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Inter- and Intramolecular π-Stacking Interactions in *cis*-Bis{1-(9-anthracene)}phosphirane Complexes of Platinum(II)

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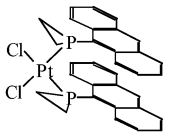
The bis{1-(9-anthracene)phosphirane}dithiolatoplatinum(II) complexes, Pt{1-(9-anthracene)phosphirane}$_2$(dithiolate), where dithiolate = 1,1-dimethoxycarbonyl-ethylene-2,2-dithiolate (dmdt) (**2**), 1,1-diethoxycarbonyl-ethylene-2,2-dithiolate (dedt) (**3**), 1-ethoxycarbonyl-1-cyano-ethylene-2, 2-dithiolate (ecdt) (**4**), and 1,1-dicyano-ethylene-2,2-dithiolate (dcdt) (**5**), were prepared from *cis*-dichlorobis{1-(9-anthracene)phosphirane}platinum(II) (**1**). Complexes **3** and **5** were characterized by X-ray crystallography and were found to have vastly different crystal and molecular structures. The crystal and molecular structure of **3** is dominated by intramolecular π-stacking between the anthracene rings of the *cis*-bis(anthracene)phosphiranes with a ring···ring separation of 3.48(6) Å. The molecular structure of **5** does not exhibit an intramolecular interaction between the anthracene rings. Instead, the crystal structure of **5** shows significant intermolecular π-stacking between the anthracene rings of the phosphirane ligands of adjacent molecules packed in the crystal lattice. The intermolecular stacking interaction results in a ring···ring separation of 3.33(4) Å. Complexes **2**–**5** were found to emit at 530 nm at low temperatures in the solid state. Complex **5** emits strongly in fluid THF or benzene solution at 430 nm.

Introduction

Square-planar complexes of platinum(II) have become important inorganic pharmaceuticals. Since *cisplatin* was discovered by Rosenberg in the 1960s to possess cytotoxic properties,[1,2] thousands of related compounds have been synthesized and studied preclinically.[3−7] DNA intercalation has also been a subject of intense study as it is widely believed to be essential for the activity of many drugs and antibiotics.[8] Ethidium bromide[9] and thiozole orange[10] show strong affinities for double-stranded DNAs, and have been particularly well-studied. The complex *cis*-dichlorobis{1-(9-anthracene)phosphirane}platinum(II) (**1**) was recently pre-



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pared in our laboratories.[11] The structure of **1** contains both a *cis*-$PtCl_2$ unit and a cleft formed by the anthracene rings of two 1-(9-anthracene)phosphirane ligands stacked parallel to each other. Anthracenylphosphines have been available for several years from the work of Schmutzler;[12] however,

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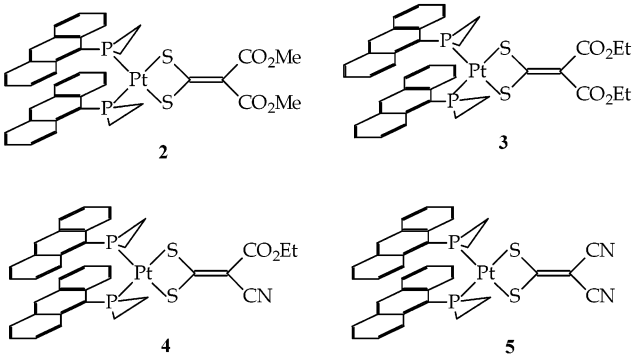
the type of intramolecular π-stacking found in **1** has not been observed previously.

In particular, we were intrigued by the fact that the two anthracene rings form a parallel stacked assembly of two anthracene rings separated by 3.4 Å, essentially the same distance as that between adjacent base pairs in the crystal structures of double-stranded DNA oligomers. Anthracene is also a strong $\pi-\pi^*$ emitter, with a quantum yield and lifetime that are quite sensitive to the local environment. In principle, the emission from the anthracene chromophores in the complex could be used to signal local environmental effects, possibly including the degree and type of metal complex−DNA binding. Here we describe synthetic and structural studies of new 1-(9-anthracene)phosphirane complexes of platinum(II). We also describe our preliminary studies of human tumor cytotoxicity of these compounds as well as their luminescence properties.

