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Expanding the Scope of Ligand Substitution from $[\text{M(S}_2\text{C}_2\text{Ph}_2)]$ ($\text{M} = \text{Ni}^{2+}, \text{Pd}^{2+}, \text{Pt}^{2+}$) to Afford New Classes of Heteroleptic Dithiolene Complexes

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**Abstract.** The scope of direct substitution of dithiolene ligand from \([M(S_2C_2Ph_2)_2] (M = Ni^{2+} (1), Pd^{2+} (2), Pt^{2+} (3))\) to produce heteroleptic species \([M(S_2C_2Ph_2)_2L_n] (n = 1, 2)\) has been broadened to include isonitriles and dithiooxamides in addition to phosphines and diimines. Collective observations regarding ligands that cleanly produce \([M(S_2C_2Ph_2)L_n]\), do not react at all, or lead to ill-defined decomposition identify soft σ donors as the ligand type capable of dithiolene substitution. Substitution of MeNC from \([Ni(S_2C_2Ph_2)(CNMe)_2]\) by \(L\) provides access to a variety of heteroleptic dithiolene complexes not accessible from 1. Substitution of dithiolene ligand from 1 involves net redox disproportionation of the ligands from radical monoanions, \(\cdot S;SC_2Ph_2\), to ene-dithiolate and dithione, the latter of which is an enhanced leaving group that is subject to further irreversible reactions.
Introduction

The emergence of metallodithiolene chemistry as a distinctive subfield of inorganic coordination chemistry was driven by research aimed at understanding the electronic structures of homoleptic bis- and tris(dithiolene) complexes, which did not yield to classical formalisms for describing a d electron count. The seminal studies in this area by Gray, Holm, Schrauzer, and later by Wieghardt, provided the foundation upon which the general concepts of ligand redox non-innocence are now expressed. Scheme 1 illustrates the several redox states accessible to a dithiolene ligand even when coordinated to a transition metal ion.

At the time these early studies were being conducted, heteroleptic dithiolene complexes were also being reported, the first being mono(dithiolene) bis(phosphine) complexes of the Group 10 metals. Several approaches to this compound type were disclosed: Oxidative addition of dithiacyclobutene to [Ni(CO)$_2$(PR$_3$)$_2$] (Eq 1);$^5$ substitution of halide by an ene-1,2-dithiolate salt (Eq 2);$^5$ displacement of dithiolene ligand from a bis(dithiolene) complex by phosphine (Eq 3).$^6$ The last of these approaches is the least obvious, inasmuch as the kinetic advantage of a chelating ligand is overtaken by monodentate ligands, even when the latter is present in sub-stoichiometric amounts. Although it has been applied in the synthesis of [M(S$_2$C$_2$R$_2$)(diimine)] (M = Ni or Pt, R = CF$_3$ or Ph, diimine = phen, diazadiene, or bipy) complexes,$^7-9$ the reaction type of Eq 3 has not been broadly investigated for its generality or for a better understanding of the factors that enable its occurrence. In this report, we present leading results from a systematic examination of this dithiolene displacement reaction, describe the properties of new sets of
heteroleptic Group 10 dithiolene complexes, and provide insight into the ligand attributes necessary for this reactivity to occur and into the fate of the displaced dithiolene ligand.

Experimental

Physical Methods. UV-vis spectra were obtained at ambient temperature with a Hewlett-Packard 8452A diode array spectrometer, while IR spectra were taken either as pressed KBr pellets or as CH$_2$Cl$_2$ solutions with a Thermo Nicolet Nexus 670 FTIR instrument in absorption mode. All $^1$H NMR spectra were recorded at 25 °C either with a Varian Unity Inova spectrometer (400 MHz) or with a Bruker Avance spectrometer (300 mHz). Spectra were referenced to the protonated solvent residual. Mass spectra (MALDI-TOF) were obtained with a Bruker Autoflex III instrument operating in positive ion mode. Electrochemical measurements were made with a CHI620C electroanalyzer workstation using a Ag/AgCl reference electrode, a platinum disk working electrode, Pt wire as auxiliary electrode, and ["Bu$_4$N][PF$_6$] as the supporting electrolyte. Under these conditions, the Cp$_2$Fe$^+$/Cp$_2$Fe reduction consistently occurred at +540 mV, and all potentials are reported relative to this couple. Elemental analyses were performed by Midwest Microlab, LLC of Indianapolis, IN or by Galbraith Laboratories, Inc. of Knoxville, TN.

Emission spectra samples were prepared in a 4:5 propionitrile/butyronitrile solvent mixture and cooled to 77 K using liquid nitrogen. Time-resolved emission spectra (450 nm - 750 nm, 10 nm steps) were collected using an Applied Photophysics LKS 60 optical system. A 355 nm excitation (< 4 ns pulse) was provided by a Quantel Brilliant B Q-switched Nd:YAG laser equipped with frequency doubling and tripling crystals. A 0.2 neutral density filter (Thorlabs) was placed before the sample to decrease the power of the excitation light source to 10 mJ/ pulse. Detection at a right angle was accomplished using a single grating monochromator (Applied Photophysics 0.25m) with PMT detector (Hamamatsu R298). Emission decays were collected using linear oversampling with a 600 MHz Agilent Infiniium oscilloscope.

