the range  $\delta$  5.44–4.32. The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of complex **7** show duplicate signals for each of the protons and carbon atoms of the dithioato ligand, which is consistent with the presence of two bridging and two chelating dithioates as depicted in Scheme 2. The salts **Q8** give rise to almost identical resonances for the protons of the anion, with one set of signals corresponding to a dithioato ligand and another set corresponding to a symmetrical dithiolato ligand.

**IR Spectra.** The solid-state infrared spectra of the platinum complexes with the (fluoren-9-ylidene)methanedithiolato ligand and its substituted derivatives show one or two bands between 1500 and 1538 cm<sup>-1</sup> assignable to the  $\nu$ (C=CS<sub>2</sub>) mode.<sup>35</sup> As is the case with the previously described gold complexes,<sup>26</sup> the observed variations in the energies of the  $\nu$ (C=CS<sub>2</sub>) bands can be attributed to the oxidation state of the metal center and the nature of the ligands attached to it, which affect the strength of the  $\pi$  component of the C=CS<sub>2</sub> bond. Usually, a higher oxidation state and/or the presence of weaker donor ligands favor the resonance form **A** of the (fluoren-9-ylidene)methanedithiolato ligand (Chart 1) and increase the energy of the  $\nu$ (C=CS<sub>2</sub>) band. Thus, the dianionic complexes **2a–c** give rise to the lowest energy for this band (around 1500 cm<sup>-1</sup>), while the Pt(II)–Pt(IV) complex **6** (1510–1520 cm<sup>-1</sup>), the monoprotonated **8** (1514 cm<sup>-1</sup>), and the neutral complexes **3a–c**, **4a–c**, and **5a–c** (1520–1538 cm<sup>-1</sup>) display appreciably higher energies. The  $\nu$ (Pt–S) band can be unequivocally assigned only for the dianionic complexes **2a–c** and appears around 340 cm<sup>-1</sup>.

**Mass Spectra.** The electrospray ionization (ESI) and/or fast atom bombardment (FAB) mass spectra of complexes (Pr<sub>4</sub>N)<sub>2</sub>**2b**, (Pr<sub>4</sub>N)<sub>2</sub>**6**, **7**, Pr<sub>4</sub>N**8**, and DMANH**8** were measured to confirm their nuclearity (see Supporting Information for details). The most abundant peak in the negative ESI mass spectrum of (Pr<sub>4</sub>N)<sub>2</sub>**2b** appears at *m/z* 450 and corresponds to the dianionic species **2b**; the isotopic distributions corresponding to the monoanion resulting from the one-electron oxidation of **2b** and the ionic association Pr<sub>4</sub>N**2b** are also observed (most intense peaks at *m/z* 900 and 1086, respec-

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tively). The isotope pattern of the ion pair  $\text{Pr}_4\text{N}6$  is observed in both the negative-ion FAB and ESI mass spectra of  $(\text{Pr}_4\text{N})_2\mathbf{6}$  at  $m/z$  1985. The fragmentation of  $\mathbf{6}$  gives fundamentally monoanionic  $\mathbf{2b}$  in FAB, while the softer ESI technique allows the observation of several dinuclear species. The positive-ion FAB mass spectrum of  $\mathbf{7}$  shows the isotope distribution corresponding to a dinuclear  $\text{M}^+$  ion at  $m/z$  1804 with a relative abundance of 35%, while the most abundant ion is the mononuclear species  $[\text{Pt}\{\text{S}_2\text{CCH}[\text{C}_{12}\text{H}_6(t\text{-Bu})_2-2,7]\}_2]^+$ , which most probably results from the fragmentation of the  $\text{M}^+$  ion. In negative mode, the FAB MS of  $\mathbf{7}$  displays the isotopic distribution of monoanionic  $\mathbf{2b}$  as the most abundant ion, while the partially deprotonated dinuclear species  $[\text{Pt}_2\{\text{S}_2\text{C}=\text{C}[\text{C}_{12}\text{H}_6(t\text{-Bu})_2-2,7]\}_2\{\text{S}_2\text{CCH}[\text{C}_{12}\text{H}_6(t\text{-Bu})_2-2,7]\}_2]^-$  and  $[\text{Pt}_2\{\text{S}_2\text{C}=\text{C}[\text{C}_{12}\text{H}_6(t\text{-Bu})_2-2,7]\}_2\{\text{S}_2\text{CCH}[\text{C}_{12}\text{H}_6(t\text{-Bu})_2-2,7]\}_2]^-$  show up with very low relative abundances at  $m/z$  1802 and 1448, respectively, indicating that they have a very low stability as compared to monoanionic  $\mathbf{2b}$ . The ionization of  $\mathbf{7}$  by the ESI technique was very poor in  $\text{CH}_2\text{Cl}_2$ , and the compound is not soluble enough in MeCN; therefore, consistent results were not obtained. The most abundant isotope distribution observed in the ESI mass spectra of  $\text{Q}8$  ( $\text{Q} = \text{Pr}_4\text{N}^+$  and  $\text{DMANH}^+$ ), obtained from freshly prepared MeCN or  $\text{CH}_2\text{Cl}_2$  solutions in negative mode, is attributable to the mononuclear anion  $\mathbf{8}$ . The pattern is similar to that of monoanionic  $\mathbf{2b}$  but shifted by one unit at higher  $m/z$ . However, its most intense peak occurs also at  $m/z$  900, and not the expected  $m/z$  901, probably because of the contribution of small amounts of monoanionic  $\mathbf{2b}$ . After ca. 5 min in solution, the ESI mass spectra of  $\text{Q}8$  show the isotopic distribution of the dianion  $\mathbf{2b}$  at  $m/z$  450, which results from the deprotonation of  $\mathbf{8}$ .

