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The ^{195}Pt NMR of L_2Pt(1,2-dithiolene) Complexes

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The syntheses and characterizations of the novel platinum(II) mono-1,2-dithiolenes (COD)Pt(dddt) (**1**), $(Ph_3P)_2$Pt(dddt) (**2**), (COD)Pt(edt) (**3**), $(Ph_3P)_2$Pt(edt) (**4**), (bipy)Pt(edt) (**5**), and (Ph_3P)(CO)Pt(dddt) (**6**) (COD = 1,5-cyclooctadiene; dddt = 5,6-dihydro-1,4-dithiin-2,3-dithiolate; edt = ethylene-1,2-dithiolate, bipy = 2,2′-bipyridyl) are reported. ^{195}Pt NMR spectral analysis was performed on the above-mentioned compounds along with the previously reported compounds (COD)Pt(dmid) (**7**), $(Ph_3P)_2$Pt(dmid) (**8**), $(Ph_3P)_2$Pt(dmit) (**9**), (COD)Pt(mnt) (**10**), $(Ph_3P)_2$Pt(mnt) (**11**), (COD)Pt(dt) (**12**), and $(Ph_3P)_2$Pt(dt) (**13**) (dmid = 1,3-dithiole-2-oxo-4,5-dithiolate; dmit = 1,3-dithiole-2-thione-4,5-dithiolate; mnt = maleonitrile-1,2-dithiolate; dt = ethane-1,2-dithiolate). ^{195}Pt NMR results show that, depending on the nature of L_2 in L_2Pt(1,2-dithiolene) complexes, the 1,2-dithiolene ligands behave as either π donors or acceptors toward the Pt metal center. ^{195}Pt NMR is also sensitive to the relative electron-withdrawing ability of the substituents on the 1,2-dithiolene backbone which results in an ordering of chemical shifts into a series independent of L_2. Support is also provided by electrochemistry, UV−vis spectroscopy, and ^{13}C NMR. X-ray structural analysis results are given for **1**, monoclinic, $P2_1/a$, $a = 10.2420(10)$ Å, $b = 10.7510(10)$ Å, $c = 13.2890(20)$ Å, $\beta = 102.870(10)$, $Z = 4$, and for **5**, monoclinic, $I2/a$, $a = 7.2294(2)$ Å, $b = 11.4574(4)$ Å, $c = 14.9103(6)$ Å, $\beta = 89.380(15)$, $Z = 4$.

Introduction

Over the past two decades there has been considerable interest in transition metal complexes of 1,2-dithiolene ligands. This interest stems from the isolobal analogy between metal dithiolene fragments and tetrathiafulvalene (TTF).[1] Charge-transfer salts of TTF and bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) have exhibited metallic and superconducting properties at low temperatures.[2] To date, only modest success has been achieved at using transition metal bis-dithiolenes to prepare electronic conductors.[3] Recently, synthetic efforts have been extended to include dimeric and oligomeric transition metal complexes bridged by 1,2-dithiolene ligands. Among the most interesting of these are tetrathiafulvalene tetrathiolate,[4−9] the first bridging ligand containing a TTF moiety and $C_2S_4^{n-}$, the simplest bridging 1,2-dithiolene ligand (Figure 1).[1,10−16]

To develop polymeric precursors to 1,2-dithiolene bridged transition metal complexes, we have chosen to investigate Pt(II) compounds which contain a single 1,2-dithiolene ligand. Platinum was chosen in order to minimize mixtures of products resulting from ligand exchange, due to slow kinetics for these reactions. In an effort to find an effective spectroscopic probe of the electronic properties of Pt(II) complexes containing 1,2-dithiolene ligands, a study of the ^{195}Pt NMR spectra of a number of these compounds was carried out.

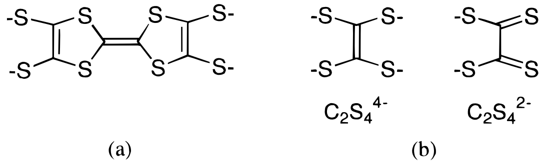

Figure 1. Tetrathiafulvalene tetrathiolate (a) and $C_2S_4^{n-}$ (b).

^{195}Pt with a spin $s = {}^1/_2$ is a nucleus well suited for NMR studies. Its natural abundance (33.8%), combined with its relatively large magnetic moment, $\mu = 1.0398$ (μ/μ_B), gives it a receptivity 19 times that of ^{13}C.[17] Chemical shifts occur over a range of about 15 000 ppm and are generally reported referenced to Na_2PtCl_6 in D_2O. Chemical shifts are usually dependent upon the oxidation state of the metal, with shifts lying

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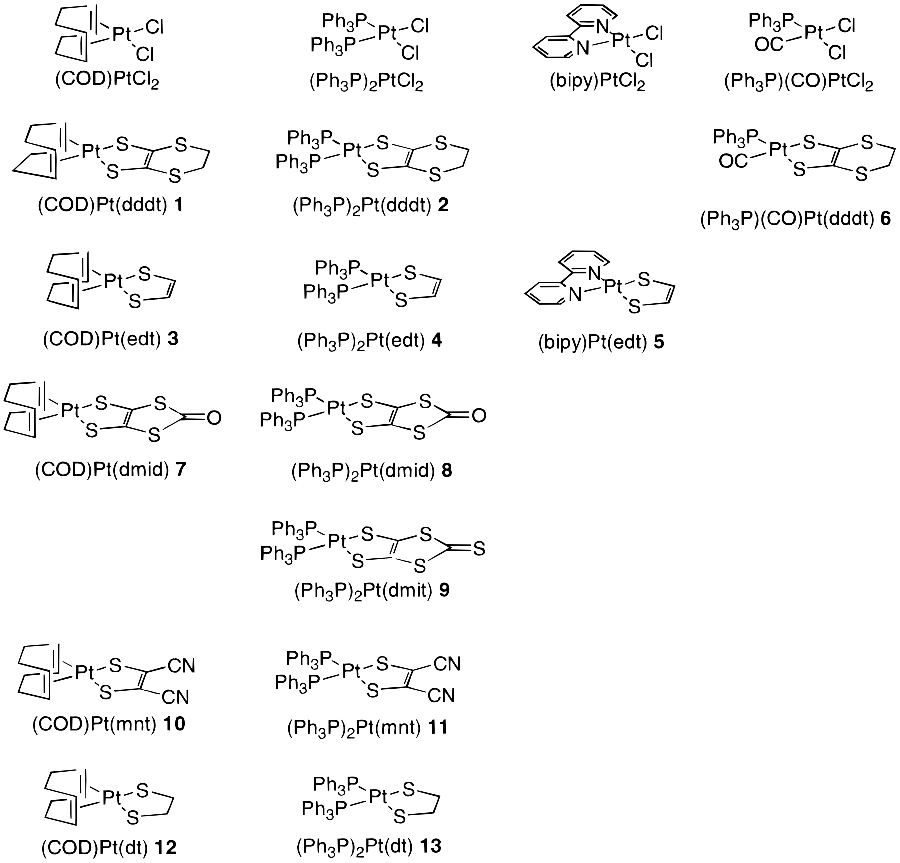

Figure 2. Platinum compounds included in this study.

in the range of 7500 to −6000 ppm for Pt(IV) compounds, −1000 to −6000 ppm for Pt(II), and −4000 ppm to −6000 ppm for Pt(0). Given this large chemical shift range, it seemed reasonable to suppose ^{195}Pt NMR would be a sensitive probe of the electronic structure of Pt 1,2-ditholene complexes and provide valuable information about the type of bonding present. There are several extensive reviews[18−21] summarizing ^{195}Pt chemical shifts. In addition, there are several reports on the ^{195}Pt NMR spectra of thioether[22,23] and thiolate[24,25] complexes. However, to our knowledge, there are no reports which deal with 1,2-dithiolene ligands coordinated to platinum.

We report here several new complexes, their characterizations including representative structural studies, and the ^{195}Pt NMR spectra for a number of platinum 1,2-dithiolene complexes (Figure 2). Correlation of ^{195}Pt NMR results with other characterizations including electrochemical properties, UV−vis spectroscopy, and ^{13}C NMR are given. Furthermore, a qualitative interpretation of these results with respect to the electron withdrawing and accepting behavior of the 1,2-dithiolene ligands is offered.

