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Article

Synthesis and Electronic Characterization of Bipyridine Dithiolate Rhodium(III) Complexes

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Five new mixed diimine 1,1′-dithiolate or dithiocarbamate ligand complexes of the form [Rh(bpy)$_2$(SS)][PF$_6$]$_n$, where bpy = 2,2′-bipyridine and SS = various substituted dialkyldithiocarbamates or 1,1′-dithiolates, were synthesized from *cis*-[Rh(bpy)$_2$(OTf)$_2$][OTf]. The triflate ligands are easily displaced by other ligands and allow these syntheses to proceed in high yields (80–90% overall) under relatively mild reaction conditions and to give high purity products. Electrochemistry shows irreversible two-electron reduction of Rh(III) to Rh(I) and a concomitant loss of one bipyridine ligand; this is followed by reversible one-electron reduction of the remaining 2,2′-bipyridine ligand. The electronic characterizations of these complexes are consistent with significant delocalization of the sulfur electron density onto the empty metal d orbitals. The 1,1′-dithiolate ligands induce larger red shifts in the absorption and emission spectra than the dithiocarbamates as the 1,1′-dithiolates have a more extensive conjugation system.

Introduction

Octahedral diimine rhodium(III) complexes are of interest because of their ability to undergo a chemically irreversible two-electron reduction involving ligand loss to form square-planar rhodium(I) complexes. This change in coordination number from six to four opens up sites for binding substrates for catalysis and has been utilized to carry out the electro-catalytic reduction of CO to methanol.[1,2] Further, octahedral diimine rhodium(III) complexes are of interest as they have been used in the process of photochemically reducing H$_2$O to H$_2$.[3–5]

Tris-diimine[6–9] and tris-dithiolate[10,11] rhodium(III) complexes have been previously reported. The tris-diimine complexes all exhibit ligand-based π–π* emission in frozen solvent matrixes at 77 K and no emission in fluid solution at room temperature.[6–9] By contrast, in frozen solvent matrixes at 77 K, the tris-dithiolate complexes exhibit metal-based d–d* emission for the Rh(Me$_2$dtc)$_3$ {Me$_2$dtc = dimethyldithiocarbamate}[10,11] and both d–d* and ligand-to-metal charge transfer (π–d*) for the Rh(SS)$_3$ {SS = sulfur analogues of β-diketones}.[10,11]

Mixed ligand dithiolate and diimine complexes of zinc, osmium, ruthenium, and platinum have exhibited interesting photophysical properties. A series of Zn(NN)(SS) complexes[12–19] exhibit emission from two states at 77 K; a phenanthroline-localized π–π* emission and a ligand-to-ligand charge-transfer (LLCT) band in which the electron is excited from the dithiolate ligand across the d^{10} metal center

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to the phenanthroline π^* orbital. The Pt(NN)(SS) complexes exhibit solvatochromic absorption bands and solution luminescence arising from a metal/dithiolate to a diimine charge-transfer excited state.[20−37] In addition, they display diimine-based $\pi−\pi^*$ emission at 77 K. By contrast, the [Os(NN)$_2$-(SS)]$^{2+}$ complexes (where SS = dithioethers)[38] and a [Ru-(NN)$_2$(SS)]$^+$ complex (where SS = diethyldithiocarbamate)[39] exhibit emission from the lowest lying metal-to-ligand charge-transfer (MLCT) excited state. For the osmium complexes, this emission falls in the visible region of the spectrum, but the ruthenium complex emission falls into the near-IR region.

These systems led us to explore the analogous diimine dithiolate system on a d^6 Rh(III) metal center in order to investigate if unique photophysical and electrochemical properties result and what ligands are lost during the two-electron Rh(III)-to-Rh(I) reduction. In mixed ligand systems, the ligand lost depends on the nature of the ligands present.[1−5,40−43] Mixed ligand systems allow one to tune the electrochemical potential and affect the reactivity of the rhodium metal center. We have recently shown that *cis*-[Rh-(bpy)$_2$(OTf)$_2$][OTf]—where bpy = 2,2′-bipyridine and OTf = trifluoromethanesulfonate acid—is a versatile intermediate for synthesizing mixed diimine ligand complexes of rhodium-(III) by a high yield synthetic pathway.[43] Here, we report on the synthesis of novel [Rh(bpy)$_2$(SS)][PF$_6$]$_n$ complexes, where SS = dimethyldithiocarbamate (Me$_2$dtc), diethyldithio-carbamate (Et$_2$dtc), dibenzyldithiocarbamate (Bz$_2$dtc), 1,1-dicyanoethylene-2,2-dithiolate (*i*-mnt), and 1-(ethoxycarbonyl)-1-cyanoethylene-2,2-dithiolate (ecda), using the triflate complex

as the starting material. Further, these compounds are pure upon precipitation from solution with 80−90% yields under mild reaction conditions.