**Molar Conductivities.** Because of their very low solubility in  $\text{Me}_2\text{CO}$ , the molar conductivities of  $(\text{Pr}_4\text{N})_2\mathbf{2a}$  and  $\text{Q}_2\mathbf{2b}$  ( $\text{Q} = \text{Et}_4\text{N}^+$ ,  $\text{Pr}_4\text{N}^+$ ) were measured in  $\text{MeNO}_2$  at concentrations of ca.  $1 \times 10^{-4}$  M. The values found ( $128\text{--}134 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ) fall in the range given by Geary<sup>36</sup> for 2:1 electrolytes in  $\text{MeNO}_2$  ( $115\text{--}250 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ); however, accurate comparisons are not possible because the concentrations employed for obtaining reference values (usually  $10^{-3}$  M) were much higher. The conductivities of the rest of the ionic compounds were measured in  $\text{Me}_2\text{CO}$  at  $5 \times 10^{-4}$  M or somewhat lower concentrations. The values found for  $(\text{pipH})_2\mathbf{2b}$  and  $(\text{Pr}_4\text{N})_2\mathbf{2c}$  ( $83$  and  $94 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ , respectively) are considerably lower than expected for 2:1 electrolytes in  $\text{Me}_2\text{CO}$  (range  $160\text{--}200 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ),<sup>36</sup> probably as a result of ion association. The conductivity of  $[\text{Pt}(\text{pip})_4]\mathbf{2b}$  ( $74 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ) is rather low relative to reference values for 1:1 electrolytes (range  $100\text{--}140 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ); although we have not found reference data for bivalent electrolytes in the literature, this value confirms the ionic nature of the compound. The salts  $\text{Q}_2\mathbf{6}$  ( $\text{Q} = \text{Et}_4\text{N}^+$ ,  $\text{Pr}_4\text{N}^+$ ,  $\text{PPN}^+$ ) gave conductivities in the range  $121\text{--}149 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ , which are close to the lower limit of the reference range given for 2:1 electrolytes; again, ion association and probably the expected low mobility of dianion  $\mathbf{6}$  may account

**Table 4.** Electronic Absorption Data for Compounds  $\mathbf{2}\text{--}\mathbf{8}$  in  $\text{CH}_2\text{Cl}_2$  Solution (ca.  $5 \times 10^{-5}$  M) at 298 K ( $\lambda > 330$  nm)

compd	$\lambda/\text{nm}$ ( $\epsilon/\text{M}^{-1} \text{cm}^{-1}$ )
$(\text{Pr}_4\text{N})_2\mathbf{2a}$	338 (12 500), 435 (sh, 7100), 501 (38 100)
$(\text{Pr}_4\text{N})_2\mathbf{2b}$	337 (28 100), 428 (12 200), 490 (57 600)
$[\text{Pt}(\text{pip})_4]\mathbf{2b}$	408 (6100), 441 (14 100), 471 (30 000)
$(\text{Pr}_4\text{N})_2\mathbf{2c}$	398 (20 500), 492 (46 100)
$\mathbf{3a}$	398 (45 400)
$\mathbf{3b}$	399 (47 800)
$\mathbf{3c}$	396 (30 000)
$\mathbf{4a}$	392 (26 600), 410 (26 900)
$\mathbf{4b}$	391 (31 900), 408 (28 800)
$\mathbf{4c}$	389 (35 500), 405 (30 900)
$\mathbf{5a}$	383 (28 000), 399 (33 100), 532 (10 800)
$\mathbf{5b}$	381 (27 800), 397 (31 400), 543 (10 000)
$\mathbf{5c}$	388 (22 100), 395 (23 500), 531 (8200)
$(\text{Pr}_4\text{N})_2\mathbf{6}^a$	399 (sh), 417
$(\text{PPN})_2\mathbf{6}$	399 (sh, 82 300), 420 (116 400)
$\mathbf{7}$	347 (12 900), 388 (11 300), 509 (2800), 574 (1900)
$\text{Pr}_4\text{N}8$	383 (27 400), 401 (35 600), 534 (15 700)
$\text{DMANH}8$	384 (22 300), 402 (28 800), 535 (11 400)

<sup>a</sup> Accurate concentration and  $\epsilon$  values could not be measured for this compound due to its very low solubility.

for these low values. The molar conductivities of the  $\text{Q}8$  salts [ $97$  ( $\text{Q} = \text{Pr}_4\text{N}^+$ ) and  $95 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$  ( $\text{Q} = \text{DMANH}^+$ )] are in good agreement with the reference values given for 1:1 electrolytes.