Experimental Section

General Procedures. ^{1}H NMR spectra were obtained at 300.075 MHz on a Varian Gemini 300 NMR spectrometer with chemical shifts reported in ppm downfield from tetramethylsilane (TMS), using the peak for $CHCl_3$ (7.26 ppm) as an internal reference. ^{31}P NMR spectra were obtained at 121.653 MHz on a Varian Gemini 300 NMR spectrometer with chemical shifts reported in ppm downfield relative to the external reference 85% H_3PO_4 in H_2O. ^{195}Pt NMR spectra were obtained at 64.497 MHz on a GN 300 MHz Omega FT-NMR spectrometer with chemical shifts reported in ppm downfield relative to the external reference 1.0 M Na_2PtCl_6 in D_2O. Typical ^{195}Pt NMR parameters were as follows: pulse width = 34 μs (90°), sweep width = 80 kHz, pulse delay = 0.5 s, 8K data points, line-broadening = 20−50 Hz. UV−vis measurements were recorded using a Hewlett-Packard 8453 UV−vis spectrophotometer. Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected. High-resolution mass spectra were obtained on a Jeol HX110HF mass spectrometer using fast atom bombardment (FAB) ionization. Elemental analyses were performed by Atlantic Microlab, Inc. (Norcross, GA).

Materials. K_2PtCl_4 (Johnson-Matthey), 1,5-cyclooctadiene (COD) (Matheson), 2,2′-dipyridyl, triphenylphosphine, 2-chloroacetaldehyde (50% solution by weight in H_2O), and 1,2-ethanedithiol (Aldrich) were used without further purification. Potassium isopropyl xanthate,[26] 1,5-cyclooctadieneplatinum(II) dichloride ((COD)PtCl$_2$),[27] *cis*-bis(triphenylphosphine)platinum(II) dichloride (*cis*-(PPh$_3$)$_2$PtCl$_2$),[27] *cis*-triphenylphosphinecarbonylplatinum(II) dichloride ((Ph$_3$P)(CO)PtCl$_2$),[28] 2,2′-bipyridylplatinum(II) dichloride ((bipy)PtCl$_2$),[29] dipotassium 5,6-dihydro-1,4-dithiin-2,3-dithiolate (K_2dddt),[30] and 4,5-dibenzoylthio-1,3-dithiole-2-thione (Bz$_2$dmit)[31] were prepared according to literature

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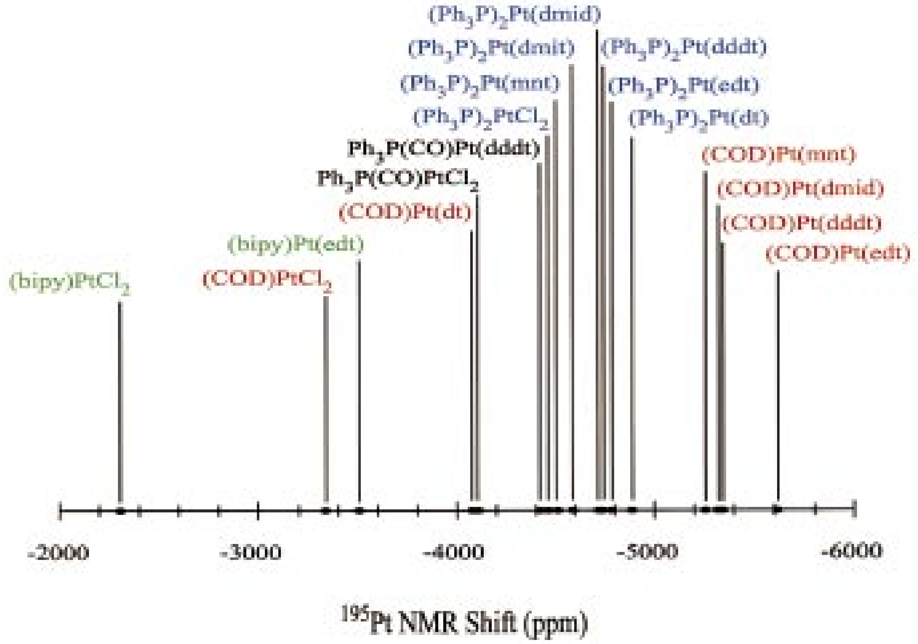

Figure 3. ^{195}Pt NMR of a variety of Pt(II) complexes. Line heights are set to an arbitrary distance for clarity.

procedures. All syntheses were carried out under Ar using standard Schlenk techniques.

1,5-Cyclooctadieneplatinum(II) 5,6-Dihydro-1,4-dithiin-2,3-dithiolate, (COD)Pt(dddt) (1). Dipotassium 5,6-dihydro-1,4-dithiin-2,3-dithiolate (K$_2$dddt) (0.67 g, 2.6 mmol) in 30 mL of anhydrous methanol was added dropwise to (COD)PtCl$_2$ (1.0 g, 2.7 mmol in 150 mL of acetone) and allowed to stir for approximately 6 h. After removal of solvent, the orange solid was dissolved in CH$_2$Cl$_2$, filtered, and passed through a short (5 cm) silica gel column with CH$_2$Cl$_2$ as eluent. An initial orange band was collected, evaporated to dryness, and recrystallized from chloroform to give 0.82 g of dark orange crystals (63% yield, mp = 180 °C (dec)). ^{1}H NMR (CDCl$_3$): δ 2.42−2.58 (m, 8H), 3.07 (s, 4H), 5.45 (s with Pt satellites, 4H, $^2J(^{195}\mathrm{Pt}{-}^1\mathrm{H}) = 57$ Hz). ^{195}Pt{^{1}H} NMR (CDCl$_3$): δ −5322 (s). High-resolution MS (FAB), exact mass calcd for $[\mathrm{C_{12}H_{16}PtS_4}]^+$ (M$^+$) 482.9783. Found: 482.9785. Anal. Calcd for $\mathrm{C_{12}H_{16}PtS_4}$: C, 29.80; H, 3.34; S, 26.52. Found: C, 29.93; H, 3.30; S, 26.36.

***cis*-Bis(triphenylphosphine)platinum(II) 5,6-Dihydro-1,4-dithiin-2,3-dithiolate, (Ph$_3$P)$_2$Pt(dddt) (2).** Triphenylphosphine (0.37 g, 1.4 mmol) was added to (COD)Pt(dddt) (0.32 g, 0.66 mmol) in 100 mL of THF and allowed to stir overnight. The light orange precipitate was filtered and washed with ether to yield 0.43 g of a light orange solid (73% yield). ^{1}H NMR (CDCl$_3$): δ 3.74 (s, 4H), 7.15 (t, 12H, $^1J(^1\mathrm{H}{-}^1\mathrm{H}) = 15$ Hz), 7.26−7.31 (m, 6H), 7.43−7.48 (m, 12H). ^{31}P NMR (CDCl$_3$): δ 14.54 (t, $^1J(^{31}\mathrm{P}{-}^{195}\mathrm{Pt}) = 2950$ Hz). ^{195}Pt NMR (CDCl$_3$): δ −4735 (t, $^1J(^{31}\mathrm{P}{-}^{195}\mathrm{Pt}) = 2940$ Hz). High-resolution MS (FAB), exact mass calcd for $[\mathrm{C_{40}H_{34}P_2PtS_4}]^+$ (M$^+$) 899.0667. Found: 899.0735. Anal. Calcd for $\mathrm{C_{40}H_{34}P_2PtS_4}$: C, 53.38; H, 3.81; S, 14.25. Found: C, 53.51; H, 3.76; S, 14.04.

1,3-Dithiole-2-one. Potassium isopropyl xanthate (70 g, 0.402 mol) was added to a 50% wt/wt solution of 2-chloroacetaldehyde/water (50 g, 0.318 mol) and water (500 mL) and stirred for 24 h. After extraction with chloroform (3 × 200 mL), the organic layer was separated and dried with MgSO$_4$ and the solvent was removed to give 44.0 g of a yellow oil which was added slowly to ca. 1 L of concentrated H$_2$SO$_4$ at 0 °C and stirred with continued cooling. After 2 h, this solution was poured onto 4 L of ice and filtered to give a brown solid, which was air-dried and recrystallized from ethanol to give 12.1 g (32% overall) of a yellow-brown solid (mp = 35 °C (lit.[32,33] 35 °C)). ^{1}H NMR (CDCl$_3$, δ 6.78, s).