Experimental Section

RhCl$_3$·xH$_2$O was obtained from Pressure Chemical and was stored in a desiccator over anhydrous CaSO$_4$ upon receipt. *cis*-[Rh(bpy)$_2$(OTf)$_2$][OTf] was synthesized as previously described.[43] Sodium 1-(ethoxycarbonyl)-1-cyanoethylene-2,2-dithiolate [Na$_2$-(ecda)] and sodium 1,1-dicyanoethylene-2,2-dithiolate [Na$_2$(*i*-mnt)] were synthesized as previously reported in the literature.[44,45] Sodium dimethyldithiocarbamate [Na(Me$_2$dtc)] and sodium dibenzyldithio-carbamate [Na(Bz$_2$dtc)] were obtained from TCI America. Sodium diethyldithiocarbamate [Na(Et$_2$dtc)] was obtained from Lancaster Synthesis. Potassium hexafluorophosphate (KPF$_6$) and tetrabutyl-ammonium hexafluorophosphate (^{n}Bu$_4$NPF$_6$) were purchased from Alfa-Aesar. Deuterated solvent, DMSO-d_6 [0.05% tetramethylsilane (TMS) (v/v)], was purchased from Cambridge Isotope Laboratories. Acetonitrile (CH$_3$CN) for spectroscopy was HPLC grade and was dried on an MBraun solvent purification system prior to use. Dimethylformamide (DMF) was Dry-Solv grade (sealed under nitrogen) and removed under nitrogen to keep it dry. ^{n}Bu$_4$NPF$_6$ was recrystallized from hot ethanol and dried under a vacuum at 70 °C for at least 3 days prior to use. Anhydrous ethanol and methanol were purchased from Aldrich. All other reagents were obtained from VWR and were used as received. All syntheses were carried out under a nitrogen atmosphere using standard Schlenk techniques.

Physical Measurements. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer. Absorption spectra were recorded in acetonitrile using an HP 8452 diode array UV−visible spectrophotometer. Emission spectra were recorded with a SPEX Fluorolog-3 fluorometer equipped with a double excitation monochromator (399 nm cutoff filters), a single emission mono-chromator, and a thermoelectrically cooled Hamamatsu R2685P photomultiplier tube. Glassy 4:1 EtOH/MeOH solutions at 77 K were prepared by inserting a quartz tube (9 mm o. d., 7 mm i. d.) into a quartz-tipped finger dewar. Emission spectra were corrected for instrument response using a manufacturer-supplied correction file from 250 to 850 nm. Cyclic voltammograms (CVs) were recorded on a computer-controlled BAS Epsilon potentiostat. CVs were obtained in dry DMF solvent with 0.1 M ^{n}Bu$_4$NPF$_6$ as the supporting electrolyte using a one-compartment, three-electrode cell with a Pt disk working electrode, Pt wire counter electrode, and a Ag/AgCl reference electrode.

[Rh(bpy)$_2$(Me$_2$dtc)][PF$_6$]$_2$·H$_2$O. *cis*-[Rh(bpy)$_2$(OTf)$_2$][OTf] (114 mg, 0.132 mmol) and Na(Me$_2$dtc) (27.2 mg, 0.152 mmol) in methanol (10 mL) were placed in a 50 mL Schlenk flask, fitted with a condenser, then stirred under nitrogen for 25 min. The solution was heated for 30 min at 35 °C to dissolve the Na(Me$_2$-dtc), 15 min at 50 °C, and 30 min at reflux. The reaction was cooled on ice for 5−10 min, 25 mL of saturated aqueous KPF$_6$ solution was added, and the mixture was stirred on ice for an additional 30 min. The solution was concentrated to 20 mL on a rotary evaporator. The product was isolated by vacuum filtration, and the resultant solid was washed with a minimum amount of water. The resulting solid was washed with diethyl ether (3 × 15 mL) and finally dried under a vacuum. Yield of light yellow powder: 90% (101 mg, 0.120 mmol). Anal. Calcd for C$_{23}$H$_{24}$F$_{12}$N$_5$OP$_2$RhS$_2$: C, 32.75; H, 2.87; N, 8.30. Found: C, 32.75; H, 2.56; N, 8.33. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.38 (d, J = 5.26 Hz, 2H), 8.98 (d, J = 8.04 Hz,

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2H), 8.88 (d, $J = 8.30$ Hz, 2H), 8.62 (t, $J = 7.93$ Hz, 2H), 8.34 (t, $J = 7.72$ Hz, 2H), 8.12 (t, $J = 6.53$ Hz, 2H), 7.79 (d, $J = 5.41$ Hz, 2H), 7.63 (t, $J = 6.23$ Hz, 2H), 3.29 (s, 6H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 201.3 (d, $^2J_{Rh-C} = 5.00$ Hz), 156.0, 154.7, 151.6, 150.3, 141.9, 141.4, 129.7, 128.7, 125.8, 125.3, 120.5, 39.4.