**Electronic Absorption Spectra.** The UV–visible absorption spectra of the platinum compounds were measured in the range  $200\text{--}700$  nm in  $\text{CH}_2\text{Cl}_2$  at 298 K. All of them display the bands arising from the fluoren-9-ylidene moiety at around 230, 250, and 300 nm.<sup>26</sup> The absorptions with  $\lambda > 330$  nm are listed in Table 4. The spectra of the dianionic complexes  $\text{Q}_2\mathbf{2a}\text{--}\mathbf{c}$  show medium-intensity bands in the  $330\text{--}340$  and  $400\text{--}430$  nm regions and a very intense band in the range  $490\text{--}501$  nm, the pattern being similar to that observed for the isoelectronic gold(III) complexes  $[\text{Au}\{\text{S}_2\text{C}=\text{C}(\text{C}_{12}\text{H}_6\text{R}_2-2,7)\}_2]^-$  ( $\text{R} = \text{H}$ ,  $t\text{-Bu}$ ,  $\text{OC}_8\text{H}_{17}$ ).<sup>26</sup> The spectra of the phosphine complexes  $\mathbf{3,4a}\text{--}\mathbf{c}$  also display very intense bands above 330 nm; for the  $\text{PPh}_3$  complexes, only one band of triangular shape is observed at around 400 nm, which resolves into two bands for the  $\text{PEt}_3$  analogues at 390 and 410 nm. The intense lowest energy absorption band observed for a number of dianionic bis(1,1-ethylenedithiolato)platinate(II)<sup>8,37</sup> and neutral 1,1-ethylenedithiolatobis(phosphine)-platinum(II)<sup>9,10</sup> complexes has been assigned to a metal-to-ligand charge-transfer (MLCT) transition for which the HOMO is a mixture of metal and dithiolate orbital character and the LUMO is a dithiolate-based  $\pi^*$  orbital. The lowest energy absorptions observed for  $\text{Q}_2\mathbf{2a}\text{--}\mathbf{c}$ ,  $\mathbf{3a}\text{--}\mathbf{c}$ , and  $\mathbf{4a}\text{--}\mathbf{c}$  can be given the same assignment on the basis of structural similarity. Their large molar extinction coefficients are comparable to those of analogous derivatives containing *i*-mnt or ecda ligands<sup>8–10,37</sup> and typical of charge-transfer transitions in 1,1-ethylenedithiolato complexes.<sup>2</sup> The lower energies observed for the MLCT absorptions in the anionic complexes  $\text{Q}_2\mathbf{2a}\text{--}\mathbf{c}$  relative to those in the neutral complexes  $\mathbf{3,4a}\text{--}\mathbf{c}$  are consistent with the expected higher d orbital energies in the anionic systems as compared to the neutral. The variations due to the phosphine ligands in  $\mathbf{3,4a}\text{--}\mathbf{c}$  are

(36) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81–122.

(37) Werden, B. G.; Billig, E.; Gray, H. B. *Inorg. Chem.* **1966**, *5*, 78–81.

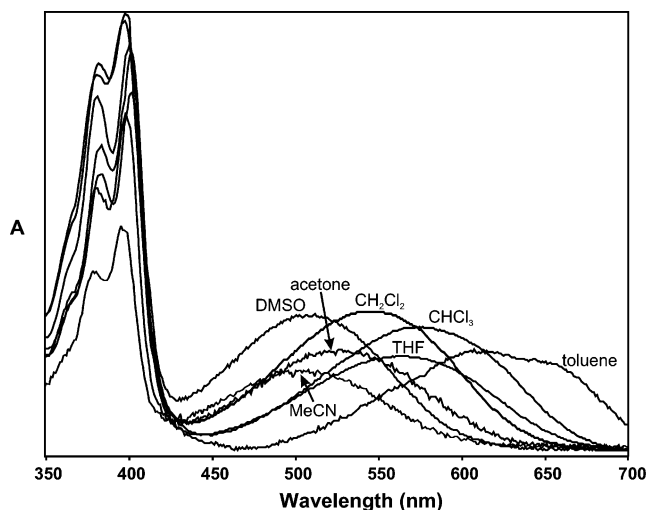
**Table 5.** Lowest Energy Absorption Band for Complexes **5a–c** as a Function of Solvent<sup>a</sup>

solvent	$\lambda_{\text{max}}$ , nm		
	<b>5a</b>	<b>5b</b>	<b>5c</b>
toluene	599	607	596
THF	552	564	553
CHCl <sub>3</sub>	560	572	557
CH <sub>2</sub> Cl <sub>2</sub>	532	543	531
Me <sub>2</sub> CO	512	528	513
dimethyl sulfoxide	494	511	497
MeCN	490	502	495

<sup>a</sup>  $5 \times 10^{-5}$  M.