1,5-Cyclooctadieneplatinum(II) Ethylene-1,2-dithiolate, (COD)-Pt(edt) (3). 1,3-Dithiole-2-one (0.160 g, 1.35 mmol) was added to sodium methoxide prepared from Na (63 mg, 2.7 mmol) and 80 mL of anhydrous methanol. After stirring 45 min, (COD)PtCl$_2$ (0.500 g, 1.34 mmol) in 100 mL of CH$_2$Cl$_2$ was added dropwise and stirred for 12 h. After removal of solvent the orange solid was taken up in CH$_2$Cl$_2$ and extracted with H$_2$O. The organic layer was dried with MgSO$_4$ and applied to a short (5 cm) silica gel column using CH$_2$Cl$_2$ as eluent. The initial orange band was collected and evaporated to dryness, giving 0.385 g of a bright orange solid (73% yield, mp = 85 °C (dec)). ^{1}H NMR (CDCl$_3$): δ 2.45−2.67 (m, 8H), 5.55 (s with Pt satellites, 4H, $^2J(^{195}\mathrm{Pt}{-}^1\mathrm{H}) = 53$ Hz), 6.83 (s with Pt satellites, 4H, $^3J(^{195}\mathrm{Pt}{-}^1\mathrm{H}) = 98$ Hz). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 30.50 (s), 90.16 (s with Pt satellites $^1J(^{195}\mathrm{Pt}{-}^{13}\mathrm{C}) = 118$ Hz) 131.56 (s with Pt satellites $^2J(^{195}\mathrm{Pt}{-}^{13}\mathrm{C}) = 29$ Hz). ^{195}Pt{^{1}H} NMR (CDCl$_3$): δ −5414 (s). High-resolution MS (FAB), exact mass calcd for $[\mathrm{C_{10}H_{14}PtS_2}]^+$ (M$^+$) 393.0185. Found: 393.0192. Anal. Calcd for $\mathrm{C_{10}H_{14}PtS_2}$: C, 30.51; H, 3.58; S, 16.29. Found: C, 30.68; H, 3.63; S, 16.37.

***cis*-Bis(triphenylphosphine)platinum(II) Ethylene-1,2-dithiolate, (Ph$_3$P)$_2$Pt(edt) (4).** Triphenylphosphine (0.400 g, 1.525 mmol) in 25 mL of CHCl$_3$ was added dropwise to (COD)Pt(edt) (**3**; 0.287 g, 0.729 mmol) in 50 mL of CHCl$_3$ and stirred for 2 h. The volume of the solution was reduced to ca. 10 mL and applied to a short (5 cm) silica gel column using CHCl$_3$ as eluent. The initial yellow band was collected and evaporated, giving 0.550 g of bright yellow solid (93% yield, mp = 235 °C (dec)). ^{1}H NMR (CDCl$_3$): δ 6.62 (d with Pt satellites, 2H, $J = 4$ Hz, $^3J(^{195}\mathrm{Pt}{-}^1\mathrm{H}) = 84$ Hz), 7.15−7.24 (t, 12H, $^3J(^1\mathrm{H}{-}^1\mathrm{H}) = 7$ Hz), 7.26−7.35 (t, 6H, $^3J(^1\mathrm{H}{-}^1\mathrm{H}) = 7$ Hz), 7.44−7.60 (m, 12H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 127.64 (t, meta, $^3J(^{13}\mathrm{C}{-}^{31}\mathrm{P}) = 6$ Hz), 128.14 (t, ethylene, $^2J(^{13}\mathrm{C}{-}^{195}\mathrm{Pt}) = 18$ Hz), 130.51 (s, para), 131.05−132.15 (m, ipso), 135.29 (t with Pt satellites, ortho, $^2J(^{31}\mathrm{P}{-}^{13}\mathrm{C}) = 6$ Hz, $^3J(^{195}\mathrm{Pt}{-}^{13}\mathrm{C}) = 16$ Hz). ^{31}P NMR (CDCl$_3$): δ 18.64 (s with Pt satellites, $^1J(^{195}\mathrm{Pt}{-}^{31}\mathrm{P}) = 2877$ Hz). ^{195}Pt NMR (CDCl$_3$): δ −4792 (triplet of doublets, $^1J(^{195}\mathrm{Pt}{-}^{31}\mathrm{P}) = 2876$ Hz, $^3J(^{195}\mathrm{Pt}{-}^1\mathrm{H}) = 83$ Hz) (see Figure 4). High-resolution MS (FAB), exact mass calcd for $[\mathrm{C_{38}H_{32}P_2PtS_2}]^+$ (M$^+$) 810.1147. Found: 810.1111. Anal. Calcd for $\mathrm{C_{38}H_{32}P_2PtS_2}$: C, 56.36; H, 3.98; S, 7.92. Found: C, 56.40; H, 3.98; S, 7.86.

2,2′-Bipyridineplatinum(II) Ethylene-1,2-dithiolate, (bipy)Pt(edt) (5). 1,3-Dithiole-2-one (0.300 g, 2.54 mmol) was added to sodium methoxide solution (sodium (0.12 g, 5.2 mmol), 100 mL of anhydrous methanol). A slurry of (bipy)PtCl$_2$ (0.500 g, 1.18 mmol) in 50 mL of

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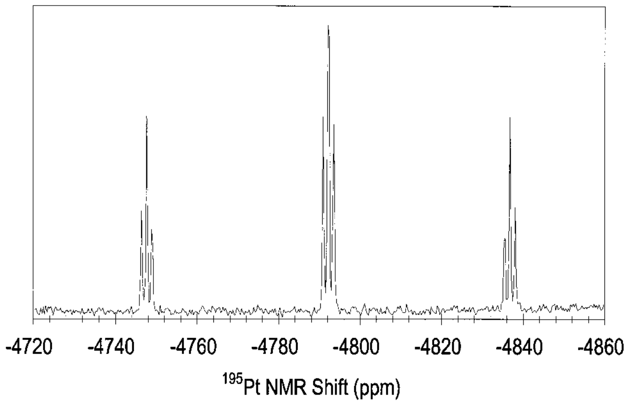

Figure 4. ^{195}Pt NMR of $(Ph_3P)_2Pt$(edt) (**4**).

a 50/50 mixture of methanol/chloroform was added, and the reagents were stirred for 18 h. The resulting blue solution was evaporated to give a solid that was extracted concurrently with CH_2Cl_2 (150 mL) and H_2O (100 mL). The aqueous layer was separated and extracted once more with CH_2Cl_2 (150 mL), and the combined organic layers were dried with $MgSO_4$, reduced to ca. 10 mL, applied to a long (30 cm) silica gel column, and eluted using a 99/1 solution of CH_2Cl_2/MeOH. The initial blue band was collected and evaporated, yielding 0.110 g of dark blue crystals (21%). ^{1}H NMR ($CDCl_3$): δ 6.29 (s with Pt satellites, 2H, $^3J(^{195}Pt-^1H) = 51$ Hz), 7.43−7.47 (m, 2H), 8.00−8.07 (m, 4H), 9.44 (d with Pt satellites, 2H, $^3J(^{195}Pt-^1H) = 21$ Hz, $^3J(^1H-^1H) = 5$ Hz). ^{195}Pt NMR ($CDCl_3$): δ −3506. High-resolution MS (FAB), exact mass calcd for $[C_{12}H_{10}N_2PtS_2]^+$ (M^+) 440.9933. Found: 440.9961. Anal. Calcd for $C_{12}H_{10}N_2PtS_2$: C, 32.65; H, 2.28; S, 14.53. Found: C, 33.17; H, 2.50; S, 14.75.