Results and Discussion

Synthesis of Platinum Bisphosphirane Dithiolate Complexes. A series of platinum bisphosphirane dithiolates (**2**−**5**) were synthesized by reacting *cis*-dichlorobis{1-(9-anthracene)phosphirane}platinum(II) (**1**) with the corresponding potassium dithiolates.



All complexes were characterized by $^{31}P\{^1H\}$ NMR, IR, Plasma Desorption Mass Spectrometry (PDMS), and microanalysis. Complexes **3** and **5** were characterized by X-ray crystallography. While the solubility of complex **1** is poor in most organic solvents, complexation with the dithiolates greatly increases the solubility of **2**−**5**, especially in polar organic solvents. In addition, these complexes are quite stable to air and moisture. Preparative TLC purification can be performed without special precautions. The $^{31}P\{^1H\}$ NMR of all the platinum bisphosphirane dithiolates **2**−**5** show characteristic $^{195}Pt-^{31}P$ couplings. Of these, the $^{31}P\{^1H\}$ NMR spectrum of bis{1-(9-anthracene)phosphirane}{1-ethoxycarbonyl-1-cyano-ethylene-2,2-dithiolate}platinum(II) (**4**) is the most complicated due to the unsymmetrical nature of the ecdt ligand. In this case, the $^1J_{(Pt-P)}$ coupling constants between the ^{195}Pt and the two chemically inequivalent phosphorus atoms are different, 3282 and 3487 Hz. The $^2J_{(PA-PB)}$ coupling constant between the two *cis*-phosphorus nuclei of **4** is small, 23.6 Hz, and consistent with the square-planar structure of the complex.[13]

Table 1. Crystal Data and Data Collection Parameters for $Pt(PC_{16}H_{13})_2(S_2C_8H_{10}O_4)$ (**3**) and $Pt(PC_{16}H_{13})_2(S_2C_4N_2)$ (**5**)

chem formula	$PtS_2P_2O_4C_{40}H_{36}$	$PtS_2P_2N_2C_{36}H_{26}$
fw	901.9	807.79
space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
a, Å	17.3638(18)	9.3043(18)
b, Å	11.654(3)	12.6638(16)
c, Å	19.651(4)	14.8719(19)
α, deg		67.233(10)
β, deg	114.393(13)	85.728(13)
γ, deg		77.769(13)
V, Å^3	3622(3)	1579.1(5)
Z	4	2
ρ_{calc}, g cm^{-3}	1.654	1.702
T, K	296	296
μ, mm^{-1}	41.51	47.51
λ, Å	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)
$R(F_o)^a$	0.033	0.024
$Rw(F_o)^b$	0.039	0.029

^{a} $R = \sum|F_o - F_c|/\sum F_o$. ^{b} $Rw = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}$, where $w = 4F_o^2/\sigma^2(F_o^2)$ and $\sigma^2(F_o^2) = [S^2(C + R^2B) + (pF_o^2)^2]/LP^2$. Here S is the scan rate, C is the total integrated peak count, R is the ratio of scan time to background counting time, B is the total background count, LP is the Lorentz−Polarization factor, and $p = 0.040$.

The $^1J_{(Pt-P)}$ coupling constant for the dichloride complex **1** (4133 Hz) is significantly larger than those for the dithiolate complexes **2**−**5** (3282−3508 Hz). The $^1J_{(Pt-P)}$ coupling constants can be rationalized by invoking the "push−pull" mechanism.[14] Chloride is not as strong a σ-donor as an alkanethiolate. As a consequence, the phosphirane phosphorus atom tends to donate more σ-electron density to the platinum center, such that the P−Pt bond gains s-character in the dichloride complex relative to the dithiolate case. The increased s-character results in higher $^1J_{(Pt-P)}$ coupling constants in **1** compared to **2**−**5**. Within the dithiolate complexes, the electron-withdrawing ability of the dithiolate substituents has the following order: −CN (**5**) > $-CO_2Me$ (**2**) ∼ $-CO_2Et$ (**3**). Thus, the compensatory σ donation from the phosphirane phosphorus atoms to platinum increases from complex **2** to **5**, and the Pt−P bond s-character and $^1J_{(Pt-P)}$ coupling constants follow that trend.