[Rh(bpy)$_2$(Et$_2$dtc)][PF$_6$]$_2$·H$_2$O. [Rh(bpy)$_2$(Et$_2$dtc)][PF$_6$]$_2$·H$_2$O was prepared as above, using *cis*-[Rh(bpy)$_2$(OTf)$_2$][OTf] (112 mg, 0.130 mmol) and Na(Et$_2$dtc) (34.4 mg, 0.153 mmol). Yield of light yellow product: 88% (100 mg, 0.115 mmol). Anal. Calcd for C$_{25}$H$_{28}$F$_{12}$N$_5$OP$_2$RhS$_2$: C, 34.46; H, 3.01; N, 8.04. Found: C, 34.76; H, 2.99; N, 8.07. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.38 (d, $J = 5.68$ Hz, 2H), 8.99 (d, $J = 7.99$ Hz, 2H), 8.88 (d, $J = 8.06$ Hz, 2H), 8.63 (t, $J = 7.90$ Hz, 2H), 8.34 (t, $J = 7.78$ Hz, 2H), 8.14 (t, $J = 6.66$ Hz, 2H), 7.81 (d, $J = 5.56$ Hz, 2H), 7.63 (t, $J = 6.55$ Hz, 2H), 3.71 (quartet, $J = 7.08$ Hz, 4H), 1.21 (t, $J = 7.11$ Hz, 6H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 200.9 (d, $^2J_{Rh-C} = 4.51$ Hz), 156.0, 154.7, 151.4, 150.3, 141.9, 141.4, 129.7, 128.7, 125.9, 125.3, 45.3, 12.0.

[Rh(bpy)$_2$(Bz$_2$dtc)][PF$_6$]$_2$. [Rh(bpy)$_2$(Bz$_2$dtc)][PF$_6$]$_2$ was prepared as above, using *cis*-[Rh(bpy)$_2$(OTf)$_2$][OTf] (108 mg, 0.125 mmol) and Na(Bz$_2$dtc) (49.3 mg, 0.167 mmol). Yield of yellow product: 87% (107 mg, 0.109 mmol). Anal. Calcd for C$_{35}$H$_{30}$F$_{12}$N$_5$P$_2$RhS$_2$: C, 43.00; H, 3.09; N, 7.16. Found: C, 42.77; H, 3.10; N, 7.02. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.36 (d, $J = 5.55$ Hz, 2H), 8.99 (d, $J = 8.05$ Hz, 2H), 8.87 (d, $J = 8.09$ Hz, 2H), 8.65 (t, $J = 7.73$ Hz, 2H), 8.33 (t, $J = 7.63$ Hz, 2H), 8.16 (t, $J = 6.69$ Hz, 2H), 7.84 (d, $J = 5.45$ Hz, 2H), 7.62 (t, $J = 6.68$ Hz, 2H), 7.37 (m, 6H), 7.22 (d, $J = 6.18$ Hz, 4H), 5.09 (d, $J = 15.83$ Hz, 2H), 4.87 (d, $J = 15.99$ Hz, 2H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 205.7 (d, $^2J_{Rh-C} = 1.24$ Hz), 156.1, 154.7, 151.4, 150.5, 142.0, 141.4, 133.4, 129.5, 128.9, 128.7, 128.3, 127.5, 125.9, 125.4, 53.7.

[Rh(bpy)$_2$(*i*-mnt)][PF$_6$]·1.5H$_2$O. [Rh(bpy)$_2$(*i*-mnt)][PF$_6$]·1.5H$_2$O was prepared as above, using *cis*-[Rh(bpy)$_2$(OTf)$_2$][OTf] (112 mg, 0.130 mmol) and Na$_2$(*i*-mnt) (29.5 mg, 0.158 mmol) in 20 mL of methanol and refluxing for 90 min. Yield of yellow product: 89% (83 mg, 0.116 mmol). Anal. Calcd for C$_{24}$H$_{19}$F$_6$N$_6$O$_{1.5}$PRhS$_2$: C, 39.63; H, 2.63; N, 11.55. Found: C, 39.73; H, 2.31; N, 11.43. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.45 (d, $J = 4.82$ Hz, 2H), 8.98 (d, $J = 7.70$ Hz, 2H), 8.86 (d, $J = 8.00$ Hz, 2H), 8.62 (t, $J = 7.47$ Hz, 2H), 8.31 (t, $J = 7.22$ Hz, 2H), 8.17 (t, $J = 6.62$ Hz, 2H), 7.79 (d, $J = 4.88$ Hz, 2H), 7.60 (t, $J = 5.83$ Hz, 2H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 208.4 (d, $^2J_{Rh-C} = 3.85$ Hz), 156.1, 154.7, 151.8, 150.2, 141.7, 141.2, 129.8, 128.6, 125.8, 125.2, 113.8, 72.6, 72.5.