X-ray Absorption Spectroscopy (XAS). X-ray absorption spectra (XAS) were measured at the Stanford Synchrotron Radiation Lightsource (SSRL). Sulfur K-edge data were obtained using the 20-pole wiggler beamline 4-3. Detailed S K-edge data collection and normalization procedures were followed as previously described.$^{10}$ Data were averaged using EXAFSPAK$^{11}$ and normalized by subtracting the spline and normalizing the postedge to 1.0. The S K pre-edge
features were modeled with lineshapes having fixed mixing ratios (1:1) of Lorentzian and Gaussian functions (pseudo-Voigt) using the program **EDG_FIT**.¹¹

**Syntheses.** The [M(S₂C₂Ph₂)₂] (M = Ni²⁺, Pd²⁺, Pt²⁺) starting materials were synthesized according to the procedure outlined by Schrauzer and Mayweg.⁶ Methyl isonitrile was prepared by the dehydration of N-methylformamide,¹² and its density was experimentally determined to be 0.78 g/mL. The tert-butyl and phenyl isonitriles were synthesized via the phase-transfer Hofmann-carblylamine reaction.¹³ The 1,4-diisopropylpiperidine-2,3-dithione (Pr₂pipdt) ligand was synthesized by a modification of the procedure documented by R. Isaksson et al.¹⁴ The IPr-HBF₄ (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) protected form of the carbene ligand was prepared and unmasked under N₂ following the protocol documented by Bantreil and Nolan.¹⁵ The free IPr ligand was stored in the glovebox. Purifications by column chromatography were conducted in open air using 60–230 μm silica (Dynamic Adsorbents) and solvents used as received from Fisher Scientific. The numbering system employed hereafter in compound identification is that defined in **Scheme 1**. The following descriptions of synthesis procedures are representative; forthcoming reports will fully detail the preparations and physical characterizations of all new compounds.

**[Ni(S₂C₂Ph₂)(CNMe)₂], 4a.** Methyl isonitrile (0.020 mL, 0.0156 g, 0.38 mmol) was added to a solution of 1 (0.100 g, 0.184 mmol) in CH₂Cl₂ (25 mL). The mixture was stirred at 25 °C for 5 h, after which time the solvent was removed under reduced pressure. The dark blue residual solid was applied directly to the top of a silica gel column packed as a slurry in hexanes. Flash elution with 1:1 CH₂Cl₂:hexanes moved a dark green band of unreacted 1, followed by a blue band of 4a. Following collection of the fraction containing 1, continued elution with 2:1 CH₂Cl₂:hexanes enabled collection of the blue fraction of 4a. This blue fraction was taken to dryness under reduced pressure. The residual solid was washed with n-pentane and then redissolved in a minimal volume of CH₂Cl₂. The resulting solution was filtered through a Celite pad and reduced to dryness again. Following drying of the solid for 1 h under reduced pressure, crystallization was accomplished by slow diffusion of Et₂O vapor into a concentrated dichloromethane solution. Yield: 0.051 g, 79%. Rₓ = 0.11 (2:1 CH₂Cl₂ :hexanes).¹⁶¹ H NMR (δ, ppm in CD₂Cl₂): 7.16-7.09 (m, 6H, Ph), 7.08-7.05 (m, 4H, Ph), 3.36 (s, 6H, Me). Solution IR (CH₂Cl₂, cm⁻¹): 2228 (vs, CN sym), 2214 (vs, CN asym). Absorption spectrum (CH₂Cl₂) λ max nm (εM): 274 (31700), 348
Cyclic voltammetry: \( 4a - e^- \rightarrow [4a]^{1+}, -0.02 \text{ V} \). Anal. Calcd for C\(_{18}\)H\(_{16}\)N\(_2\)S\(_2\)Ni: C, 56.42; H, 4.22; N, 7.31. Found: C, 56.20; H, 3.92; N, 7.24.

\[ \text{[Pd(S}_2\text{C}_2\text{Ph}_2)(\text{CNBu}_2)]} \], \( 5c \). Procedures similar to that described above for the synthesis and purification of \( 4a \) were employed but with 0.40 mL (0.338 mmol) of \( \text{tert-} \)butylisonitrile and 0.100 g (0.169 mmol) of \( 2 \) in 25 mL CH\(_2\)Cl\(_2\), ultimately affording red crystals of \( 5c \). Yield: 0.056 mg, 71\%. Rf = 0.38 (2:1 CH\(_2\)Cl\(_2\):hexanes). \(^1\)H NMR (δ, ppm in CD\(_2\)Cl\(_2\)): 7.14-7.11 (m, 6H, Ph), 7.09-7.06 (m, 4H, Ph), 1.56 (s, 18H, \(^1\)Bu). Solution IR (CH\(_2\)Cl\(_2\), cm\(^{-1}\)): 2213 (vs, CN\(_{sym}\)), 2197 (vs, CN\(_{asym}\)). Absorption spectrum (CH\(_2\)Cl\(_2\) \( \lambda_{max} \) nm (\( \epsilon_M \)): 240 (32500), 336 (17300), 498 (620), 419 (860). Cyclic voltammetry: \( 5c - e^- \rightarrow [5c]^{1+}, +0.06 \text{ V} \).