Crystal and Molecular Structure of Bis{1-(9-anthracene)phosphirane}{1,1-diethoxycarbonyl-ethylene-2,2-dithiolate}platinum(II) (3). The molecular structure of complex **3** exhibits intramolecular anthracene ring π-stacking quite similar to that first observed in complex **1**.[11] X-ray data and collection parameters for **3** are given in Table 1. Bond distances and angles appear in Table 2. An ORTEP drawing of the complex is presented in Figure 1. A notable difference between the structures of **1** and **3** is the relatively narrow S(31)−Pt−S(32) bond angle, 74.29(5)°, in the chelated dithiolate complex **3**, compared to the unconstrained Cl−Pt−Cl bond angle, 86.7(2)°, found in **1**. This, however, does not have a pronounced effect on the P−Pt−P angles, which are 100.90(5)° (**3**) and 99.62(14) (**1**). Within the phosphirane rings, the C−C−P angles, 65.3(4)−65.9(3)°, and C−P−C angles, 48.6(2)−49.3(3)°, attest to a high degree of ring strain. These metrical parameters agree within experimental error with those previously reported for complex **1**. The

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Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for $Pt(PC_{16}H_{13})_2(S_2C_8H_{10}O_4)$ (**3**)[a]

Bond Distances

atom 1−atom 2	distance	atom 1−atom 2	distance
Pt−S(31)	2.3290(14)	P(2)−C(21)	1.813(5)
Pt−S(32)	2.3190(13)	P(2)−C(215)	1.809(5)
Pt−P(1)	2.2612(13)	P(2)−C(216)	1.814(5)
Pt−P(2)	2.2645(13)	C(30)−C(31)	1.355(7)
S(31)−C(30)	1.754(5)	C(31)−C(32)	1.468(7)
S(32)−C(30)	1.752(5)	C(31)−C(36)	1.461(7)
P(1)−C(11)	1.821(5)	C(115)−C(116)	1.511(11)
P(1)−C(115)	1.812(6)	C(215)−C(216)	1.490(8)
P(1)−C(116)	1.813(6)		

Bond Angles

atom 1−atom 2−atom 3	angle	atom 1−atom 2−atom 3	angle
S(31)−Pt−S(32)	74.29(5)	C(21)−P(2)−C(215)	104.8(2)
S(31)−Pt−P(1)	93.66(5)	C(21)−P(2)−C(216)	105.6(2)
S(31)−Pt−P(2)	165.42(5)	C(215)−P(2)−C(216)	48.6 (2)
S(32)−Pt−P(1)	167.76(5)	S(31)−C(30)−S(32)	106.4(3)
S(32)−Pt−P(2)	91.19(5)	S(31)−C(30)−C(31)	126.4(4)
P(1)−Pt−P(2)	100.90(5)	S(32)−C(30)−C(31)	127.3(4)
Pt−S(31)−C(30)	89.33(18)	Pt−P(2)−C(21)	131.69(16)
Pt−S(32)−C(30)	89.71(17)	Pt−P(2)−C(215)	118.04(18)
Pt−P(1)−C(11)	126.73(17)	Pt−P(2)−C(216)	118.96(18)
Pt−P(1)−C(115)	119.7(2)	P(1)−C(115)−C(116)	65.4(4)
Pt−P(1)−C(116)	120.2(2)	P(1)−C(116)−C(115)	65.3(4)
C(11)−P(1)−C(115)	108.3(3)	P(2)−C(215)−C(216)	65.9(3)
C(11)−P(1)−C(116)	107.9(3)	P(2)−C(216)−C(215)	65.6(3)
C(115)−P(1)−C(116)	49.3(3)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

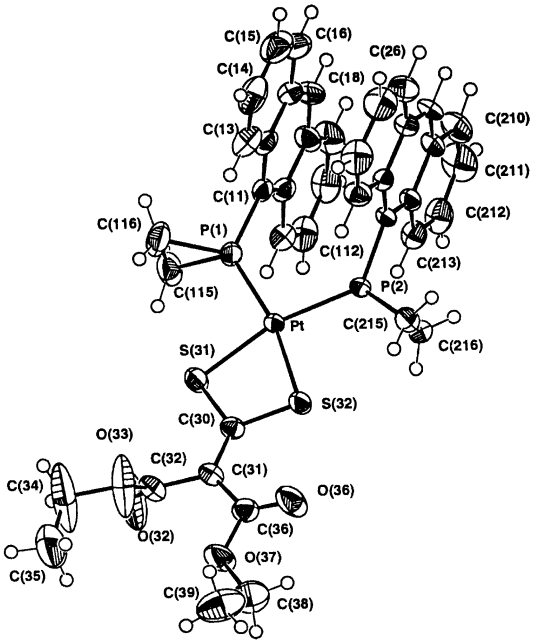

Figure 1. ORTEP diagram of the molecular structure of $Pt(PC_{16}H_{13})_2(S_2C_8H_{10}O_4)$ (**3**) with thermal ellipsoids that represent 50% probability. Hydrogen atoms are included at calculated positions with fixed thermal parameters.