[Rh(bpy)$_2$(ecda)][PF$_6$]·2H$_2$O. [Rh(bpy)$_2$(ecda)][PF$_6$]·2H$_2$O was prepared as above, using *cis*-[Rh(bpy)$_2$(OTf)$_2$][OTf] (112 mg, 0.130 mmol) and Na$_2$(ecda) (37.0 mg, 0.139 mmol) in 20 mL of methanol and refluxing for 90 min. Yield of bright yellow-orange solid: 80% (81 mg, 0.103 mmol). Anal. Calcd for C$_{26}$H$_{25}$F$_6$N$_5$O$_4$PRhS$_2$: C, 39.86; H, 3.22; N, 8.94. Found: C, 39.95; H, 2.84; N, 8.88. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.49 (quartet, $J = 5.74$ Hz, 2H), 8.96 (d, $J = 8.24$ Hz, 2H), 8.86 (d, $J = 8.04$ Hz, 2H), 8.59 (t, $J = 7.78$ Hz, 2H), 8.30 (t, $J = 5.20$ Hz, 2H), 8.15 (t, $J = 6.47$ Hz, 2H), 7.78 (t, $J = 6.37$ Hz, 2H), 7.60 (t, $J = 6.31$ Hz, 2H), 4.05 (quartet, $J = 5.51$ Hz, 2H), 1.16 (t, $J = 7.05$ Hz, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 205.8 (d, $^2J_{Rh-C} = 4.02$ Hz), 162.6, 156.2, 156.1, 154.5, 154.3, 151.8, 151.7, 149.9, 149.7, 141.4, 141.0, 129.5, 128.5, 125.6, 125.0, 116.6, 115.3, 114.7, 94.6, 59.6, 14.3.

Results and Discussion

Synthesis. We exploited the reactivity of the triflate ligands to develop a general, high-yield synthesis of mixed diimine dithiolate rhodium(III) complexes under mild reac-

Scheme 1. Synthesis of [Rh(bpy)$_2$(SS)][PF$_6$]$_n$
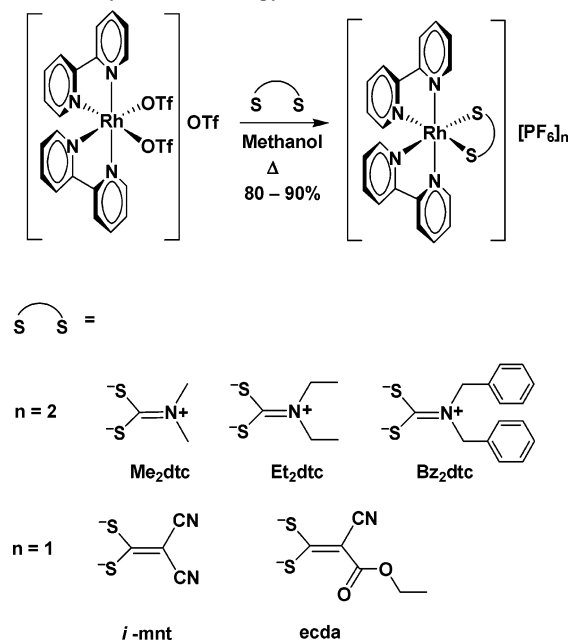
tion conditions (Scheme 1). These reactions were carried out in refluxing methanol in the presence of a slight excess of the SS ligand (~1.2 molar excess). Reaction times were 75 min for the dialkyldithiocarbamates and 90 min for the 1,1′-dithiolates. It was found, for the dialkyldithiocarbamates, that a stepwise increase in the reaction temperature from ~35 to 65 °C resulted in less decomposition of the dithiocarbamate ligands and cleaner products. In all reactions, it was necessary to remove the methanol prior to filtration to prevent methanol from being trapped in the crystal matrix. The dithiolate ligands cleanly replaced the triflates and did not substitute for the 2,2′-bipyridine ligands, thus eliminating the need for chromatography. Washing the product in diethyl ether followed by filtration was carried out to reduce the number of water molecules trapped in the crystal matrix. After drying the compounds overnight in a vacuum oven at 70 °C, the desired compounds were obtained in 80−90% yields. No further purification was required.