small, but the lower MLCT energies observed for **4a–c** relative to **3a–c** are attributable to the higher electron-donating character of PEt<sub>3</sub>, which raises the energy of the HOMO.<sup>10</sup> When compared with analogous complexes containing 1,1-ethylenedithiolates with electron-withdrawing groups, the energies of the MLCT transitions in **Q<sub>2</sub>2a–c** and **3,4a–c** are considerably lower. Thus, in the cases of **Q<sub>2</sub>2a–c**, the MLCT band is up to 4250 cm<sup>-1</sup> lower than that of the anionic complexes [Pt(*i*-mnt)<sub>2</sub>]<sup>2-</sup> (413 nm)<sup>37</sup> and [Pt(ecda)<sub>2</sub>]<sup>2-</sup> (424 nm)<sup>8</sup> and only comparable to those found for the closely related (cyclopentadienyliidene)methanedithiolato derivative (516 nm)<sup>23</sup> and dithiolene complexes such as [Pt(mnt)<sub>2</sub>]<sup>2-</sup> (474 nm)<sup>38</sup> and [Pt(qdt)<sub>2</sub>]<sup>2-</sup> (510 nm).<sup>39</sup> Likewise, the MLCT energies observed for the phosphine complexes **3a–c** and **4a–c** are about 3840 or 3080 cm<sup>-1</sup>, respectively, lower than those of [Pt(ecda)(PPh<sub>3</sub>)<sub>2</sub>] (346 nm) and [Pt(ecda)(PCy<sub>3</sub>)<sub>2</sub>] (364 nm) but similar to that of [Pt(mnt)(PPh<sub>3</sub>)<sub>2</sub>] (410 nm).<sup>10</sup> Although the nature of the dithiolato ligands is expected to affect both the HOMO and LUMO energies, the considerably reduced HOMO–LUMO gap in complexes **Q<sub>2</sub>2a–c**, **3a–c**, and **4a–c** with respect to the analogous derivatives with *i*-mnt and ecda is most probably the result of an appreciably higher HOMO energy, due to the strong electron-donating character of the (fluoren-9-ylidene)methanedithiolato ligands.

The spectra of the diimine complexes **5a–c** show three absorption bands above 330 nm. In CH<sub>2</sub>Cl<sub>2</sub> solution, the first two bands are observed at 380 and 400 nm, with little variations along the series, and have high molar extinction coefficients (22 100–33 100 M<sup>-1</sup> cm<sup>-1</sup>), while the third band is very broad, stretching from 420 to 620 nm approximately, and centered at 532 (**5a**), 543 (**5b**), or 531 (**5c**) nm, with molar extinction coefficients of 10 800, 10 000, or 8200 M<sup>-1</sup> cm<sup>-1</sup>, respectively. The higher energy bands are insensitive to solvent variations and most probably arise from electronic transitions within the dithiolato ligand.<sup>23</sup> In contrast, the broad, lowest energy absorption band is strongly solvent-dependent and can be assigned to the Pt(d)/S(p)- $\pi^*$  diimine solvatochromic transition typically observed for Pt(II) diimine dithiolates.<sup>15</sup> The UV–visible spectra of **5a–c** in a variety of organic solvents showed that this band shifts to lower energy as solvent polarity decreases (Table 5; Figure 3). The plots of the lowest absorption energies against the Pt(NN)-(SS) solvent parameter introduced by Cummings and Eisen-

**Figure 3.** Absorption spectra of complex **5b** in solvents of different polarity (absorbance not to scale).

berg<sup>15</sup> gave good linear correlations ( $R^2 > 0.93$ ; see Supporting Information) and yielded solvatochromic shifts of 0.21 (**5a**), 0.23 (**5b**), and 0.22 (**5c**) (in cm<sup>-1</sup> × 10<sup>-3</sup>), which are generally lower than those reported for the solvatochromic transitions of other Pt(II) diimine dithiolates. As is the case for the MLCT transitions observed for **Q<sub>2</sub>2a–c**, **3a–c**, and **4a–c**, the energies of the solvatochromic transition in **5a–c** in CH<sub>2</sub>Cl<sub>2</sub> are much lower than in analogous Pt(II) complexes containing dbbpy and 1,1-ethylenedithiolates with electron-withdrawing functional groups. For example, the solvatochromic absorptions of [Pt-(tbcd)(dbbpy)] (437 nm), [Pt(cpdt)(dbbpy)] (434 nm)<sup>15</sup> (cpdt = 1-diethylphosphonate-1-cyanoethylene-2,2-dithiolate), and [Pt{S<sub>2</sub>C=C(COMe)<sub>2</sub>}(dbbpy)] (452 nm)<sup>14</sup> are about 3300 cm<sup>-1</sup> higher in energy. Only analogous complexes with dithiolenes such as 2,3-toluenedithiolate (tdt, 563 nm) and maleonitriledithiolate (mnt, 497 nm) display a similar energy for this transition. Since the energy of the diimine-based LUMO is not expected to vary significantly with modifications of the dithiolato ligands,<sup>15</sup> the reduced HOMO–LUMO gap in complexes **5a–c** with respect to their analogues tbcd, cpdt, or 2,2-diacetyl-1,1-ethylenedithiolate must be attributed to a considerably higher energy of the mixed metal/dithiolato HOMO.

The salts **Q<sub>2</sub>6** (Q = Pr<sub>4</sub>N<sup>+</sup> and PPN<sup>+</sup>) have almost identical absorption spectra. A very intense absorption is observed at 420 nm, which probably overlaps higher energy bands (weakly pronounced shoulders are observed at 400 and 370 nm). The assignment of this band is uncertain, but its intensity and energy suggest a MLCT transition, as observed for the previously discussed complexes.

The absorptions of the dithiolato complex **7** above 300 nm occur as broad bands centered at 347, 388, 509, and 577 nm and have molar extinction coefficients of  $\epsilon = 12\,900$ , 11 300, 2800, and 1900 M<sup>-1</sup> cm<sup>-1</sup>, respectively. The first two bands are most probably the result of the perturbation of the band observed for the free dithiolate **1b** at 346 nm ( $\epsilon = 12\,000$  M<sup>-1</sup> cm<sup>-1</sup>), which arises from n- $\pi^*$  transitions within the CS<sub>2</sub><sup>-</sup> group.<sup>26</sup> The low intensity and energy of the 509 and 577 nm bands are typical of metal-centered d–d transitions.