crystal structure of **3** reveals the dominant intramolecular anthracene ring packing, with the anthracene rings nearly parallel to the **b**−**c** plane. The strong intramolecular interactions contrast with a loose intermolecular packing, which involves mostly nonbonding interactions between the phosphirane ring carbons and carboethoxy groups of the dithiolate ligands of adjacent molecules. The separation between least-squares planes defined by the two intramolecularly stacked anthracene rings is 3.48(6) Å.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for $Pt(PC_{16}H_{13})_2(S_2C_4N_2)$ (**5**)[a]

Bond Distances

atom 1−atom 2	distance	atom 1−atom 2	distance
Pt−S(31)	2.3351(10)	P(2)−C(215)	1.811(5)
Pt−S(32)	2.3404(10)	P(2)−C(216)	1.806(4)
Pt−P(1)	2.2591(10)	N(32)−C(32)	1.151(6)
Pt−P(2)	2.2644(10)	N(33)−C(33)	1.142(6)
S(31)−C(30)	1.736(4)	C(30)−C(31)	1.375(5)
S(32)−C(30)	1.720(4)	C(31)−C(32)	1.417(6)
P(1)−C(11)	1.804(4)	C(31)−C(33)	1.420(6)
P(1)−C(115)	1.809(4)	C(115)−C(116)	1.510(7)
P(1)−C(116)	1.813(5)	C(215)−C(216)	1.494(8)
P(2)−C(21)	1.807(4)		

Bond Angles

atom 1−atom 2−atom 3	angle	atom 1−ato m 2−atom 3	angle
S(31)−Pt−S(32)	74.56(4)	Pt−P(2)−C(216)	131.58(16)
S(31)−Pt−P(1)	167.34(3)	C(21)−P(2)−C(215)	106.7(2)
S(31)−Pt−P(2)	92.28(4)	C(21)−P(2)−C(216)	106.4(2)
S(32)−Pt−P(1)	92.84(4)	C(215)−P(2)−C(216)	48.8(3)
S(32)−Pt−P(2)	166.64(4)	S(31)−C(30)−S(32)	110.1(2)
P(1)−Pt−P(2)	100.26(4)	S(31)−C(30)−C(31)	124.1(3)
Pt−S(31)−C(30)	87.43(13)	S(32)−C(30)−C(31)	125.8(3)
Pt−S(32)−C(30)	87.65(14)	N(32)−C(32)−C(31)	179.6(9)
Pt−P(1)−C(11)	126.36(13)	N(33)−C(33)−C(31)	177.1(5)
Pt−P(1)−C(115)	119.94(15)	P(1)−C(115)−C(116)	65.5(2)
Pt−P(1)−C(116)	121.10(15)	P(1)−C(116)−C(115)	65.5(2)
C(11)−P(1)−C(115)	106.77(19)	P(2)−C(215)−C(216)	65.4(3)
C(11)−P(1)−C(116)	108.65(19)	P(2)−C(216)−C(215)	65.8(3)
C(115)−P(1)−C(116)	49.3(2)		
Pt−P(2)−C(21)	117.10(13)		
Pt−P(2)−C(215)	127.92(16)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Crystal and Molecular Structure of Bis{1-(9-anthracene)Phosphirane}{1,1-dicyano-ethylene-2,2-dithiolate}-platinum(II) (5). The molecular structure of **5** reveals none of the intramolecular anthracene π-stacking evident in the structures of complexes **1** and **3**. The structure does reveal that one anthracene phosphirane ligand has rotated by 180° away from the other, completely breaking the intramolecular stacking arrangement. X-ray data and collection parameters are given in Table 1. Bond distances and angles appear in Table 3. An ORTEP drawing of the complex is presented in Figure 2. The coordination geometry about the platinum centers in **3** and **5** is similar. The Pt−P and Pt−S bond lengths in the two structures as well as the P−Pt−P and S−Pt−S bond angles agree within experimental error. The origin of the dramatic difference between the intramolecular stacked structures of **1** and **3** and the open structure of **5** can be seen in the unit cell packing diagram, Figure 3. Here significant intermolecular π-stacking of the anthracene rings of adjacent molecules is clearly evident. The closest anthracene ring approach in the intermolecular stacking arrangement occurs between the ring defined by carbon atoms C11−C114 and the equivalent ring, related by a crystallographic inversion center, on an adjacent molecule in the unit cell. One possible explanation for the shift from intra- to intermolecular anthracene ring stacking is that the more open Cl−Pt−Cl bond angle prevents the two intramolecular stacked anthracene rings from moving away from each other