NMR Spectroscopy. The data from the ^{1}H and ^{13}C NMR spectra are all consistent with the given complexes. The [Rh-(bpy)$_2$(SS)]$^{n+}$ complexes have approximately C_2 symmetry, and the ^{1}H NMR show the expected eight aromatic signals for the bipyridine protons and the appropriate aliphatic protons for the R$_2$dtc and ecda ligands. In addition, there are some unusual features. The [Rh(bpy)$_2$(Bz$_2$dtc)]$^{2+}$ complex shows two doublets for the methylene protons.[46,47] This arises from the approximate C_2 symmetry of the molecule, which causes the methylene protons attached to the same carbon atom to be inequivalent; thus, these protons occur at different chemical shift values and couple to each other with a J value of 15.9 Hz. ^{13}C NMR spectra all show a doublet for the CS$_2$ signal between 201 and 208 ppm due to the ^{103}Rh (100%

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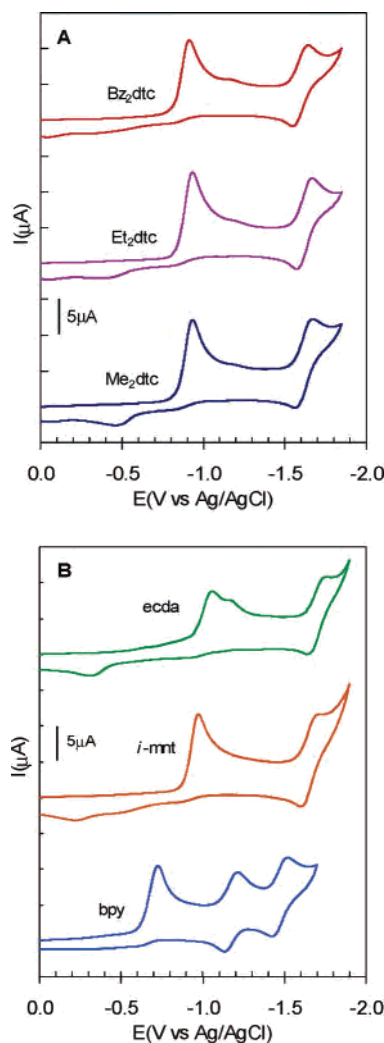
Table 1. Electronic Data for [Rh(bpy)$_2$(SS)][PF$_6$]$_n$

SS	E_{pc}/V^a [Rh(III) − Rh(I)]	$E_{1/2}/V^a$ [bpy/bpy$^-$]	λ_{abs}/nm ($\epsilon/10^4$ M^{-1}cm^{-1})^b	λ_{em}/nm^c
Me$_2$dtc	−0.93	−1.62	246 (4.74), 304 (2.56), 314 (2.54)	787
Et$_2$dtc	−0.93	−1.62	246 (4.61), 302 (2.51), 314 (2.45)	776
Bz$_2$dtc	−0.91	−1.60	244 (4.91), 280 (2.81), 302 (2.68), 312 (2.42)	765
i-mnt	−0.97	−1.66	244 (3.99), 306 sh (3.34), 316 (3.66), 334 (2.35)	~840
ecda	−1.06, −1.18^d	−1.70	242 (3.98), 306 sh (3.16), 314 (3.52), 340 (2.54)	>850^e
bpy^f	−0.73	−1.17, −1.46	242 (3.84), 306 (3.66), 320 (3.63)	450, 484, 519, 554
Cl$_2^g$	−0.80	−1.16, −1.45	230 (4.00), 302 (2.33), 312 (2.73), 402 sh (0.0096)	683

^{a} Cyclic voltammetry in dry DMF with 0.1 M ^{n}Bu$_4$PF$_6$ using Ag/AgCl (0.29 V vs NHE) reference electrode; 200 mV/s scan rate. The ferrocene/ferrocenium redox potential occurs at 0.57 V under these conditions. ^{b} UV-vis absorbance spectra in CH$_3$CN at room temperature in 1 cm quartz cells. ^{c} Emission spectra at 77 K in 4:1 EtOH/MeOH glass in quartz tubes; excitation at 320 nm. Uncertainties in maxima are ±5 nm. ^{d} A shoulder at low scan rates; this becomes a discernible peak at scan rates of 500 mV/s or above. ^{e} Emission maximum is beyond the 850 nm detection limit of our instrument. ^{f} Reference 43. ^{g} Reference 42.

abundant, $I = {}^1/_2$) splitting through the sulfur to the carbon.[48] This two-bond splitting is observed when the Rh−S−C bond angle is approximately 90°.[49] Two-bond splitting was not observed for the bipyridine ligands as the Rh−N−C bond angle is ∼120° and the more electronegative nitrogen makes the predicted splitting too small to be observed.