\[ \text{[Pt(S}_2\text{C}_2\text{Ph}_2)(\text{CNPh})_2]} \], \( 6e \). Procedures similar to that described above for the synthesis and purification of \( 4a \) were employed but with 0.28 mL (2.95 mmol) of phenylisonitrile and 0.100 g (0.147 mmol) of \( 3 \) in CH\(_2\)Cl\(_2\) (25 mL), ultimately producing yellow crystals of \( 6e \). Yield: 0.03770 g, 59\%. Rf = 0.66 (2:1 CH\(_2\)Cl\(_2\):hexanes). \(^1\)H NMR (δ, ppm in CD\(_2\)Cl\(_2\)): 7.53-7.48 (m, 10H, PhCN), 7.16-7.14 (m, 6H, Ph), 7.13-7.11 (m, 4H, Ph). Solution IR (CH\(_2\)Cl\(_2\), cm\(^{-1}\)): 2199 (vs, CN\(_{sym}\)), 2172 (vs, CN\(_{asym}\)). Absorption spectrum (CH\(_2\)Cl\(_2\) \( \lambda_{max} \) nm (\( \epsilon_M \)): 274 (35800), 390 (4070). Cyclic voltammetry: \( 6e - e^- \rightarrow [6e]^{1+}, +0.19 \text{ V} \). Anal. Calcd for C\(_{28}\)H\(_{20}\)N\(_2\)S\(_2\)Pt: C, 52.24; H, 3.14; N, 4.35. Found: C, 52.52; H, 3.15; N, 4.50.

\[ \text{[Ni(S}_2\text{C}_2\text{Ph}_2)(\text{Pr}_2\text{pipdt})]} \], \( 7 \). A solution of \(^1\)Pr\(_2\)pipdt (0.300 g, 1.30 mmol) in MeC≡N (5 mL) was added to a solution of \( 1 \) (0.708 g, 1.30 mmol) in CH\(_2\)Cl\(_2\) (25 mL), and the resulting mixture was stirred for 6 h at 25 °C. Unreacted starting material and excess ligand were separated from the product by flash column chromatography on silica (2:1 CH\(_2\)Cl\(_2\):hexanes). Dark green \( 7 \) was eluted subsequently using 100\% CH\(_2\)Cl\(_2\). The solvent was removed under reduced pressure, and the residual solid was washed with \( n \)-pentane. Following redissolution in a minimal volume of CH\(_2\)Cl\(_2\) and filtration of that solution through Celite, \( 7 \) was crystallized by the slow introduction of Et\(_2\)O by vapor diffusion. Yield: 0.281 g, 63\%. Rf = 0.24 (CH\(_2\)Cl\(_2\)). \(^1\)H NMR (δ, ppm in CD\(_2\)Cl\(_2\)): 7.26-7.24 (m, 6H, Ph), 7.14-7.12 (m, 4H, Ph), 3.33-3.31 (m, 2H, \(^1\)Pr), 3.37-3.35 (t, 4H, CH\(_2\)), 1.40-1.39 (d, 12H, \(^1\)Pr). Absorption spectrum (CH\(_2\)Cl\(_2\) \( \lambda_{max} \) nm (\( \epsilon_M \)): 319 (11900), 940 (6020). Cyclic voltammetry: \( 7 - e^- \rightarrow [7]^{1+}, -0.19 \text{ V} \); \( 7 + e^- \rightarrow [7]^{1-}, -1.30 \text{ V} \). MALDI MS: \( m/z \) C\(_{24}\)H\(_{28}\)N\(_2\)NiS\(_4\): 530.049, Observed: 530.024. Anal. Calcd for C\(_{24}\)H\(_{28}\)N\(_2\)NiS\(_4\): C, 54.23; H, 5.32; N, 5.27. Found: C, 54.06; H, 5.28; N, 5.27.
A solution of 3,4,7,8-tetramethyl-1,10-phenanthroline (0.050 g (0.189 mmol) was introduced to a solution of 1 (0.189 mmol) in CH$_2$Cl$_2$ (25 mL), and the resulting mixture was stirred overnight at 25°C. The unreacted starting material and excess ligand were separated from the product by flash column chromatography (2:1 CH$_2$Cl$_2$ : hexanes) followed by elution of the dark purple product using 100% CH$_2$Cl$_2$. The solvent was removed under reduced pressure, and the crude solid product was washed with n-pentane. The product was dissolved in a minimum amount of 1,2-dichloroethane, filtered through Celite and crystallized by slow diffusion of tert-butyl methyl ether vapor into the concentrated solution of 1,2-dichloroethane. Yield: 0.04436 g, 71%. R$_f$ = 0.67 (CH$_2$Cl$_2$). $^1$H NMR (δ, ppm in CD$_2$Cl$_2$): 8.74 (s, 2H, phen), 7.98 (s, 2H, phen), 7.19-7.16 (m, 6H, Ph), 7.10-7.08 (m, 4H, Ph), 2.62 (s, 6H, Me), 2.49 (s, 6H, Me). Absorption spectrum (CH$_2$Cl$_2$) λ$_{max}$ nm ($\varepsilon_M$): 275 (32000), 367 (6500), 567 (5200), 868 (2850). MALDI MS: m/z C$_{30}$H$_{26}$N$_2$NiS$_2$: 538.084, Observed: 538.393.