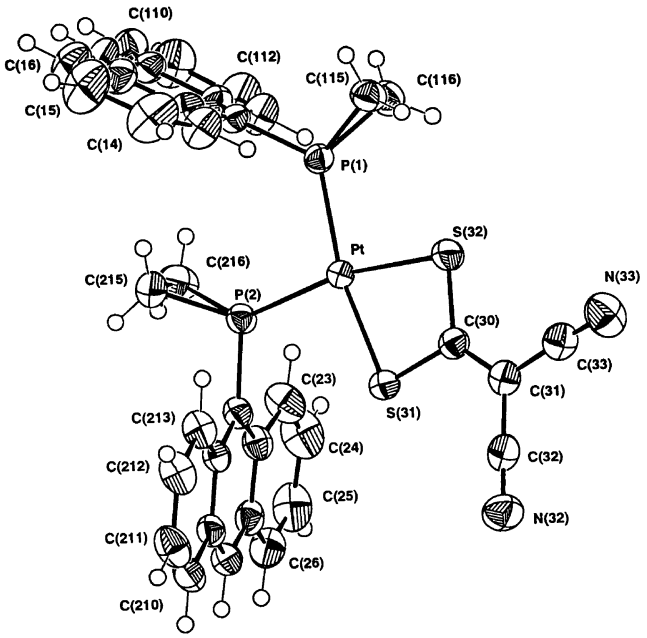

Figure 2. ORTEP diagram of the molecular structure of $Pt(PC_{16}H_{13})_2(S_2C_4N_2)$ (**5**). Thermal ellipsoids represent 50% probability. Hydrogen atoms are included at calculated positions with fixed thermal parameters.

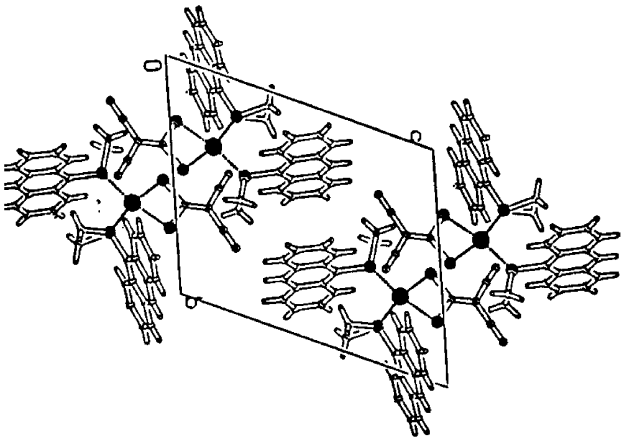

Figure 3. Unit cell packing diagram for $Pt(PC_{16}H_{13})_2(S_2C_4N_2)$ (**5**). The intermolecular stacking occurs between molecules related by an inversion center.

and toward the intermolecular stacked arrangement in the crystal packing. This explanation fails to account for the sharp differences in the structures of **3** and **5**, which have similar S−Pt−S angles. Instead, it appears to be the bulk of the ancillary groups of the dithiolate ligands that are coming into play. The smaller cyano group of the dcdt ligand may allow the anthracene rings of adjacent complexes to move relatively more freely toward intermolecular π-stacking, while the bulkier carboethoxy groups of the dedt ligand prevent close intermolecular approaches and leave intramolecular π-stacking as the only option. Nonetheless, the large structural differences between **1** and **3**, on one hand, and **5**, on the other, for rather similar ligand sets suggests that the overall energy differences between inter- vs intramolecular π-stacking must be small. It is noteworthy that the relative strength of the π-interaction must be significant relative to all other interactions, since it can be realized through either inter- or intramolecular stacking.