(38) Shupack, S. I.; Williams, R.; Gray, H. B.; Billig, E.; Clark, R. J. H. *J. Am. Chem. Soc.* **1964**, *86*, 4594–4602.(39) Cummings, S. D.; Eisenberg, R. *Inorg. Chem.* **1995**, *34*, 2007–2014.



**Table 6.** Excitation and Emission Data for (Pr<sub>4</sub>N)<sub>2</sub>2a–c, 3a–c, and 4a–c in DMF/CH<sub>2</sub>Cl<sub>2</sub>/MeOH (1:1:1 v/v/v) Glasses at 77 K<sup>a</sup>

compd	$\lambda_{\text{exc}}$	$\lambda_{\text{em}}^b$
(Pr <sub>4</sub> N) <sub>2</sub> 2a	454, <i>511</i>	587, 599, 642 <sup>c</sup>
(Pr <sub>4</sub> N) <sub>2</sub> 2b	456, <i>510</i>	589, 602 <sup>c</sup>
(Pr <sub>4</sub> N) <sub>2</sub> 2c	458, <i>507</i>	584, 596, <sup>c</sup> 638 <sup>c</sup>
3a	376, 395, 416	562, 614, 676 <sup>c</sup>
3b	376, 394, 416	567, 618, 681 <sup>c</sup>
3c	373, 416	561, 611, 672 <sup>c</sup>
4a	372, 405, 416	561, 610, 673 <sup>c</sup>
4b	372, 389, 410	561, 612, 674 <sup>c</sup>
4c	372, 391, 414	566, 618, 682 <sup>c</sup>

<sup>a</sup> In nm. The most intense peak is italicized. <sup>b</sup> At the lowest energy excitation maximum. <sup>c</sup> Shoulder.

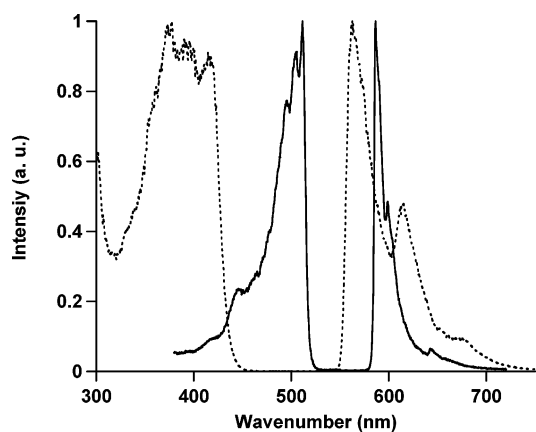
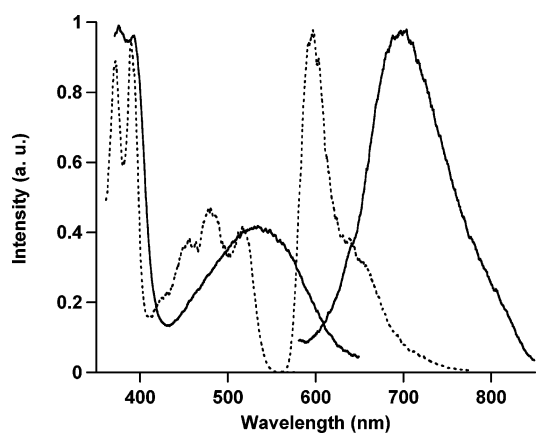
The absorption spectra of Pr<sub>4</sub>N8 and DMANH8 are almost identical in CH<sub>2</sub>Cl<sub>2</sub> solution and show three bands at 380, 400, and 534 nm, which, surprisingly, are very similar in energy, intensity, and shape to those of the diimine derivatives 5a–c. The analogous gold(III) mixed dithiolato/dithioato complexes [Au{S<sub>2</sub>C=C(C<sub>12</sub>H<sub>6</sub>R<sub>2</sub>-2,7)}{S<sub>2</sub>CCH-(C<sub>12</sub>H<sub>6</sub>R<sub>2</sub>-2,7)}] (R = H, *t*-Bu, OC<sub>8</sub>H<sub>17</sub>)<sup>26</sup> give rise to similar absorptions at slightly higher energies. The two higher energy bands are therefore assignable to transitions within the dithiolato ligand. The lowest energy broad band at 534 nm is essentially not solvent-dependent, consistent with little or no change in polarity between the ground and excited states. Its origin is uncertain and can only be tentatively assigned. Since a similar band is not observed in the spectra of the bis(dithiolato) complexes Q<sub>2</sub>2a–c or the dithioato derivative 7, it is clear that its existence requires the presence of both dithiolato and dithioato ligands. Also, the higher energy observed for this band in the analogous gold complexes suggests a transition involving a HOMO of significant metal orbital character. Given that the rest of the dithiolato complexes described here share a common HOMO of mixed metal/dithiolate orbital character, it is reasonable that the transition responsible for this band involves a HOMO of similar orbital nature. The LUMO is possibly a dithioato-based  $\pi^*$  orbital, which is expected to lie at a lower energy than a similar dithiolate  $\pi^*$  orbital,<sup>40</sup> and thus the transition could be described as a particular type of MMLCT.