[Ni(S$_2$C$_2$Ph$_2$)(Me$_2$phen)], 10. A solution of 3,4,7,8-tetramethyl-1,10-phenanthroline (0.050 g (0.189 mmol) was introduced to a solution of 1 (0.189 mmol) in CH$_2$Cl$_2$ (25 mL), and the resulting mixture was stirred overnight at 25°C. The unreacted starting material and excess ligand were separated from the product by flash column chromatography (2:1 CH$_2$Cl$_2$ : hexanes) followed by elution of the dark purple product using 100% CH$_2$Cl$_2$. The solvent was removed under reduced pressure, and the crude solid product was washed with n-pentane. The product was dissolved in a minimum amount of 1,2-dichloroethane, filtered through Celite and crystallized by slow diffusion of tert-butyl methyl ether vapor into the concentrated solution of 1,2-dichloroethane. Yield: 0.04436 g, 71%. R$_f$ = 0.67 (CH$_2$Cl$_2$). $^1$H NMR (δ, ppm in CD$_2$Cl$_2$): 8.74 (s, 2H, phen), 7.98 (s, 2H, phen), 7.19-7.16 (m, 6H, Ph), 7.10-7.08 (m, 4H, Ph), 2.62 (s, 6H, Me), 2.49 (s, 6H, Me). Absorption spectrum (CH$_2$Cl$_2$) λ$_{max}$ nm ($\varepsilon_M$): 275 (32000), 367 (6500), 567 (5200), 868 (2850). MALDI MS: m/z C$_{30}$H$_{26}$N$_2$NiS$_2$: 538.084, Observed: 538.393.

[Ni(S$_2$C$_2$Ph$_2$)(Me$_2$DAD$_{Mes}$)], 11. A solid portion of N,N'-dimesityl-2,3-butanediimine (diazadiene, Me$_2$DAD$_{Mes}$) (0.023 g, 0.070 mmol) was added to a CH$_2$Cl$_2$ solution of 4a (0.0270 g, 0.070 mmol), which occasioned an immediate color change from blue to green. The resulting mixture was allowed to stir for 3 h at 25°C, after which time the solvent was removed under reduced pressure. The residual solid was purified by chromatography on a silica column packed as a slurry in hexanes. Unreacted diazadiene ligand was separated first by flash elution with 100% hexanes; continued elution with the 2:1 CH$_2$Cl$_2$:hexanes moved 11 as a green band.
Following collection of 11, the solvent was removed under reduced pressure, and the remaining solids were washed with n-pentane. Redissolution in a minimal amount of CH$_2$Cl$_2$, filtration through Celite and slow crystallization by introduction of Et$_2$O via vapor diffusion afforded 11 as green-yellow columns. Yield: 0.0444 g, 67%. R$_f$ = 0.80 (2:1 CH$_2$Cl$_2$:hexanes). $^1$H NMR (δ, ppm in CD$_2$Cl$_2$): 7.03-7.02 (m, 6H, Ph), 7.01-6.99 (m, 4H, Ph), 6.92 (s, mesityl CH), 2.35 (s, 6H, mesityl CH$_3$), 2.33 (s, 12H, mesityl CH$_3$), 2.27 (s, 6H, diene CH$_3$). Absorption spectrum (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ nm ($\epsilon_M$): 234 (44000), 270 (17500), 316 (13900), 478 (1200), 776 (6600). Cyclic voltammetry: 11 $\rightarrow$ e$^-$ $\rightarrow$ [11]$^{1+}$, 0.00 V; 11 + e$^-$ $\rightarrow$ [11]$^{1-}$, -1.71 V. MALDI MS: m/z C$_{60}$H$_{38}$N$_2$NiS$_2$: 620.183, Observed: 620.058.