Electrochemistry. Known rhodium(III) diimine complexes all undergo a chemically irreversible two-electron reduction from Rh(III) to Rh(I) with a concomitant change in coordination number and geometry from octahedral (CN = 6) to square planar (CN = 4). The chemical irreversibility of the initial reduction wave arises from ejection of a ligand after electrochemical reduction of the parent compound. This reduction is followed by two reversible one-electron reductions of the diimine ligands.[40,41] Electrochemical potentials for the five [Rh(bpy)$_2$(SS)][PF$_6$]$_n$ complexes are given in Table 1, and the cyclic voltammograms are shown in Figure 1. The *cis*-[Rh(bpy)$_3$][PF$_6$]$_3$ data are in agreement with data of DeArmond et al.,[40] with differences being attributable to changes in counterion, solvent, and reference electrode. Four of our [Rh(bpy)$_2$(SS)][PF$_6$]$_n$ complexes have a chemically irreversible two-electron wave between −0.91 and −1.06 V followed by one chemically reversible, one-electron bipyridine reduction (Scheme 2). The first wave is assigned as a two-electron reduction based on the fact that the height of the forward wave is twice that of the forward wave for the reversible bipyridine reduction. The chemically irreversible two-electron wave corresponds to the Rh(III) to Rh(I) reduction and the concomitant loss of a ligand as a result of the preference of Rh(I) d^8 complexes for the four-coordinate square-planar geometry. For the ecda complex, the first reduction is split into two peaks which become more distinct at higher scan rates. These data are consistent with the previously proposed reduction mechanism for [Rh(bpy)$_2$Cl$_2$]$^+$ and [Rh(bpy)$_3$]$^{3+}$.[40,41] The Rh(III) complex accepts one electron to form the Rh(II) complex, which rapidly loses a bipyridine and picks up a solvent molecule to achieve an 18-electron, five-coordinate complex. This complex then picks up the second electron, making it Rh(I), which rapidly loses the solvent molecule to form the four-coordinate, 16-electron, square-planar geometry preferred by a d^8 metal.
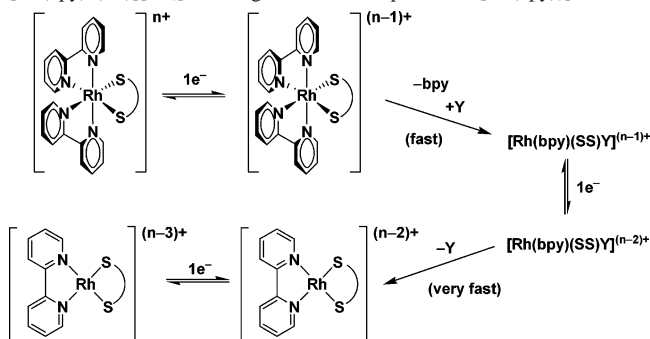
(48) Van Gaal, H. L. M.; Diesveld, J. W.; Pijpers, F. W.; Van der Linden, J. G. M. *Inorg. Chem.* **1979**, *18*, 3251.
(49) Silverstein, R. M.; Webster, F. X. *Spectroscopic Identification of Organic Compounds*, 6th ed.; John Wiley & Sons: New York, 1998.

Figure 1. Cyclic voltammograms in 0.1 M ^{n}Bu$_4$NPF$_6$/DMF, scan rate = 200 mV/s, potentials reported vs the Ag/AgCl (0.29 V vs NHE) reference electrode at room temperature. The ferrocene/ferrocenium cation potential occurs at 0.57 V under the same conditions.

The remaining bipyridine then undergoes an electrochemically reversible, one-electron reduction.

Comparison of the cathodic peak potentials (E_{pc}) for the chemically irreversible two-electron wave of the [Rh(bpy)$_2$(SS)][PF$_6$]$_n$ complexes to that of [Rh(bpy)$_3$]$^{3+}$ shows that this reduction is significantly more negative for the mixed diimine dithiolate complexes than for [Rh(bpy)$_3$]$^{3+}$. These data are consistent with the presence of the strongly electron-donating

Scheme 2. Proposed Electrochemical Reduction Pathway for [Rh(bpy)₂(SS)][PF₆]ₙ Analogous to that Proposed for [Rh(bpy)₃]³⁺ [40]

Figure 2. UV-vis absorption spectra of [Rh(bpy)₂(SS)][PF₆]ₙ in CH₃CN.