**Excitation and Emission Spectra.** The compounds (Pr<sub>4</sub>N)<sub>2</sub>2a–c, 3a–c, 4a–c, 5a–c, 7, and Q8 (Q = Pr<sub>4</sub>N<sup>+</sup>, DMANH<sup>+</sup>) are photoluminescent at 77 K, and their excitation and emission spectra have been measured both in the solid state (KBr dispersions) and in DMM (DMF/CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 1:1:1), PrCN glasses, or frozen CH<sub>2</sub>Cl<sub>2</sub> solutions. Room-temperature luminescence in the solid state was observed for all of them, whereas only the diimine complexes 5a–c and the mixed dithiolato/dithioato complex Q8 emit in fluid CH<sub>2</sub>Cl<sub>2</sub> solution at 298 K. The results of the measurements in solution are summarized in Tables 6 and 7, and representative excitation and emission spectra are shown in Figures 4–6. The solid-state excitation and emission data at 298 and 77 K are given in the Supporting Information. No detectable luminescence was observed for the Q<sub>2</sub>6 salts.

**Table 7.** Excitation and Emission Data for 5a–c, 7, and Q8 in Solution<sup>a</sup>

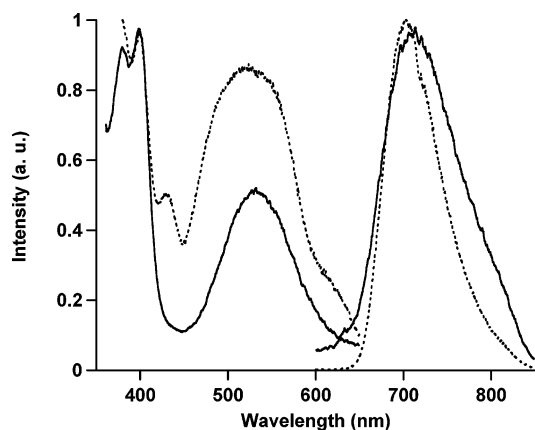
compd	298 K <sup>b</sup>			77 K <sup>c</sup>	
	$\lambda_{\text{exc}}$	$\lambda_{\text{em}}$	$\Phi_{\text{em}}^d$	$\lambda_{\text{exc}}$	$\lambda_{\text{em}}$
5a	380, 398, 537	700	2.0	377, 397, 450, 478, 516	595, 657 <sup>e</sup>
5b	380, 396, 548	711	1.7	377, 397, 457, 490, 524	608, 661 <sup>e</sup>
5c	376, 394, 535	698	2.3	371, 391, 456, 480, 516	626, 652 <sup>e</sup>
7				400, 513, 569	714
Pr <sub>4</sub> N8	378, 398, 530	711	1.5	400, 432, 521	703
DMANH8	381, 400, 534	720	1.4	381, 404, 535	704

<sup>a</sup> In nm. The most intense peak is italicized. Emission spectra are registered at the lowest energy excitation maximum. <sup>b</sup> In CH<sub>2</sub>Cl<sub>2</sub>. <sup>c</sup> In PrCN glass (5a–c) or frozen CH<sub>2</sub>Cl<sub>2</sub> solutions (7, Q8). <sup>d</sup>  $\times 10^4$ . <sup>e</sup> Shoulder.

**Figure 4.** Excitation and emission spectra of (Pr<sub>4</sub>N)<sub>2</sub>2a in CH<sub>2</sub>Cl<sub>2</sub> (—) and 3a in DMM glass at 77 K (···) (normalized intensity).**Figure 5.** Excitation and emission spectra of 5c in CH<sub>2</sub>Cl<sub>2</sub> at 298 K (—) and PrCN glass at 77 K (···) (normalized intensity). Emission spectra are registered at the lowest energy excitation wavelength.

The emission spectra of the dianionic complexes (Pr<sub>4</sub>N)<sub>2</sub>2a–c in DMM glasses at 77 K display a sharp maximum in the range 584–589 nm and less intense shoulders at 600 and 640 nm. When recorded in frozen CH<sub>2</sub>Cl<sub>2</sub> solutions, the spectra are almost identical with those obtained from DMM glasses, but the shoulders resolve as sharp peaks for 2a,c (Figure 4). These peaks could correspond to vibronic progressions, since the spacings (332–375 and 1450–1508 cm<sup>-1</sup>) approximately coincide with the energies found for the  $\nu(\text{Pt-S})$  and  $\nu(\text{C=CS}_2)$  modes in the solid state IR spectra. The corresponding excitation spectra show the absolute maximum at around 510 nm, which relates to the MLCT band observed in the room-temperature absorption

(40) Piovesana, O.; Sestili, L. *Inorg. Chem.* **1979**, *18*, 2126–2129.