$[\text{Ni(S}_2\text{C}_2\text{Ph}_2)(\text{IPr})(\text{CNMe})]$, 12. Under a protecting atmosphere of N$_2$, a 25 mL Schlenk flask was charged with a Teflon-coated stir bar, free IPr ligand (0.050 g, 0.130 mmol), and anhydrous THF (10 mL) delivered via gas-tight syringe. To this homogeneous stirring solution was then added via cannula a solution of 4a (0.020 g, 0.052 mmol) in 10 mL THF. The resulting purple-colored mixture was stirred at 25°C overnight under N$_2$. The solvent was removed under reduced pressure, and the residual solid was purified by flash column chromatography from a silica column eluted with 2:1 CH$_2$Cl$_2$:hexanes. Crystallization of the purple solid obtained after removal of the eluting solvents was accomplished by the diffusion of hexanes vapor into a concentrated 1,2-dichloroethane solution. Yield: 0.0272 g, 71%. R$_f$ = 0.18 (2:1 CH$_2$Cl$_2$: hexanes). $^1$H NMR (δ, ppm in CD$_2$Cl$_2$): 7.58 (s, 2H, IPr C(H)=C(H)), 7.57-7.54 (m, 6H, dithiolene Ph), 7.41-7.19 (m, 4H, dithiolene Ph), 7.15-7.00 (m, 6H, IPr Ph), 3.17 (s, 3H, isonitride CH$_3$), 2.89-2.97 (m, 4H, IPr CH), 1.34 (d, 12H, IPr CH$_3$), 1.13 (d, 12H, IPr CH$_3$). Solution IR (CH$_2$Cl$_2$, cm$^{-1}$): 2190 (vs, CN). Absorption spectrum (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ nm ($\epsilon_M$): 350 (11600), 560 (410), 867 (120). Cyclic voltammetry: 12 $\rightarrow$ e$^-$ $\rightarrow$ [12]$^{1+}$, -0.13 V; [12]$^{1+}$ $\rightarrow$ e$^-$ $\rightarrow$ [12]$^{2+}$, +0.76 V, irreversible. MALDI MS: m/z C$_{43}$H$_{59}$N$_3$NiS$_2$: 729.272, Observed: 729.182. Anal. Calcd for C$_{43}$H$_{59}$N$_3$NiS$_2$: C, 70.68; H, 6.76; N, 5.75. Found: C, 70.60; H, 7.31; N, 5.46.

$[\text{Et}_4\text{N}]_2[\text{Ni(S}_2\text{C}_2\text{Ph}_2)(\text{CN})_2]$, $[\text{Et}_4\text{N}]_2[13]$. Under an atmosphere of Ar, tetraethylammonium cyanide (0.650, 4.2 mmol) was added to a solution of 4a (0.800 g, 2.1 mmol) in CH$_3$NO$_2$ (15 mL). This mixture was heated to 100 °C with stirring, and a color change from blue to orange was observed after several minutes. After 30 min of heating and stirring, the reaction mixture was cooled to ambient temperature. To assist completion of the ligand substitution, the displaced MeNC was collected in a liquid N$_2$-cooled trap under lowered pressure until the volume of the
solution was reduced by ~1 mL. Heating at 100 °C and stirring under Ar were then continued overnight. Following complete cooling to ambient temperature, the CH$_3$NO$_2$ was fully removed under vacuum to afford a red-brown solid residue. This residue was washed with Et$_2$O (2 x 10 mL) and then redissolved in 10 mL MeCN. The MeCN solution was filtered through a celite pad into a Schlenk tube, and the filtrate was then frozen. An equal volume of Et$_2$O was added via syringe, and the tube was allowed to thaw slowly and the solvents to mix by diffusion over a period of days. Red-brown crystals of [Et$_4$N]$_2$[13] appeared at the solvent interface after several days and were isolated by decanting the mother liquor. The crystals remaining were washed with n-pentane and dried under vacuum. Yield: 0.12 g, 0.196 mmol, 9.3%. $^1$H NMR (δ, ppm in CD$_2$Cl$_2$): 7.25-7.04 (m, 6H, Ph), 7.03-7.25 (m, 6H, Ph), 3.46-3.38 (q, 16H, N(CH$_2$CH$_3$)$_4^+$), 1.39-1.33 (t, 24H, N(CH$_2$CH$_3$)$_4^+$). Solution IR (CH$_3$CN, cm$^{-1}$): 2100 (vs, C≡N sym), 2095 (vs, C≡N asym). Absorption spectrum (CH$_2$Cl$_2$) $\lambda_{max}$ nm ($\varepsilon_M$): 490 (220), 380 (5380).