Emission Properties of Platinum Complexes. All of the platinum bisphosphirane dithiolate complexes **2**−**5** reported here emit at low temperature in the solid state. Solid samples were placed in small vials and the vials were inserted into a liquid nitrogen dewar for a short period. Short-wavelength UV was then used to irradiate the samples. All samples showed a strong green emission. Complex **5** shows the brightest emission. In all cases, the emission occurs at ca. 530 nm, and is likely metal-to-ligand charge transfer (MLCT) in origin, similar to that reported by Eisenberg and coworkers.[15−17] The emission spectrum of bis{1-(9-anthracene)-phosphirane}{1,1-dicyano-ethylene-2,2-dithiolate}platinum-(II) (**5**) was measured at room temperature in THF solution. Emission at 450 nm was produced via excitation at 420 nm. This is rare for a square-planar platinum diphosphine dithiolate complex. The blue emission and very small Stokes shift is likely ligand-based emission of the anthracene rings, as it is similar to that observed for the free 1-(9-anthracene)-phosphirane ligand and anthracene itself.[18] More detailed studies of the photochemistry and photophysics of these complexes will be the subject of future studies.

Human Tumor Cytotoxicity Studies. In view of the presence of potentially intercalating anthracene rings held in a parallel stacked arrangement at a distance of 3.4 Å, well matched to the separation of adjacent base pairs in DNA, the biological activity of **1**−**5** was assayed. The human tumor cytotoxicity assay is a quick colorimetric assay used to screen possible antitumorigenic agents against a variety of established human tumor cell lines in vitro. The cytotoxicity of complex **1**−**5** was tested for six common human tumor cell lines: A-549 (lung carcinoma); MCF-7 (breast carcinoma); HT-29 (colon adenocarcinoma); A-498 (kidney carcinoma); PC-3 (prostate adenocarcinoma); and PACA-2 (pancreatic carcinoma). Adriamycin was included as a positive control. After two-week trial periods, none of these complexes showed active cytotoxicity. It appears that the relatively large hydrophobic organic ligands used to form these complexes contribute to low solubilities in the aqueous media required for cytotoxicity studies. Complexes related to those described here, but with ligands designed to impart greater solubility, may be promising for future work.

Conclusions

The bis{1-(9-anthracene)phosphirane}dithiolateplatinum-(II) complexes **2**−**5** display a delicate balance between adopting intra- or intermolecular anthracene ring stacked structures. Very modest modifications of the substituents of the dithiolate ligands appear to be sufficient to direct the anthracene ring stacking toward either the intra- or intermolecular stacked arrangement. Although these complexes possess functionality known to be involved in DNA intereactions, no evidence of significant interactions with DNA has been identified to date.

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Experimental Section

General. All reactions and manipulations were carried out under a nitrogen atmosphere with a nitrogen-filled drybox (Vacuum Atmospheres) or standard Schlenk line techniques. K_2PtCl_4 was obtained on loan from Johnson-Matthey. Anhydrous methanol was purchased from Aldrich Chemical Co. and used without further purification. Other solvents were degassed and purified by distillation under nitrogen from the appropriate drying agents (calcium hydride for methylene chloride and acetonitrile, sodium metal for toluene). Deuterated NMR solvents were purchased from Cambridge Isotope Labs.

^{1}H and ^{31}P{^{1}H} NMR spectra were recorded on a QE-300 spectrometer at 300.6 and 121.4 MHz. Chemical shifts were reported in ppm. ^{1}H NMR spectra were referenced to external TMS via residue solvent peaks. ^{31}P{^{1}H} NMR spectra were referenced to external 85% H_3PO_4. Infrared spectra were recorded on a Perkin-Elmer 1710 FTIR spectrophotometer with a 1700/PC Data Station. Plasma desorption mass spectra (PDMS) were obtained on a Bioion 20R plasma desorption mass spectrometer. A solution of the analyte was electrosprayed onto the nitrocellulose-coated Mylar target, which was immediately inserted into the mass spectrometer. Data were collected for 30 min at an acceleration potential of 17 000 V. Emission spectra were recorded on a PTI Ls-100 Luminescence System.

trans-Bis(benzonitrile)dichloroplatinum(II),[19] dmdt (potassium-1,1-dimethoxycarbonyl-ethylene-2,2-dithiolate), dedt (potassium-1,1-diethoxycarbonyl-ethylene-2, 2-dithiolate), ecdt (potassium-1-ethoxycarbonyl-1-cyano-ethylene-2,2-dithiolate), dcdt (potassium-1,1-dicyano-ethylene-2,2-dithiolate),[20] and 1-(9-anthracene)-phosphirane[11] were prepared by published literature procedures.