Triphenylphosphinecarbonylplatinum(II) 5,6-Dihydro-1,4-dithiin-2,3-dithiolate, $(Ph_3P)(CO)Pt$(dddt) (6). Dipotassium 5,6-dihydro-1,4-dithiin-2,3-dithiolate (K_2dddt) (0.12 g, 0.45 mmol) in 30 mL of anhydrous methanol was added dropwise to *cis*-$(Ph_3P)(CO)PtCl_2$ (0.25 g, 0.45 mmol in 150 mL of $CHCl_3$) and stirred for approximately 6 h. The resulting solution was evaporated, yielding an orange solid which was dissolved in CH_2Cl_2, filtered, and then passed through a short (5 cm) silica gel column with CH_2Cl_2 as eluent. An initial orange band was collected, evaporated, and recrystallized from chloroform to give 0.27 g of dark orange crystals (89% yield, mp = 170 °C (dec)). ^{1}H NMR ($CDCl_3$): δ 3.01−3.03 (m, 4H), 7.42−7.76 (m, 15H). ^{195}Pt NMR ($CDCl_3$): δ −4467 (d, $^1J(^{195}Pt-^{31}P) = 2569$ Hz). High-resolution MS (FAB), exact mass calcd for $[C_{23}H_{19}OPPtS_4]^+$ (M^+) 664.9704. Found: 664.9740. Anal. Calcd for $C_{23}H_{19}OPPtS_4$: C, 41.50; H, 2.88; S, 19.27. Found: C, 41.29; H, 2.84; S, 19.39.

1,5-Cyclooctadieneplatinum(II) Maleonitrile-1,2-dithiolate, (COD)-Pt(mnt) (10). Compound **10** was synthesized from (COD)$PtCl_2$ and Na_2mnt according to literature procedures[34] and characterized by ^{1}H NMR and mass spectroscopy. ^{1}H NMR ($CDCl_3$): δ 2.55−2.68 (m, 8H), 5.65 (s with Pt satellites, 4H, $^2J(^{195}Pt-^1H = 54$ Hz). $^{195}Pt\{^1H\}$ NMR ($CDCl_3$): δ −5253 (s). UV−vis (CH_2Cl_2) λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 242 (15 930) 275 sh (8130) 336 (5680) 345 (5470). MS (FAB) (M^+) 443.

***cis*-Bis(triphenylphosphine)platinum(II) Maleonitrile-1,2-dithiolate, $(Ph_3P)_2Pt$(mnt) (11).** Compound **11** was synthesized using a variation of literature procedure.[35] Triphenylphosphine (0.26 g, 1.0 mmol) was dissolved in 25 mL of $CHCl_3$ and added dropwise to a solution of (COD)Pt(mnt) (**10**, 0.20 g, 0.45 mmol) in 50 mL of $CHCl_3$. The solution was stirred for 2 h. The volume of the solution was reduced to ca. 10 mL and applied to a short (5 cm) silica gel column using $CHCl_3$ as eluent. The initial yellow band was collected and evaporated to dryness, giving 0.35 g of a yellow solid (91% yield). ^{1}H NMR ($CDCl_3$): δ 7.21 (t, 12H, $^3J(^1H-^1H) = 7$ Hz), 7.34−7.42 (m, 18H). ^{31}P NMR ($CDCl_3$): δ 16.20 (t, $^1J(^{31}P-^{195}Pt) = 2913$ Hz). ^{195}Pt NMR ($CDCl_3$): δ −4551 (t, $^1J(^{195}Pt-^{31}P) = 2916$ Hz). UV−vis (CH_2Cl_2) λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 250 (38 300), 283 sh (16 310) 367 (6180). MS (FAB) (M + H) 859.

1,5-Cyclooctadieneplatinum(II) Ethane-1,2-dithiolate, (COD)Pt-(dt) (12). To 1,2-ethanedithiol (0.022 mL, 0.27 mmol) in 25 mL of THF, and Na (0.050 g, 2.2 mmol) was added and allowed to completely react with the dithiol. Excess Na was removed, and (COD)$PtCl_2$ (0.10 g, 0.27 mmol) in 25 mL of $CHCl_3$ was added dropwise. The yellow solution was stirred for 15 min and evaporated, and the remaining yellow solid was dissolved in a minimal amount of $CHCl_3$. This was chromatographed on a short (5 cm) silica gel column with $CHCl_3$ as the eluent. The first yellow band was collected and evaporated to give 0.076 g of a yellow crystalline solid (72% yield, mp = 140−145 °C (dec)). ^{1}H NMR ($CDCl_3$): δ 2.28−2.43 (m, 4H), 2.52−2.55 (m, 4H), 2.80 (s with Pt satellites, 4H, $^3J(^{195}Pt-^1H) = 51$ Hz), 5.16 (s with Pt satellites, 4H, $^2J(^{195}Pt-^1H) = 52$ Hz). ^{13}C NMR ($CDCl_3$): 30.75 (s), 40.93 (s with Pt satellites, $^2J(^{195}Pt-^{13}C) = 17$ Hz), 95.14 (s with Pt satellites, $^1J(^{195}Pt-^{13}C) = 111$ Hz). $^{195}Pt\{^1H\}$ NMR ($CDCl_3$): δ −4070. High-resolution MS (FAB), exact mass calcd for $[C_{10}H_{16}PtS_2]^+$ (M^+) 395.0341. Found: 395.0349. Anal. Calcd for $C_{10}H_{16}PtS_2$: C, 30.37; H, 4.08; S, 16.22. Found: C, 30.44; H, 4.10; S, 16.13.

***cis*-Bis(triphenylphosphine)platinum(II) 1,2-Ethanedithiolate, $(Ph_3P)_2Pt$(dt) (13).** Compound **13** was synthesized according to literature procedures,[36] and its identity was verified by mp, ^{1}H NMR, and high-resolution mass spectrometry (mp = 246−248 °C (lit.[36] 244−246 °C)). ^{1}H NMR ($CDCl_3$): δ 2.70 (t, 4H, $^3J(^{195}Pt-^1H) = 45$ Hz), 7.15 (t, 12H, $^3J(^1H-^1H) = 7$ Hz), 7.27 (t, 6H, $^3J(^1H-^1H) = 7$ Hz), 7.45 (t, 12H, $^3J(^1H-^1H) = 8$ Hz). ^{31}P NMR ($CDCl_3$): δ 20.71 (t, $^1J(^{31}P-^{195}Pt) = 2883$ Hz). ^{195}Pt NMR ($CDCl_3$): δ −4881 (t of quintets, $^1J(^{195}Pt-^{31}P) = 2886$ Hz, $^3J(^{195}Pt-^1H) = 46$ Hz). High-resolution MS (FAB), exact mass calcd for $[C_{38}H_{34}P_2PtS_2]^+$ (M^+) 811.1225. Found: 811.1228.

Crystal Structure Determinations. Crystals of **1** were grown by the slow evaporation of a chloroform solution at room temperature, yielding an orange platelike crystal. Crystals of **5** were grown by the slow evaporation of an acetonitrile solution at room temperature, yielding a very dark blue rectangular prism-like crystal. X-ray measurements for **1** were made on a Rigaku AFC-6S diffractometer at the University of North Carolina, Chapel Hill. X-ray measurements for **5** were made on an Enraf-Nonius CAD4 diffractometer. The nonstandard space group for **5** was chosen to make β near orthogonal and reduce correlations in the least-squares refinement. The unit cell dimensions were determined by a symmetry constrained fit of 41 (**1**) and 24 (**5**) well-centered reflections, and their Friedel pairs were measured at $\pm\theta$ values with $40° < 2\theta < 44°$ for **1** and $36° < 2\theta < 40°$ for **5**. For **1**, a hemisphere of intensity data was collected using a bisecting $\theta/2\theta$ scan mode at room temperature and for **5** a unique quadrant of intensity data was collected using a bisecting $\theta/2\theta$ scan mode. For **1**, three standard intensity checks were measured every 100 reflections. For **5**, three standard intensity check reflections were measured every 4800 s of X-ray exposure time. For **5**, the crystal orientation was checked every 400 reflections. Scaling the data was accomplished using a 5 point smoothed curved routine fit to the intensity check reflections. The intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction was performed using ψ scan data.