**4,5-diphenyl-1,3-dithiol-2-cyclohexylimine.** Four equivalents of cyclohexylisonitrile (0.05 mL, 0.368 mmol) were added to a dilute solution of 1 (0.0500 g, 0.092 mmol) in CH$_2$Cl$_2$ (500 mL). The mixture was stirred for 5 h at 25°C, after which time the formation of the product was confirmed by TLC (*vide infra*) with UV lamp visualization. The solvent was then reduced in volume using a rotary evaporator, and a minimal amount of silica (~0.5 g) was added to the
flask. The resulting slurry was taken to dryness. The dry-loaded silica was applied directly to the top of a silica gel column packed as a slurry in hexanes, and the column was then eluted with 1:1 CH$_2$Cl$_2$:hexanes. A fraction of unreacted 1 was collected. The column was continued with the same solvent mixture until incipient elution of 4b (~35 mL). This portion of the eluent was then taken to dryness under reduced pressure, and the residual solid was washed with n-pentane. Crystallization was accomplished by diffusion of Et$_2$O vapor into a CH$_2$Cl$_2$ solution, yielding
Table 2. Selected bond lengths (Å), angles (deg.) for 1a, 2c, 3e, and [13]2+.\(^a\)

<table>
<thead>
<tr>
<th></th>
<th>1a</th>
<th>2c</th>
<th>3e</th>
<th>[13]2+</th>
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</thead>
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<tr>
<td>Δ(^b)</td>
<td>0.288</td>
<td>0.265</td>
<td>0.310</td>
<td>0.287</td>
</tr>
<tr>
<td>C–C(_{chelate})</td>
<td>1.348[1]</td>
<td>1.351(2)</td>
<td>1.345(5)</td>
<td>1.345(2)</td>
</tr>
<tr>
<td>C–M–C</td>
<td>89.91[5]</td>
<td>93.33(7)</td>
<td>92.13(16)</td>
<td>90.70(7)</td>
</tr>
<tr>
<td>θ(^c)</td>
<td>6.9, 12.2</td>
<td>11.7</td>
<td>4.0</td>
<td>4.7</td>
</tr>
</tbody>
</table>

\(^a\)Chemically identical, crystallographically independent values are averaged. Square brackets represent uncertainties propagated according to the general formula for uncertainty in a function of several variables, as detailed in Taylor, J. R. An Introduction to Error Analysis; University Science Books: Sausalito, California, 1997, pp 73-77. \(^b\)Δ = (M–S\(_{ave}\)) – (M–C\(_{ave}\)). \(^c\)θ = angle between MS- planes.

clear to off-white crystals. Yield: 0.0032 g, 9.89%. Melting point = 143-147 °C. R\(_f\) = 0.24 (1:1 CH\(_2\)Cl\(_2\):hexanes). \(^1\)H NMR (δ, ppm in CD\(_2\)Cl\(_2\)): 7.21-7.10 (m, 6H, Ph), 7.10-7.09 (m, 4H, Ph), 3.64–3.62 (m, 1H, Cy), 1.96-1.49 (m, 10H, Cy). Solution IR (CH\(_2\)Cl\(_2\), cm\(^{-1}\)): 1600 (vs, C≡N).

Results and Discussion

A motivating premise to this study was that ligands possessing the good σ-donor and modest π-acid characteristics of a typical phosphine would be those most likely to substitute dithiolene in the fashion illustrated in Eq 3. Arsines notably fail to react with 1 under the mild conditions in which phosphines, with the same set of ancillary alkyl or aryl groups, readily displace a dithiolene ligand (Scheme 2). Isonitriles, however, are plausible candidates that meet the criterion of holding phosphine-like basicity and π-acidity. Solutions of [M(S\(_2\)C\(_2\)Ph\(_2\))] (M = Ni\(^{2+}\), Pd\(^{2+}\), Pt\(^{2+}\)) in CH\(_2\)Cl\(_2\) readily react with C≡N–R (R = Me, Cy, tBu, 1-adamantyl, Ph) to afford [M(S\(_2\)C\(_2\)Ph\(_2\))(C≡N–R)] (M = Ni\(^{2+}\), 4a-e; M = Pd\(^{2+}\), 5a-e; M = Pt\(^{2+}\), 6a-e) in yields of ~70%. The only previously reported Group 10 compounds of this type are [M(S\(_2\)C\(_2\)(CN)\(_2\))(C≡NMe)\(_2\)] which have been prepared by addition of MeNC, followed by Na\(_2\)[S\(_2\)C\(_2\)(CN)\(_2\)], to aqueous NiCl\(_2\) or MCl\(_4\) (M = Pd\(^{2+}\), Pt\(^{2+}\))\(^\text{17}\) solutions. Structural characterizations of [M(S\(_2\)C\(_2\)(CN)\(_2\))(C≡NMe)\(_2\)] (M = Ni\(^{2+}\), Pd\(^{2+}\)) by X-ray crystallography have been reported,\(^\text{16}\) while a structure of [Pt(S\(_2\)C\(_2\)(CN)\(_2\))(C≡NMe)\(_2\)] was later described as a 1:1 co-crystallite with (NC)\(_2\)C\(_2\)S\(_2\)C≡NMe in a sample prepared serendipitously by the reaction of [Pt(C≡NMe)\(_4\)][PF\(_6\)]\(_2\) with [t\(_8\)Bu\(_4\)N]\(_2\)[Cu(S\(_2\)C\(_2\)(CN)\(_2\))]\(_2\).\(^\text{18}\) Heteroleptic dithiolene-isonitride compounds that have been reported with other transition metals include [Mo(S\(_2\)C\(_2\)H\(_2\))(C≡N\(_8\)Bu)\(_2\)]\(^\text{19}\).
[W(S₂C₂Me₂)₂(C≡N'Bu)₂], [M(arene-1,2-dithiolate)(C≡NR)] (M = Mo, W) and [Ru(S₂C₆H₄)(C₆Me₆)(C≡N'Bu)], but none of their syntheses proceeds by displacement of dithiolene ligand from a homoleptic compound by C≡NR.