Synthesis of *cis*-Dichlorobis{1-(9-anthracene)phosphirane}-dicholoroplatinum(II) (1). Complex **1** was prepared by our previously published procedure,[11] or more conveniently starting from *trans*-bis(benzonitrile)dichloroplatinum(II)[19] as follows. A 2-mL methylene chloride solution of 21.0 mg (0.044 mmol) of pure *trans*-bis(benzonitrile)dichloroplatinum(II) was added to a 2-mL methylene chloride solution containing 23.1 mg (0.098 mmol) of 1-(9-anthracene)phosphirane. The yellow solution was then stirred at ambient temperature. Precipitate started to form in 1 h. After an additional 5 h, the solution was taken to dryness under vacuum. The residue was washed with diethyl ether and recrystallized from methylene chloride and diethyl ether to give a yellow microcrystalline solid (**1**), spectroscopically identical with material reported earlier.[11] ^{31}P{^{1}H} NMR (CD_2Cl_2) δ −180.6 {d, $^1J_{(Pt-P)}$ = 4133 Hz}. ^{1}H NMR (CD_2Cl_2) δ 1.26 (m, 2H, P(CH_2)), 2.20 (td, 2H, P(CH_2)), 7.09 (t, 4H), 7.25 (t, 4H), 7.44 (d, 4H), 7.61(s, 2H), 8.20 (d, 4H). IR (KBr) ν(small ring C−H) 3045 (m). PDMS (*m*/*z*) 738.

Synthesis of Bis{1-(9-anthracene)phosphirane}{1,1-dimethoxycarbonyl-ethylene-2,2-dithiolate}platinum(II) (2). The complex *cis*-dichlorobis{1-(9-anthracene)phosphirane}platinum(II) (**1**) (36.9 mg, 0.05 mmol) was partially dissolved in 5 mL of methylene chloride. Two equivalents of dmdt (potassium-1,1-dimethoxycarbonyl-ethylene-2, 2-dithiolate) (17.1 mg, 0.06 mmol) in 1 mL of methanol was then added dropwise to the solution. The reaction mixture was stirred at ambient temperature overnight and then taken to dryness. The residue was extracted with methylene chloride and the methylene chloride solution was dried in vacuo to give a yellow powder. Recrystallization from methylene chloride and ethanol gave yellow needles of bis{1-(9-anthracene)phosphirane}{1,1-dimethoxycarbonyl-ethylene-2,2-dithiolate}platinum(II) (**2**): 39.5 mg, 91%. ^{31}P{^{1}H} NMR ($CDCl_3$) δ −183.5 (d, $^1J_{(Pt-P)}$ = 3303 Hz). ^{1}H NMR ($CDCl_3$) δ 1.26 (td, 2H, P(CH_2)), 2.23 (td, 2H, P(CH_2)), 3.83 (s, 6H), 7.03 (t, 4H), 7.23 (t, 4H), 7.48 (d, 4H), 7.62 (s, 2H), 8.21 (d, 4H). IR (KBr) ν(small ring C−H) 3045 (m); ν(C−H) 2943 (m); ν(C═O) 1719 (s), 1688 (s); ν(C═CS_2) 1492 (s), 1010(s). PDMS (*m*/*z*) 873. Anal. Calcd for $C_{38}H_{32}O_4P_2S_2Pt$: C, 52.23; H, 3.69. Found: C, 51.95; H, 3.66.