The data were reduced and graphics produced using routines from the NRCVAX set of programs.[37] The calculated structure factors were fit to the data using full matrix least-squares based on F. All non-H atoms were allowed to refine with anisotropic displacement parameters (ADP's). The hydrogen atoms were included in the structure factor calculation but not refined. Carbon−hydrogen distances were set to 0.96 Å, and the isotropic displacements (U(H)) were set according to the expression $U(H) = U(C) + 0.01$ Å^2. The hydrogen positional and displacement parameters were updated after every other cycle of least-squares refinement. The calculated structure factors included corrections for anomalous dispersion from the usual tabulation.[38] In the final refinement, a secondary extinction correction was included. The

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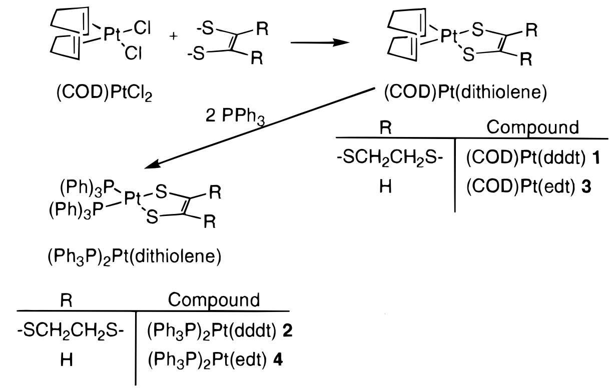
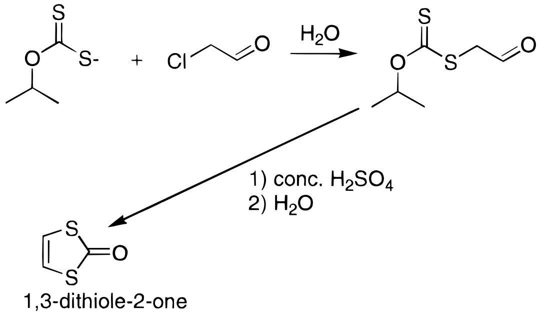
Scheme 1



R	Compound
-SCH$_2$CH$_2$S-	(COD)Pt(dddt) **1**
H	(COD)Pt(edt) **3**

R	Compound
-SCH$_2$CH$_2$S-	(Ph$_3$P)$_2$Pt(dddt) **2**
H	(Ph$_3$P)$_2$Pt(edt) **4**

Scheme 2



structures were solved using SIR92[39] and all non-H atoms were recovered from the initial *E* map.

Results and Discussion

Synthesis. The platinum(II) mono-1,2-dithiolenes (COD)Pt(dddt) (**1**), (Ph$_3$P)$_2$Pt(dddt) (**2**), (COD)Pt(edt) (**3**), and (Ph$_3$P)$_2$Pt(edt) (**4**) (COD = 1,5-cyclooctadiene; dddt = 5,6-dihydro-1,4-dithiin-2,3-dithiolate; edt = ethylene-1,2-dithiolate) were synthesized as shown in Scheme 1. (bipy)Pt(edt) (**5**), and (Ph$_3$P)(CO)Pt(dddt) (**6**) (bipy = 2,2′-bipyridyl; CO = carbonyl) were synthesized in an analogous fashion with (bipy)PtCl$_2$ and (Ph$_3$P)(CO)PtCl$_2$ as the starting platinum compounds. (COD)Pt(dt) (**12**) has been previously reported as the product of a transmetalation reaction involving (cp)$_2$Ti(SCH$_2$CH$_2$S) and (COD)PtCl$_2$.[40] Direct synthesis from the dithiol was performed, but no experimental details were given. We report here experimental details for the direct synthesis of **12**. A new synthesis for 1,3-dithiol-2-one, the precursor to the edt^{2-} ligand, that uses inexpensive starting materials and involves only two steps has been developed (Scheme 2). This compound was synthesized previously by a transformation of the 1,3-dithiol-2-thione using mercuric acetate.[32] The disadvantages of that method include the expense of the 1,3-dithiol-2-thione and the use of a mercuric salt.

^{195}Pt NMR. The ^{195}Pt NMR spectra for compounds **1**−**13** as well as the parent dichlorides (COD)PtCl$_2$, *cis*-(Ph$_3$P)$_2$PtCl$_2$, and (Ph$_3$P)(CO)PtCl$_2$ were obtained. These results are shown in Table 1 and Figure 3. The spectra obtained for the triphenylphosphine complexes were well defined and exhibited $^1J(^{195}\mathrm{Pt}-^{31}\mathrm{P})$ coupling in the range of 2500−3000 Hz, and, for **4** and **13**, $^3J(^{195}\mathrm{Pt}-^1\mathrm{H})$ coupling to the protons on the sulfur ligand was observed. Line widths were in the range of 10−50 Hz. As an example, the spectrum of **4** is given in Figure 4. It consists of a triplet of triplets with $^1J(^{195}\mathrm{Pt}-^{31}\mathrm{P})$ = 2877 Hz and $^3J(^{195}\mathrm{Pt}-^1\mathrm{H})$ = 83 Hz. The spectra for the COD complexes were also well resolved with slightly larger line widths of 50−80 Hz. Spectra for the COD compounds were obtained with ^{1}H decoupling to increase signal strength via multiplet collapse due to their low solubility relative to the triphenylphosphine complexes. ^{1}H decoupling precluded the observation of $^3J(^{195}\mathrm{Pt}-^1\mathrm{H})$ in the edt **3** and dt **12** compounds. The spectra of (bipy)Pt(edt) **5** consisted of a broad singlet with a line width of ∼420 Hz. This large broadening is due to the substantial nuclear quadrupole moment for ^{14}N combined with its coupling and relaxation characteristics.[21] As a result, coupling between ^{195}Pt and ^{14}N or ^{1}H was not seen for **5**.

Examination of the chemical shift data presented in Figure 3 reveals several interesting observations. First, all of the chemical shifts for the compounds that possess a sulfur-containing ligand are upfield from the corresponding dichloride compounds, as expected for the coordination of a less electronegative donor atom.

Second, for the triphenylphosphine complexes, the chemical shifts of the 1,2-dithiolene complexes (−4550 to −4800 ppm) are downfield of (Ph$_3$P)$_2$Pt(dt) (**13**) (−4880 ppm), a 1,2-dithiolate. The only difference between a 1,2-dithiolate and a 1,2-dithiolene is the π system which exists in the 1,2-dithiolene due to the C═C double bond and the lone pairs on sulfur. Therefore the downfield shift of the 1,2-dithiolenes relative to 1,2-dithiolates must be due to interactions between the π system of the 1,2-dithiolenes and the platinum metal. 1,2-Dithiolenes have filled and empty π orbitals of the proper symmetry to interact with the 5d orbitals of Pt (Figure 5) and therefore can act as both a π donor and acceptor. If a 1,2-dithiolene acts as a π *acceptor*, electron density on the metal would decrease, and a downfield change of the chemical shifts relative to the dt^{2-} complex **13** should occur. This is what is observed for the triphenylphosphine complexes. Triphenylphosphine is a strong σ donor and has little π acceptor ability. Pt(II) is a d^8 metal, and the only empty d orbital on the metal is $d_{x^2-y^2}$. It is a σ^* orbital and has the wrong symmetry to interact as an acceptor with the π system of the 1,2-dithiolenes. Therefore, in the bis(triphenylphosphine) complexes the only π type interaction which is possible is donation of electron density from the d orbitals of platinum to the empty π^* orbital of the 1,2-dithiolene, whereby it acts as a π acceptor.

For the COD compounds, the 1,2-dithiolene complexes (−5250 to −5410 ppm) are upfield of (COD)Pt(dt) (**12**) (−4070 ppm). This is the opposite of what was observed for the triphenylphosphine complexes. If a 1,2-dithiolene ligand behaves as a π *donor* to platinum, an upfield change in the chemical shift relative to the dt^{2-} complex **12** should be observed. Although COD forms a σ donor bond, it is also a very good π acceptor. The π^* orbitals of the olefin have the proper symmetry to interact with the filled d orbitals of platinum. This allows a mixing of the π^* orbitals of COD, the $d_{xz,yz}$ orbitals of platinum and the π orbitals of the 1,2-dithiolene ligand which results in an upfield shift for the (COD)Pt(1,2-dithiolenes) relative to the dt complex **12**. It is also important to note that if there was no significant π interaction between the dithiolenes and the platinum, then the COD complexes would be downfield of the corresponding triphenylphosphine complexes (as it is in the dichlorides). However, this is not the case.