Compounds 4a-e, 5a-e, and 6a-e are air-stable and amenable to purification by column chromatography on silica and to crystallization by vapor diffusion techniques. Representative examples (4a, 5c, 6e) have been characterized structurally by X-ray crystallography; thermal ellipsoid plots and crystal data are presented in Figure 1 and Table 1, respectively. The structural data, summarized as averaged values where possible, reveal the dithiolene ligands to be fully reduced and show the expected tendency toward greater square planarity, gauged by the angle (θ) between C₂M and S₂M planes, as one moves from Ni to Pd to Pt (Table 2).

The C≡N–R functional group is a useful reporter in the vibrational spectra of these compounds. Table 3 presents the symmetric and anti-symmetric stretching frequencies for these compounds in CH₂Cl₂ solution alongside values for the free isonitrile ligand. For fixed M, υC≡N in the coordination compounds trend in the same way as, but occur at markedly higher energies than, the corresponding free ligands. This observation indicates an absence of metal-to-ligand π-backbonding and instead shows that the divalent metal ion accentuates, presumably by an inductive effect, limiting form (a) of the isonitrile ligand in Scheme 3, which maximizes the C-N bond order.

Table 3. Symmetric and antisymmetric υCN (cm⁻¹) for [M(S₂C₂Ph₂)(CNR)₂] compounds in CH₂Cl₂.

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Pd</th>
<th>Pt</th>
<th>Free ligand</th>
</tr>
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<tbody>
<tr>
<td>MeNC</td>
<td>2214, 2228</td>
<td>2230, 2246</td>
<td>2223, 2246</td>
<td>2168</td>
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<tr>
<td>CyNC</td>
<td>2189, 2204</td>
<td>2203, 2217</td>
<td>2202, 2230</td>
<td>2144</td>
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<tr>
<td>'BuNC</td>
<td>2180, 2197</td>
<td>2197, 2213</td>
<td>2188, 2214</td>
<td>2140</td>
</tr>
<tr>
<td>AdNC</td>
<td>2175, 2196</td>
<td>2198, 2211</td>
<td>2192, 2219</td>
<td>2133</td>
</tr>
<tr>
<td>PhNC</td>
<td>2162, 2182</td>
<td>2182, 2198</td>
<td>2172, 2199</td>
<td>2130</td>
</tr>
</tbody>
</table>
Compounds 4a-d manifest a characteristic blue color of modest intensity arising from a near invariant band at 600 nm (639 for 4e). This transition is a HOMO → LUMO excitation, the former MO being composed largely from a dithiolene C₂S₂ π-type MO and the latter being a σₚ combination of the metal dₓ²−ᵧ² and ligand orbitals. The shift to lower energy for 4e is attributed to a delocalizing effect by the phenyl substituent upon the C≡N multiple bond. Compounds 5a-e reveal spectral features uniformly shifted ~100 nm to higher energy, which imparts a distinctive red hue to their solutions. The effect arises from the inherently higher energy of the Pd 4d orbitals compared to their Ni 3d counterparts and continues with the Pt series (6a-e), which are yellow (Figure 2, top). The sulfur K-edge X-ray absorption spectra for 4a-e and 6a-e (Figure 2, middle) trend in a way that is qualitatively similar to the visible absorption spectra. The lowest
energy band is a superposition of S 1s → LUMO, LUMO+1 transitions. This band is well-separated from the rising edge energy for M= Ni, but for M = Pt, an analogous shift to higher energy by 1 – 1.5 eV produces significant overlap with excitations attributed to intraligand dithiolene transitions.\(^{25}\)

Compounds 6a-e exhibit yellow luminescence in low temperature glasses. Time-resolved emission spectra of the complexes in propionitrile/butyronitrile (4:3) at 77 K (\(\lambda_{ex} = 355\) nm) have maxima between 550 and 600 nm and excited state lifetimes of 55 ± 3 \(\mu\)s for 6a and 6c (Figure 2, bottom). The arylisocyanide complex, 6e, has an emission maximum approximately 20 nm to the red of the alkyl derivatives and a much shorter excited state lifetime (1.2 \(\mu\)s). The combination of spectroscopic and computational results suggests the emissive state is either of dithiolene (nb) to metal (\(\sigma^*\)) or dithiolene to metal-isocyanide (\(\sigma^*\)) charge transfer character. Given the long lifetimes, the emitting state is very likely of triplet spin multiplicity. Related dithiolene-diimine complexes are known to be similarly emissive,\(^{26}\) but typically with lower energy emission maxima, and have been subject to considerable study as chromophores in light-to-electricity\(^7,27-29\) or light-to-chemical energy conversion systems\(^{30-32}\) and as sensors of various
Table 4. Oxidation potentials (V) for [M(S$_2$C$_2$Ph$_2$)(C≡NR)$_2$] $\text{-} \text{e}^{-} \rightarrow$ [M(S$_2$C$_2$Ph$_2$)(C≡NR)$_2$]$^{+}$. in CH$_2$Cl$_2$ vs. Cp$_2$Fe$^{+}$/Cp$_2$Fe with 0.10 M [Bu$_4$N][PF$_6$] supporting electrolyte.