Figure 3. Emission spectra of [Rh(bpy)₂(SS)][PF₆]ₙ in 4:1 EtOH/MeOH at 77 K; λ_{ex} = 320 nm, 400 nm cuton filter.

sulfur ligands on the rhodium center and delocalization of electron density from the sulfur p orbitals to the rhodium d orbitals, thus making the bipyridine attached to the rhodium center harder to reduce. This has also been seen in Pt(NN)-(SS)[27,34,35] and [Ru(bpy)₂(SS)]⁺ complexes.[38,50]

In all five compounds reported, the reversible $E_{1/2}$ values for the one-electron bipyridine-based reduction are shifted to more negative potentials by ∼480 mV relative to the first reversible bipyridine reduction potential of [Rh(bpy)₃]³⁺ (Table 1 and Figure 1). This strongly suggests that the bipyridine ligand is lost after the initial reduction of Rh(III) to Rh(I). If the SS ligand had been lost, then the resulting four-coordinate complex would be [Rh(bpy)₂]⁺ and would give the same two one-electron bipyridine reduction potentials as seen for [Rh(bpy)₂]⁺ generated from the [Rh(bpy)₃]³⁺ complex.[40,41] Since this was not observed, we believe that the [Rh(bpy)(SS)]ᵐ (where $m = 0$ or -1) species was formed for all five dithiocarbamate and dithiolate ligands. The bipyridine reduction potentials of our [Rh(bpy)(SS)]ᵐ complexes are very similar to those seen in the Pt(NN)(SS) complexes where the HOMO is described as being of mixed Pt (d)/S (p).[27,34,35] This suggests that, in this [Rh(bpy)(SS)]ᵐ system, there is significant mixing of the rhodium d orbital and the sulfur p orbitals on the dithiocarbamate and dithiolate ligands.

Electronic Spectroscopy. All five [Rh(bpy)₂(SS)]ⁿ⁺ complexes show the three 2,2′-bipyridine-based $\pi-\pi^*$ absorptions at 246, 304, and 314 nm (Table 1 and Figure 2). The [Rh(bpy)₂(Bz₂dtc)]²⁺ complex shows an additional absorbance at 280 nm due to the $\pi-\pi^*$ absorbance of the benzene ring. The [Rh(bpy)₂(i-mnt)]⁺ and [Rh(bpy)₂(ecda)]⁺ complexes show additional transitions at 334 and 340 nm, respectively. The molar absorptivities of ∼24 000 suggest that these are interligand $\pi-\pi^*$ charge transfer (LLCT) transitions (from a filled dithiolate π orbital to an unoccupied π^* diimine orbital) or a mixed metal/ligand-to-ligand (dithiolate-to-diimine) interligand $\pi-\pi^*$ charge transfer (MMLL′CT) as is seen in the case of the Pt(NN)(SS) complexes[27,34] rather than MLCT excited states as are seen for [Ru(NN)₂(SS)]⁺ complexes.[38,39,50] Assignment of the additional band as a MMLL′CT state would be consistent with delocalization of the dithiolate ligand electron density into the metal d* orbitals
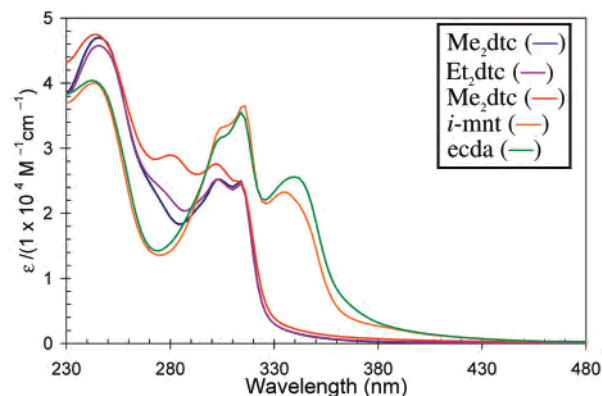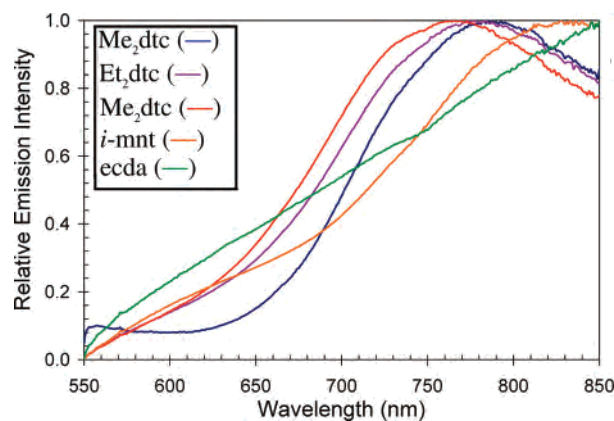
as these bands are only present in the case of the i-mnt and ecda ligands. Clearly, solvent-dependent studies of these complexes must be undertaken to determine the nature of these excited states.