Bis{1-(9-anthracene)phosphirane}{1,1-diethoxycarbonyl-ethylene-2,2-dithiolate}platinum(II) (3). This complex was prepared in a manner analogous to that described above for complex **2**, but with the dithiolate dedt (potassium-1,1-diethoxycarbonyl-ethylene-2,2-dithiolate). Bis{1-(9-anthracene)phosphirane}{1,1-diethoxycarbonyl-ethylene-2,2-dithiolate}platinum(II) (**3**): yield, 93% (yellow needles). ^{31}P{^{1}H} NMR ($CDCl_3$) δ −183.3 (d, $^1J_{(Pt-P)}$ = 3293 Hz). ^{1}H NMR ($CDCl_3$) δ 1.21 (td, 2H, P(CH_2)), 2.19 (td, 2H, P(CH_2)), 1.33 (t, 6H, CH_3), 4.30 (q, 4H, CH_2), 7.04 (dd, 4H), 7.23 (t, 4H), 7.48 (d, 4H), 7.64 (s, 2H), 8.21 (d, 4H). IR (KBr) ν(small ring C−H) 3048 (w); ν(C−H) 2981 (m); ν(C═O) 1713 (s), 1679 (s); ν(C═CS_2) 1496 (s), 1081 (s). PDMS (*m*/*z*) 902. Anal. Calcd for $C_{40}H_{36}O_4P_2S_2Pt$: C, 53.27; H, 4.02. Found: C, 52.88; H, 3.93.

Bis{1-(9-anthracene)phosphirane}{1-ethoxycarbonyl-1-cyano-ethylene-2,2-dithiolate}platinum(II) (4). This complex was prepared in a manner analogous to that described above for complex **2**, but with the dithiolate ecdt (potassium-1-ethoxycarbonyl-1-cyano-ethylene-2,2-dithiolate). Bis{1-(9-anthracene) phosphirane}{1-ethoxycarbonyl-1-cyano-ethylene-2,2-dithiolate}platinum(II) (**4**): yield, 86% (yellow disks). ^{31}P{^{1}H} NMR ($CDCl_3$) δ −184.7 (d, $^1J_{(Pt-P)}$ = 3282.2 Hz, $^2J_{P-P}$ = 23.6 Hz), −182.9 (d, $^1J_{(Pt-P)}$ = 3486.9 Hz, $^2J_{P-P}$ = 23.6 Hz). ^{1}H NMR ($CDCl_3$) δ 1.30 (td, 2H, P(CH_2)), 2.20 (m, 2H, P(CH_2)), 1.36 (t, 3H, CH_3), 4.30 (q, 2H, CH_2), 7.04 (dd, 4H), 7.23 (t, 4H), 7.48 (d, 4H), 7.64 (s, 2H), 8.21 (d, 4H). IR (KBr) ν(small ring C−H) 3050 (w); ν(C−H) 2983 (m); ν(CN) 2206 (s); ν(C═O) 1693 (vs), 1679 (s); ν(C═CS2) 1465 (s), 911 (s). PDMS (*m*/*z*) 902. Anal. Calcd for $C_{38}H_{31}O_2NP_2S_2Pt$: C, 53.39; H, 3.66. Found: C, 53.26; H, 3.59.

Bis{1-(9-anthracene)phosphirane}{1,1-dicyano-ethylene-2,2-dithiolate}platinum(II) (5). This complex was prepared in a manner analogous to that described above for complex **2**, but with the dithiolate dcdt (potassium-1,1-dicyano-ethylene-2,2-dithiolate). Bis{1-(9-anthracene)phosphirane}{1,1-dicyano-ethylene-2,2-dithiolate}platinum(II) (**5**): yield, 94% (yellow needles). ^{31}P{^{1}H} NMR ($CDCl_3$) δ −183.7 (d, $^1J_{(Pt-P)}$ = 3508.0 Hz). ^{1}H NMR ($CDCl_3$) δ 1.39 (m, 2H, P(CH_2)), 2.16 (m, 2H, P(CH_2)), 7.10 (t, 4H), 7.28 (t, 4H), 7.54 (d, 4H), 7.73 (s, 2H), 8.17 (d, 4H). IR (KBr) ν(small ring C−H) 3046 (w); ν(C−H) 2991 (m); ν(CN) 2210 (vs); ν(C═CS2) 1455 (vs), 912 (s), 891 (s). PDMS (*m*/*z*) 807.4. Anal. Calcd for $C_{36}H_{26}N_2P_2S_2Pt$: C, 53.53; H, 3.24. Found: C, 53.42; H, 3.09.

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Supporting Information Available: A description of experimental procedures, tables of crystal data, atomic positional and thermal parameters, bond distances and angles, and unit cell packing diagrams for **3** and **5**, as well as crystallographic CIF data. This material is available free of charge via the Internet at http://pubs.acs.org.

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