**Figure 6.** Excitation and emission spectra of  $\text{Pr}_4\text{N}8$  in  $\text{CH}_2\text{Cl}_2$  at 298 K (—) and 77 K (···) (normalized intensity). Emission spectra are registered at the lowest energy excitation wavelength.

spectra. The solid-state emission spectra display broad maxima that are generally red-shifted with respect to the solution emissions.<sup>41</sup> The phosphine derivatives **3a–c** and **4a–c** give rise to very similar emission spectra in DMM glasses at 77 K, with the absolute maximum at around 560 nm, a less intense peak at 610 nm, and a shoulder at 670 nm. The spacings between these peaks range from 1432 to 1518  $\text{cm}^{-1}$  along the series, approaching in some cases the energy of the  $\nu(\text{C}=\text{CS}_2)$  mode. The excitation spectra collected at any of the emission peaks are identical and show three maxima in the range 372–416 nm, which brackets the wavelength range observed for the MLCT absorptions (Figure 4). The solid-state emission spectra of **3a–c** and **4a–c** undergo only slight variations with respect to the spectra in DMM glass. The luminescence of complexes of the types bis(1,1-ethylenedithiolato)platinate(II)<sup>8</sup> and 1,1-ethylenedithiolatobis(phosphine)platinum(II)<sup>9,10</sup> has been assigned as having the same orbital nature as the MLCT absorptions but originating from a triplet excited state. The above-mentioned excitation and emission data of **Q22a–c**, **3a–c**, and **4a–c** and the relatively large Stokes shifts observed ( $\sim 2600 \text{ cm}^{-1}$  for **Q22a–c**,  $\sim 6500 \text{ cm}^{-1}$  for **3a–c** and **4a–c**) support the same assignment for these complexes. The emission energies of the anionic complexes **Q22a–c** are intermediate between those of the analogous complexes with *i*-mnt (521 nm) and ecda (509 nm) and those of the dithiolene complexes with mnt (712 nm) and qdt (643 nm).<sup>8</sup> The emissions of the phosphine derivatives in solution at 77 K are also lower in energy than those of  $[\text{Pt}(\text{ecda})(\text{PPh}_3)_2]$  (495 nm) and approach the energy observed for  $[\text{Pt}(\text{mnt})(\text{PPh}_3)_2]$  (597 nm).<sup>10</sup> The emission energies of **Q22a–c**, **3a–c**, and **4a–c** are consistent with the low energies of the MLCT absorptions, which have been discussed above.

The diimine complexes **5a–c** are emissive in fluid  $\text{CH}_2\text{Cl}_2$  solution at 298 K, which is typical of platinum diimine dithiolates;<sup>12–14</sup> excitation at the charge-transfer-to-diimine wavelength maximum results in broad emissions that are maximized around 700 nm (Figure 5, Table 7). The corre-

sponding excitation spectra closely reproduce the absorption spectra, with two intense and narrow bands at 380 and 400 nm and a broad and less intense band at 537 (**5a**), 548 (**5b**), or 535 (**5c**) nm, which coincides in energy with the charge-transfer-to-diimine absorption. The room-temperature emission quantum yields are low ( $(1.7\text{--}2.3) \times 10^{-4}$ ) but comparable to those found for other Pt(II) dithiolates containing dbbpy in  $\text{CH}_2\text{Cl}_2$ .<sup>15</sup> The emission energies at 298 K did not vary significantly when the spectra were recorded in PrCN. However, at 77 K in PrCN glass the emission band sharpens and blue-shifts to around 600 nm and a shoulder appears at 660 nm. Comparable blue-shifts on going from fluid  $\text{CH}_2\text{Cl}_2$  solutions to PrCN glasses have been found for other Pt(II) diimine dithiolates and ascribed to a common rigidochromic effect observed for many diimine complexes.<sup>15,42</sup> In all cases, the excitation spectra at 77 K were identical when collected at the emission maximum or at the shoulder wavelength. The two higher intensity peaks at 380 and 400 nm, which correspond to dithiolate-based absorptions, are practically unaltered relative to the room-temperature excitation spectra. However, the band corresponding to the charge-transfer-to-diimine absorption, which is broad at 298 K, shows some structure at 77 K, with three relative maxima. It is also solvent dependent, undergoing the expected blue-shift on going from  $\text{CH}_2\text{Cl}_2$  to the more polar PrCN solvent. Excitation at any of these maxima produced the same emission spectra. The emissions of previously described Pt(II) diimine complexes containing 1,1-ethylenedithiolates have been assigned as originating from multiple emitting states, which include a triplet state with the same orbital parentage as the charge-transfer-to-diimine absorption and a diimine-based  $\pi\text{--}\pi^*$  triplet state.<sup>13,18</sup> The present luminescence data for **5a–c** at 77 K are consistent with an assignment to charge-transfer-to-diimine excited states but do not allow us to precisely establish a mixed origin for their emissions. Also, the relatively large Stokes shifts observed support a triplet multiplicity for the emitting states. The emission energies of **5a–c** are up to  $2900 \text{ cm}^{-1}$  (at 298 K in  $\text{CH}_2\text{Cl}_2$ ) or  $3700 \text{ cm}^{-1}$  (at 77 K in PrCN) lower than those of the analogous *tbcd*, *cpdt*,<sup>15</sup> and 2,2-diacetyl-1,1-ethylenedithiolate<sup>14</sup> derivatives but are similar to the emission energy of the 3,4-toluenedithiolate complex.<sup>15</sup>