Rhodium(III) diimine complexes only exhibit emission at low temperatures in frozen solvent glasses or in the solid state.[51,52] [Rh(bpy)₃]³⁺ exhibits emission from a ligand-based $\pi-\pi^*$ state, while [Rh(bpy)₂X₂]⁺—where X = Cl, Br, or I,[51,52]—and Rh(Me₂dtc)₃[10,11] exhibit emission from a metal-based d−d* state. The emission spectra of all five [Rh(bpy)₂-(SS)]ⁿ⁺ complexes are all typical of d−d* transitions; they exhibit broad featureless emissions in the near-IR region of the spectrum that are only present at 77 K in a frozen 4:1 EtOH/MeOH glass matrix (Figure 3). No emission is observed at room temperature either in fluid solution or in the solid state. However, there are some marked differences between rhodium(III) diimine complexes containing dialkyldithiocarbamate ligands and those containing 1,1′-dithiolate ligands. The emission maxima (λ_{em}) for the [Rh(bpy)₂(Me₂-dtc)]²⁺, [Rh(bpy)₂(Et₂dtc)]²⁺, and [Rh(bpy)₂(Bz₂dtc)]²⁺ complexes occur between 765 and 787 nm and are significantly red shifted relative to the emission maximum for [Rh-(bpy)₂Cl₂][PF₆] (see Table 1). This shift to lower energy is indicative of the delocalization of electron density from the dithiocarbamates ligands onto the metal center. Within this

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(51) Carstens, D. H. W.; Crosby, G. A. *J. Mol. Spectrosc.* **1970**, *34*, 113.
(52) Kalyanasundaram, K. *Photochemistry of Polypyridine and Porphyrin Complexes*; Academic Press: San Diego, CA, 1992.

series of dithiocarbamate complexes, the emission maxima blue-shift from 787 nm for [Rh(bpy)$_2$(Me$_2$dtc)]$^{2+}$ to 765 nm for [Rh(bpy)$_2$(Bz$_2$dtc)]$^{2+}$. This indicates that there may be Rh (d)/S (p) mixing and greater delocalization for the methyl group and significantly less Rh (d)/S (p) mixing and, consequently, less delocalization for the benzyl group.

Among the 1,1′-dithiolate complexes, the [Rh(bpy)$_2$(*i*-mnt)]$^+$ emission maximum occurs at about 840 nm, while the [Rh(bpy)$_2$(ecda)]$^+$ complex exhibits emission beyond the limit of our detection system (>850 nm). This red-shifting of the emission maximum indicates greater delocalization of electron density and a concomitant lowering of the energy of the emitting excited state and is consistent with the larger conjugated system in the case of the dithiolate ligands where the conjugation extends onto the cyano and ethyl ester groups. The fact that both the lowest-energy absorption band and emission maxima are shifted to lower energy from the *i*-mnt to ecda complex lends further support to the notion of a larger conjugated system.

Conclusions. We have synthesized five diimine dithiolate and diimine dithiocarbamate rhodium(III) complexes in high yield and high purity under mild reaction conditions utilizing the *cis*-[Rh(bpy)$_2$(OTf)$_2$][OTf] intermediate. The electrochemistry of these [Rh(bpy)$_2$(SS)][PF$_6$]$_n$ complexes is consistent with the two-electron reduction of the rhodium metal center and concomitant loss of one of the bipyridine ligands to form [Rh(bpy)(SS)]^m, which then undergoes one reversible 2,2′-bipyridine-based reduction. The 1,1′-dithiolate ligands induce more negative reduction potentials of the 2,2′-bipyridine in the rhodium(III) complex than do the corresponding dithiocarbamate ligands. Similarly, the emission maxima of the 1,1′-dithiolate complexes are at lower energy than the corresponding dithiocarbamate complexes. The absorption spectra of the 1,1′-dithiolate complexes exhibit an additional absorbance at ∼340 nm which is absent in the dithiocarbamate ligands and may indicate the presence of a MMLL′CT band. The electronic properties of these complexes are consistent with significant delocalization of the sulfur electron density onto the empty metal d orbitals as seen by the red shift of the absorption bands and that of the d−d* emission relative to [Rh(bpy)$_2$Cl$_2$][PF$_6$]. We are currently undertaking studies to characterize the nature of this delocalization and determine what factors affect it.