We chose to examine the mixed ligand system of a good σ donor (Ph$_3$P) and a good π acceptor (CO) with the expectation

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Table 1. ^{195}Pt NMR Data and Appropriate Coupling Constants

compound	^{195}Pt NMR shift^a	$^1J(^{195}Pt-^{31}P)$ in Hz^b	$^2J(^{195}Pt-^1H)$ in Hz^c
(bipy)PtCl$_2$	−2315[41]	–	–
(bipy)Pt(edt) **5**	−3506	–	–
(Ph$_3$P)(CO)PtCl$_2$	−4090 (d)	3067	–
(Ph$_3$P)(CO)Pt(dddt) **6**	−4467 (d)	2569	–
cis-(Ph$_3$P)$_2$PtCl$_2$	−4429,−4409[58](t)	3682,3678[59]	–
(Ph$_3$P)$_2$Pt(mnt) **11**	−4551 (t)	2916, 2913	–
(Ph$_3$P)$_2$Pt(dmit) **9**	−4597 (t)	2961, 2951	–
(Ph$_3$P)$_2$Pt(dmid) **8**	−4723 (t)	2969, 2975	–
(Ph$_3$P)$_2$Pt(dddt) **2**	−4735 (t)	2940, 2950	–
(Ph$_3$P)$_2$Pt(edt) **4**	−4792 (tt)	2876, 2877	$^3J(^{195}Pt-^1H) = 83^d$
(Ph$_3$P)$_2$Pt(dt) **13**	−4880 (t-quin)	2886, 2883	$^3J(^{195}Pt-^1H) = 45^e$
(COD)PtCl$_2$	−3330,−3360[60](s)	–	69
(COD)Pt(dt) **12**	−4070 (s)	–	52,$^3J(^{195}Pt-^1H) = 51^e$
(COD)Pt(mnt) **10**	−5253 (s)	–	54
(COD)Pt(dmid) **7**	−5313 (s)	–	54
(COD)Pt(dddt) **1**	−5322 (s)	–	57
(COD)Pt(edt) **3**	−5414 (s)	–	53,$^3J(^{195}Pt-^1H) = 98^d$

^{a} In ppm downfield of 1.0 M Na$_2$PtCl$_6$ in D$_2$O. ^{b} First number is as measured in the ^{195}Pt NMR spectra, second number is as measured in the ^{31}P NMR spectra. ^{c} Coupling to olefinic COD protons. ^{d} Coupling to protons on edt. ^{e} Coupling to protons on dt.

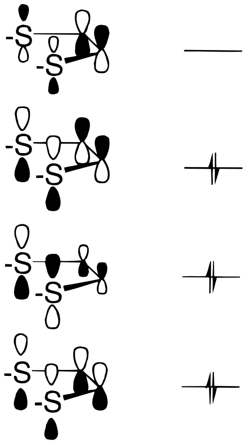

Figure 5. π-Orbitals of a 1,2-dithiolene ligand.[1]

that we might see an "average" effect. We did not see this, in fact, and found that (Ph$_3$P)(CO)Pt(dddt) (**6**) is only 377 ppm upfield of (Ph$_3$P)(CO)PtCl$_2$. In retrospect, we should have realized that the role of the dithiolenes in π-bonding is to produce a delocalized five-membered ring with the metal. The single triphenylphosphine trans to one sulfur prevents this effect. In addition, the NMR data for (bipy)PtCl$_2$,[41] and (bipy)Pt(edt) **5** have been examined and the chemical shift for compound **5** lies ∼1200 ppm upfield of the parent dichloride. This behavior resembles that of the COD complexes mentioned above with a large upfield shift for the 1,2-dithiolene complexes. This is expected because like COD, bipy has π* orbitals which can accept electron density from the filled d orbitals of Pt.

Finally, the ordering of the chemical shifts of the 1,2-dithiolene complexes is the same for both the triphenylphosphine complexes and the COD complexes and is consistent with the π type interactions discussed above. For both the triphenylphosphine and COD complexes the chemical shift series is mnt^{2-} > dmit^{2-} > dmid^{2-} > dddt^{2-} > edt^{2-}. In addition, this ordering correlates with the relative electron withdrawing ability of the substituents on the 1,2-dithiolene backbone and also with the one-electron oxidation potentials of Ni bis-1,2-dithiolene complexes ($ML_2^{2-} \rightarrow ML_2^{1-}$) which are ligand based.[42−46]

In the bis-triphenylphosphine complexes, the relative ability of the 1,2-dithiolene ligands to act as π acceptors should correspond to the electron withdrawing ability of the substituents on the dithiolene backbone. Therefore, the most electron withdrawing ligand should have the largest downfield chemical shift relative to (Ph$_3$P)$_2$Pt(dt) (**13**) and the least electron withdrawing ligand the smallest. This correlation is observed (Figure 3), with the largest downfield shift relative to **13** occurring for (Ph$_3$P)$_2$Pt(mnt) (**11**) which has cyano groups attached to the dithiolene C═C double bond and the smallest downfield shift occurring for (Ph$_3$P)$_2$Pt(edt) (**4**) which has no substituents. For the COD complexes, the size of the *upfield* chemical shift relative to (COD)Pt(dt) (**12**) should correspond *inversely* to the electron-withdrawing ability of the substituents with the most electron-withdrawing substituents having the smallest upfield change and the least electron-withdrawing substituents having the largest. This is observed for the COD complexes (Figure 3). It is interesting to note that different behavior of the 1,2-dithiolene ligands in the bis(triphenylphosphine) and COD complexes results in the same series of chemical shifts for these compounds.

The relative magnitude of the changes in chemical shifts should also be noted. For the triphenylphosphine complexes the 1,2-dithiolenes are ∼120−360 ppm upfield of (Ph$_3$P)$_2$PtCl$_2$ and **13** is 451 ppm upfield. For the COD compounds, the 1,2-dithiolene complexes are ∼1920−2090 ppm upfield of (COD)PtCl$_2$ and **12** is 740 ppm upfield. This large difference in the magnitude of the chemical shift differences is indicative of the fact that 1,2-dithiolene ligands are much better electron donors than acceptors.

Electrochemistry. Cyclic voltammetric experiments also support the existence of π interactions. Table 2 shows that the one electron oxidation potential of (COD)Pt(dmid) (**7**) is approximately 0.34 V more positive than (Ph$_3$P)$_2$Pt(dmid) **8** or (Ph$_3$P)$_2$Pt(dmit) (**9**).[47] Previous work[48] has shown that, similar

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Table 2. Cyclic Voltammetric $E_{1/2}$ Potentials (V) for (COD)Pt(dmid) (**7**), $(Ph_3P)_2$Pt(dmid) (**8**), and $(Ph_3P)_2$Pt(dmit) (**9**)[a]

complex	$E_{1/2}$
(COD)Pt(dmid) **7**	0.86
$(Ph_3P)_2$Pt(dmid) **8**	0.53
$(Ph_3P)_2$Pt(dmit) **9**	0.51

[a] Relative to Ag/AgCl in CH_3CN. Conditions: scan rate, 100 mV/s; working electrode, platinum disk (r = 0.8 mm); reference electrode, Ag/AgCl in acetonitrile; counter electrode, platinum wire; 100 mM Bu_4NBF_4 electrolyte under Ar at room temperature. Experimental details have been previously published.[47]

Table 3. λ_{max} for the 1,2-Dithiolene ($\pi \rightarrow \pi^*$) Transition in Na_2dmit, $(Ph_3P)_2$Pt(dmit) (**9**), (COD)Pt(dmit), Na_2mnt, $(Ph_3P)_2$Pt(mnt) (**11**), and (COD)Pt(mnt) (**10**)

compound (solvent)	λ_{max} (nm)	ϵ_{max} ($M^{-1}cm^{-1}$)
Na_2dmit (methanol)[51]	514	–[a]
$(Ph_3P)_2$Pt(dmit) **9** (CH_2Cl_2)	464	11000
(COD)Pt(dmit) (CH_2Cl_2)	406	8300
Na_2mnt (H_2O, methanol[50])	371, 372	10710, 12000
$(Ph_3P)_2$Pt(mnt) **11** (CH_2Cl_2, $CHCl_3$[35])	367, 366	6180, 6200
(COD)Pt(mnt) **10** (CH_2Cl_2, CH_3CN[53])	345, 346	5470, 6208

[a] ϵ not reported.