The dithioato complex **7** emits at 714 nm in frozen  $\text{CH}_2\text{Cl}_2$  solution at 77 K. The excitation spectrum closely reproduces the absorption profile in the range 380–620 nm. The emission and excitation spectra of this compound in toluene glass at 77 K were identical with those obtained in frozen  $\text{CH}_2\text{Cl}_2$  solution. Luminescence data of related dithioato complexes of platinum are not available for comparison. The possible origins of this emission include charge-transfer to dithioato and metal-centered transitions. The  $\text{Pr}_4\text{N}^+$  and  $\text{DMANH}^+$  salts of the mononuclear mixed dithioato/dithiolato complex **8** are emissive in fluid  $\text{CH}_2\text{Cl}_2$  solution at 298 K when excited at the lowest-energy absorption wavelength (Figure 6). The emission band is broad and maximized at 711 ( $\text{Pr}_4\text{N}^+$ ) or 720 ( $\text{DMANH}^+$ ) nm. The

(41) An emission band is observable at 542 or 544 nm in the solid-state spectra of **2a,c** at room temperature, probably arising from intraligand transitions.

(42) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85–277.

corresponding excitation spectra are almost superimposable on the absorption spectra at 298 K. For the measurements at 77 K, the most suitable solvent was CH<sub>2</sub>Cl<sub>2</sub> because the salts **Q8** underwent partial deprotonation in glass-forming solvents or mixtures such as EtOH/MeOH, PrCN, and DMM and were not soluble in toluene. The emission band in frozen CH<sub>2</sub>Cl<sub>2</sub> solutions is sharper and slightly blue-shifted, and the excitation spectra are similar to those at room-temperature in fluid CH<sub>2</sub>Cl<sub>2</sub> solution. The transition responsible for the emission of **Q8** has probably the same orbital nature as the lowest energy absorption, which we have tentatively assigned to a MMLLCT. Further studies on the luminescence of similar mixed dithiolato/dithioato platinum complexes are underway to confirm this assignment.

## Conclusions

The first series of platinum complexes with (fluoren-9-ylidene)methanedithiolate and its 2,7-di-*tert*-butyl- and 2,7-dimethoxy-substituted analogues has been prepared from chloroplatinum precursors and dithioates **1a–c**. The electronic absorption and emission data of the anionic complexes **2a–c** and the neutral phosphine complexes **3a–c** and **4a–c** are consistent with previous assignments for related 1,1-ethylenedithiolato complexes, which ascribe the lowest energy absorptions and the emissions to charge-transfer transitions involving a HOMO of mixed metal/dithiolate orbital character and a dithiolate-based  $\pi^*$  LUMO. The diimine derivatives **5a–c** display solvatochromic behavior and room-temperature luminescence in fluid solution, which can be ascribed to the charge-transfer-to-diimine transition typically observed for platinum diimine dithiolates. Both the absorption and emission energies of **2a–c**, **3a–c**, **4a–c**, and **5a–c** are generally much lower than those of analogous complexes containing 1,1-ethylenedithiolates with electron-withdrawing functional groups and, in most cases, compare well with those of similar complexes with 1,2-dithiolene ligands. These low energies can be generally attributed to relatively high HOMO energies, which in turn are a consequence of the strong electron-donating character of the (fluoren-9-ylidene)methanedithiolato ligands. The R substituents on the fluoren-9-ylidene moiety do not have a

significant influence on the absorption and emission energies but are decisive for the stability of the oxidation and protonation products of the anionic complexes **2a–c**. Thus, only in the case of the complex **2b**, containing the di-*tert*-butyl-substituted dithiolato ligand, did the oxidation and protonation reactions give products of definite composition. The oxidation of **2b** with [FeCp<sub>2</sub>]PF<sub>6</sub>, FeCl<sub>3</sub> or FeCl<sub>2</sub>/O<sub>2</sub> resulted in the formation of a dinuclear mixed Pt(II)–Pt(IV) dithiolato complex (**6**) for which there is no precedent. The behavior of **2b** toward oxidation contrasts with that of complexes of the type [Pt(1,2-dithiolene)<sub>2</sub>]<sup>2–</sup>, which usually give stable, monomeric platinum(III) complexes.<sup>43</sup> The protonation of both dithiolato ligands in **2b** resulted in the formation of the neutral dinuclear dithioato complex **7**, while by protonating one of the ligands, the monomeric, anionic mixed dithiolato/dithioato complex **8** was obtained. The anion **8** is a new type of species which displays room-temperature luminescence in fluid solution.

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**Supporting Information Available:** <sup>1</sup>H NMR spectra of (Pr<sub>4</sub>N)<sub>2</sub>**6**, <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of (PPN)<sub>2</sub>**6**, mass spectra of (Pr<sub>4</sub>N)<sub>2</sub>**2b**, (Pr<sub>4</sub>N)<sub>2</sub>**6**, **7**, Pr<sub>4</sub>**N8**, and DMANH**8**, plots of the lowest absorption energies of **5a–c** vs the Pt(NN)(SS) solvent parameter, solid-state excitation and emission data for (Pr<sub>4</sub>N)<sub>2</sub>**2b**, **3a–c**, **4a–c**, **5a–c**, **7**, Pr<sub>4</sub>**N8**, and DMANH**8** (KBr dispersions), and crystallographic data in CIF format for **3b**, **5c**·CH<sub>2</sub>Cl<sub>2</sub>, and (Ph<sub>4</sub>P)<sub>2</sub>**6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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