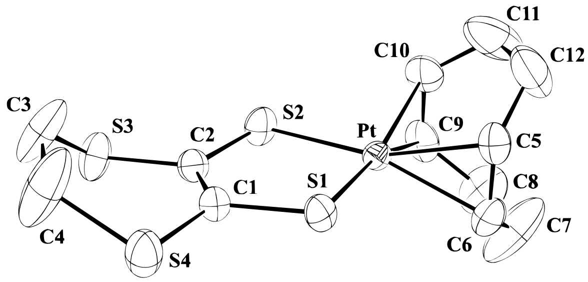

Figure 6. Molecular structure and atom labeling scheme for (COD)-Pt(dddt) (**1**). ADP ellipsoids drawn at 50% probability level. Hydrogens omitted for clarity.

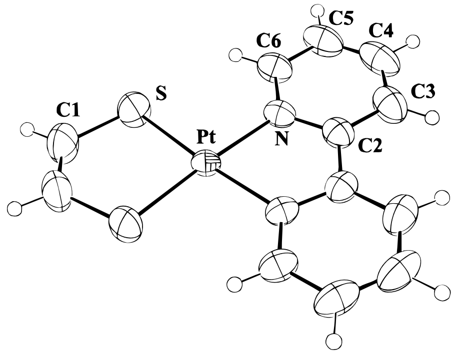

Figure 7. Molecular structure and atom labeling scheme for (bipy)-Pt(edt) (**5**). ADP ellipsoids drawn at 50% probability level. Hydrogens set to arbitrary radii for clarity.

Table 4. Single Crystal X-ray Analysis Parameters for **1** and **5**

	(COD)Pt(dddt) **1**	(bipy)Pt(edt) **5**
empirical formula	$C_{12}H_{16}PtS_4$	$C_{12}H_{10}N_2PtS_2$
fw	483.82	441.43
T (°C)	20	20
λ (Å)	Mo Kα (0.709 30)	Mo Kα (0.710 73)
space group	$P2_1/a$ (No. 14)	$I2/a$ (No. 15)
a (Å)	10.2420(10)	7.2294(2)
b (Å)	10.7510(10)	11.4574(4)
c (Å)	13.289(2)	14.9103(6)
β (deg)	102.870(10)	90.341(5)
V (Å^3)	1426.5(3)	1235.00(7)
Z	4	4
ρ, calcd (g cm^{-3})	2.253	2.374
μ (cm^{-1})	104.8	117.8
R_F, R_{wF}[a]	0.043, 0.047	0.026, 0.032
GOF[b]	1.53	1.07

[a] $R_F = \sum(|F_o - F_c|)/\sum F_o$, $R_{wF} = [\sum w(|F_o - F_c|)^2/\sum wF_o^2]^{1/2}$, where $w = [s^2(F) + gF^2]^{-1}$. [b] GOF $= [\sum w(|F_o - F_c|)^2/(\text{no. of reflcns} - \text{no. of params})]$.

to transition metal bis(1,2-dithiolenes),[49] these oxidations are primarily π 1,2-dithiolene ligand based. The fact that it is more difficult to oxidize the COD complexes than the bis(triphenylphosphine) complexes is consistent with an increased π donation from the dithiolene to the platinum in the COD compounds. This results in a lowering in energy of the 1,2-dithiolene ligand π orbital which increases its oxidation potential.

Spectroscopy. Further support is given by the analysis of the UV–vis spectra of the COD and triphenylphosphine complexes of dmit^{2-} and mnt^{2-} (Table 3). In both mnt^{2-} [34,50] and dmit^{2-} [51] there exists a low-energy charge-transfer band which has been assigned to a ligand ($\pi \rightarrow \pi^*$) transition. When the spectrum of $(Ph_3P)_2$Pt(dmit) (**9**) is compared to that of Na_2dmit, a blue shift of about 47 nm is observed (Table 3). For $(Ph_3P)_2$Pt(mnt) (**11**) relative to Na_2mnt there is a blue shift of only 4 nm. However, for (COD)Pt(dmit) (**8**) and (COD)Pt(mnt) (**10**), the spectra exhibit much larger blue shifts of 105 and 26 nm, respectively, for the ligand ($\pi \rightarrow \pi^*$) band, as would be expected for large π donor behavior of the 1,2-dithiolenes in the COD complexes. In addition, it is interesting to note the differences in the relative magnitude of blue shift between the mnt and dmit COD complexes. The much smaller blue shifts of the mnt complexes are consistent with its poorer electron donor properties than dmit due to the strongly electron withdrawing nature of the cyano groups.

Although we were unable to obtain the ^{195}Pt NMR spectrum of (COD)Pt(dmit) due to its low solubility,[47] we can infer from the NMR shifts of the other (COD)Pt(1,2-dithiolenes) and the previously discussed trends for both the (COD)Pt(1,2-dithiolenes) and $(Ph_3P)_2$Pt(1,2-dithiolenes) that its NMR shift would be approximately −5280 ppm. This predicted chemical shift is consistent with the UV–vis observations.

^{13}C NMR. The ^{13}C NMR spectra of the edt^{2-} complexes were acquired in order to determine the effect of the π interactions between the 1,2-dithiolene ligand and the metal center on the chemical shifts of the 1,2-dithiolene C=C double bond or the $^2J(^{195}\text{Pt}-^{13}\text{C})$ coupling constant. For (COD)Pt(edt) (**3**), the chemical shift of the ethylene carbons of edt is 131.6 ppm with $^2J(^{195}\text{Pt}-^{13}\text{C}) = 29$ Hz. For $(Ph_3P)_2$Pt(edt) (**4**), the chemical shift is 128.1 ppm with $^2J(^{195}\text{Pt}-^{13}\text{C}) = 18$ Hz. These results are consistent with 1,2-dithiolene π donation in the COD complexes and π acceptor behavior in the triphenylphosphine complexes. An increased interaction with the Pt center for **3** is indicated by an increase in the coupling constant relative to **4**.

X-ray Crystal Structure Analysis. Single-crystal X-ray diffraction studies of compounds **1** and **5** were done to look for structural characteristics which would demonstrate the donor/acceptor properties of the 1,2-dithiolene ligands in these complexes. ORTEP[52] diagrams are presented in Figures 6 and 7 respectively, crystallographic parameters are given in Table 4, and selected bond lengths and angles are in Tables 5 and 6.

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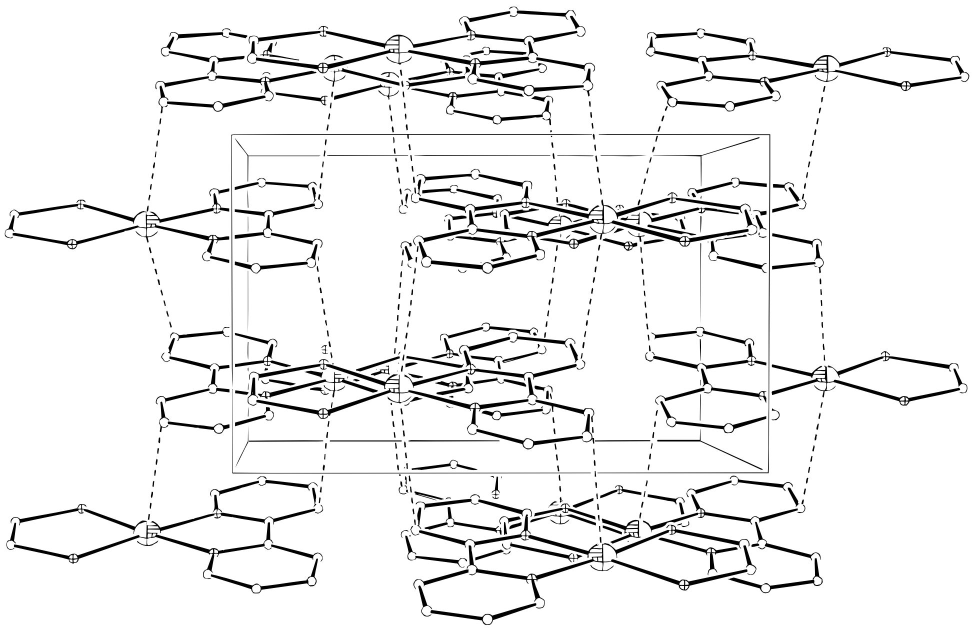

Figure 8. Molecular stacking diagram for **5** viewed approximately down the *c* axis. Pt−C3(bipy) bond length = 3.481(6) Å. Hydrogens omitted and atomic displacements set to arbitrary radii for clarity.

Table 5. Selected Bond Lengths (Å) and Bond Angles (deg) for (COD)Pt(dddt) (**1**)

Pt−S1	2.272(2)	S3−C2	1.751(10)	C5−C12	1.479(16)
Pt−S2	2.258(2)	S3−C3	1.809(12)	C6−C7	1.482(17)
Pt−C5	2.184(10)	S4−C1	1.742(10)	C7−C8	1.42(2)
Pt−C6	2.201(10)	S4−C4	1.811(12)	C8−C9	1.486(17)
Pt−C9	2.208(9)	C1−C2	1.352(13)	C9−C10	1.392(16)
Pt−C10	2.190(9)	C3−C4	1.404(18)	C10−C11	1.489(19)
S1−C1	1.763(10)	C5−C6	1.406(15)	C11−C12	1.42(2)
S2−C2	1.747(9)				

S1−Pt−S2	89.02(8)	C9−Pt−C10	36.9(4)	Pt−C5−C12	109.9(8)
S1−Pt−C5	92.8(3)	Pt−S1−C1	103.8(3)	C6−C5−C12	127.5(11)
S1−Pt−C6	92.6(3)	Pt−S2−C2	104.3(3)	Pt−C6−C5	70.7(6)
S1−Pt−C9	163.0(3)	C2−S3−C3	98.5(5)	Pt−C6−C7	107.2(7)
S1−Pt−C10	160.1(3)	C1−S4−C4	104.1(6)	C6−C7−C8	121.1(11)
S2−Pt−C5	160.1(3)	S1−C1−S4	113.3(5)	C7−C8−C9	117.3(10)
S2−Pt−C6	162.3(3)	S1−C1−C2	120.8(7)	Pt−C9−C8	109.3(7)
S2−Pt−C9	92.1(3)	S4−C1−C2	125.8(8)	Pt−C9−C10	70.9(6)
S2−Pt−C10	90.9(3)	S2−C2−S3	115.9(5)	C8−C9−C10	126.1(10)
C5−Pt−C6	37.4(4)	S2−C2−C1	121.8(7)	Pt−C10−C9	72.2(5)
C5−Pt−C9	91.8(4)	S3−C2−C1	122.2(7)	Pt−C10−C11	109.1(7)
C5−Pt−C10	80.7(4)	S3−C3−C4	119.5(9)	C10−C11−C12	118.6(10)
C6−Pt−C9	81.3(4)	S4−C4−C3	119.8(9)	C5−C12−C11	118.1(11)
C6−Pt−C10	93.5(4)	Pt−C5−C6	71.9(6)	C5−C6−C7	124.7(12)

Table 6. Selected Bond Lengths (Å) and Bond Angles (deg) for (bipy)Pt(edt) (**3**)

Pt−S	2.2504(14)	N−C6	1.351(6)	C3−C4	1.393(10)
Pt−N	2.049(4)	C1−C1a	1.346(14)	C4−C5	1.360(11)
S−C1	1.743(7)	C2−C2a	1.469(10)	C5−C6	1.379(7)
N−C2	1.362(7)	C2−C3	1.386(8)	S−Pt−Sa	88.67(6)

Pt−N−C6	125.7(4)	C2a−C2−C3	124.2(5)	S−Pt−N	96.04(12)
C2−N−C6	118.8(4)	C2−C3−C4	118.8(6)	S−Pt−Na	175.25(12)
S−C1−C1a	121.0(5)	C3−C4−C5	120.2(5)	N−Pt−Na	79.26(16)
N−C2−C2a	114.8(4)	C4−C5−C6	118.8(5)	Pt−S−C1	104.6(2)
N−C2−C3	121.0(5)	N−C6−C5	122.4(5)	Pt−N−C2	115.5(3)

The average Pt−C (2.196 Å) and Pt−S (2.265 Å) bond lengths for (COD)Pt(dddt) (**1**) are similar to those for the previously reported (COD) platinum 1,2-dithiolene complexes, (COD)Pt(dmit) (**8**, 2.198 and 2.290 Å)[47] and (COD)Pt(mnt) (**10**, 2.21 and 2.27 Å).[53] The central C=C double bond in the dddt ligand has a length of 1.35 Å and the average S−C (C=C) bond length is 1.751 Å. These dddt bond lengths are consistent with other previously characterized dddt containing compounds.[54] The cyclooctadiene moiety has two elongated C=C double bonds (1.406 and 1.392 Å) similar to other (COD)Pt(1,2-dithiolenes).[47,53]

For (bipy)Pt(edt) (**5**) the Pt−N and Pt−S bond lengths are 2.049 and 2.250 Å, respectively. For the edt ligand, the central C=C double bond length is 1.346 Å and the S−C bond length is 1.743 Å. For the bipy ligand, the average ring C−N bond length is 1.356 Å and the average ring C−C bond length is 1.380 Å. The C−C bond length between rings is 1.469 Å. In addition, **5** exhibits a short intermolecular Pt−C contact between the platinum center of one molecule and the C3 carbon of another at −*x*, −*y*, 1 − *z*. This forms a one-dimensional chain

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Table 7. Pt−S Bond Lengths for a Series of L_2Pt(1,2-dithiolenes)

compound	Pt−S bond length (Å)
(bipy)Pt(mnt)[57]	2.250(4)
(bipy)Pt(edt) **5**	2.2504(14)
(COD)Pt(mnt) **10**[53]	2.266(3)
(COD)Pt(dddt) **1**	2.265(3)
(COD)Pt(dmit)	2.2895(7)
$(Ph_3P)_2Pt$(dmit) **9**	2.3256(16)
$(Ph_3P)_2Pt$(dmid) **8**	2.3222(11)

along [100] with alternating Pt and C with a Pt−C stacking distance of 3.481 Å which is shown in Figure 8, as viewed approximately down the crystallographic *c* axis. This may be consistent with a weak axial interaction between the filled d_{z^2} orbital of platinum and the π^* antibonding orbital of C3 in the bipyridine ring. A search of the Cambridge Crystallographic Database shows that the platinum−C6(6′)(2,2′-bipyridyl) contact in **5** is shorter than any others which have been reported,[55] with the next shortest being 3.51 Å.[56]

Analysis of the molecular structures for these and previously reported L_2Pt(1,2-dithiolenes) shows that only the Pt−S bond lengths (Table 7) change significantly. It does not appear that the π type interactions which are evident in the ^{195}Pt NMR are represented by changes in the Pt−S bond lengths. For the bipy compounds, there is no difference between (bipy)Pt(mnt)[57−60] (2.250(4) Å) and (bipy)Pt(edt) (**5**, 2.250(1) Å) even though mnt^{2-} and edt^{2-} lie at the ends of the series of 1,2-dithiolene ligands based on their electron withdrawing abilities. This is also true for the bis-triphenylphosphine and 1,5-cyclooctadiene compounds. In fact, the ordering of the Pt−S bond lengths varies only with L_2 as $(PPh_3)_2$ > COD > bipy. This trend can be explained in terms of the trans-influence of the L_2 ligands where a strong trans-influence ligand lengthens the M−X bond trans to it. The variation of the Pt−S bond lengths appear to be dominated by the ligand trans to the 1,2-dithiolenes and any effects due to π interactions are not seen.

Conclusion

A systematic study of L_2Pt(1,2-dithiolene) compounds clearly demonstrates that in complexes where L_2 is a good σ donor and a poor π acceptor, such as bis-triphenylphosphine, the dithiolene ligand behaves as a weak π acceptor and small downfield chemical shifts relative to the 1,2-dithiolate dt^{2-} are observed. In cases where L_2 is a good π acceptor as in the COD case, the 1,2-dithiolenes π donor ability is seen and there is a large upfield shift for the ^{195}Pt chemical shifts of the 1,2-dithiolene complexes relative to the dt^{2-} complexes. In addition, ^{195}Pt NMR is sensitive to the effects of electron-withdrawing groups on the dithiolene backbone and an ordered series of chemical shifts is observed (mnt^{2-} > $dmid^{2-}$ > $dmit^{2-}$ > $dddt^{2-}$ > edt^{2-}), regardless of the identity of L_2.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for complexes **1** and **5** are available free of charge on the Internet at http://pubs.acs.org.

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