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Pd</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeNC</td>
<td>-0.02</td>
<td>+0.07</td>
<td>+0.10</td>
</tr>
<tr>
<td>CyNC</td>
<td>+0.02</td>
<td>+0.07</td>
<td>+0.13</td>
</tr>
<tr>
<td>'BuNC</td>
<td>+0.05</td>
<td>+0.06</td>
<td>+0.12</td>
</tr>
<tr>
<td>AdNC</td>
<td>+0.03</td>
<td>+0.05</td>
<td>+0.10</td>
</tr>
<tr>
<td>PhNC</td>
<td>+0.08</td>
<td>+0.13</td>
<td>+0.19</td>
</tr>
</tbody>
</table>

sorts.\textsuperscript{33} Preliminarily, for reasons not yet unidentified, room temperature solutions of 6a-e are not emissive.

As is typically observed for [M(S$_2$C$_2$R$_2$)(PR$_3$)$_2$] complexes, compounds 4a-e, 5a-e, 6a-e display as single reversible oxidation followed by an irreversible oxidation process at higher potentials (Table 4). The reversible oxidation is attributed to oxidation of the dithiolene ligand to a radical monoanion from an ene-1,2-dithiolate: Ph$_2$C$_2$S$_2^{2-}$ + e$^{-}$ → Ph$_2$C$_2$S,S$^{-}$. In all cases, the PhNC complexes have the higher potentials for this process, possibly because the phenyl substituent exerts a modest delocalizing effect upon the charge density for the molecule as a whole. For a fixed ligand set, oxidation potentials increase in going from Ni$^{2+}$ → Pd$^{2+}$ → Pt$^{2+}$, suggesting greater positive character to the heavier metal ions and more covalency between metal and ligand in the nickel complexes.

Use of a dithiooxamide ligand, such as the readily prepared $^{i}$Pr$_2$pipdt ($^{i}$Pr$_2$pipdt = 1,4-diisopropylpiperidine-2,3-dithione), also results in facile substitution to afford mixed ene-dithiolate, α-dithione complexes (Scheme 2, 7-9), which feature distinctive, low energy inter-ligand intervalence charge transfer transitions. Figure 3 presents the structure of the M = Ni compound (7), as determined by X-ray diffraction. Compounds of this type, so called “push-pull” complexes, have elicited interest for possible applications arising from their nonlinear optical properties. Previously reported examples of this compound type have the S=CS$_2$C$_2$S$_2^{2-}$ (dimercapoisotrithione ligand(2-), dmit) and have made by an alternate, less direct route involving the transfer of dmit(2-) from [$^{i}$Bu$_4$N][M(dmit)$_2$] to [M(R$_2$pipdt)Cl$_2$] and displacement of Cl$^{-}$ upon mixing solution samples.\textsuperscript{34-36}

Ligands that do not displace dithiolene from [M(S$_2$C$_2$Ph$_2$)$_2$] include [C≡N]$^{1-}$, which instead reduces the compound by one electron (Scheme 2), presumably forming cyanogen as byproduct. The [Ni(S$_2$C$_2$Ph$_2$)$_2$]$^{1-}$ anion was identified structurally as its Et$_4$N$^+$ salt.\textsuperscript{37} Introduction of either
NO(g) or NH₃(g) to CH₂Cl₂ solutions of 1 leads to intractable brown solid, the result of ill-defined decomposition(s). Carbon monoxide, the quintessential π acid, notably fails to produce any reaction with 1 in chlorobenzene solutions heated to ~85 °C for 2 h. This observation indicates that the requisite ligand characteristic for dithiolene displacement is not π-acidity but rather σ basicity of the right degree. The absence of π-backbonding that is evident by the νC≡N values in Table 3 for 4a-e, 5a-e and 6a-e substantiates this notion. Both Me₄phen and Me₂DADMes₂ (Scheme 2) displace a dithiolene ligand from 1, although the latter ligand forms only minor amounts of the dithiolene diimine complex in room temperature reactions. The modest amounts of 11 formed directly from 1 (~6%), compared to yields of ~70% for 10, may arise from the ligand’s preference for a trans disposition of the imine bonds about the diazadiene C–C single bond and consequently the existence of a barrier against the conformation that present both imine nitrogen atoms for chelation.³⁸

The monodentate nature of the isonitrile ligands, the absence of metal-to-ligand π-backbonding in 4-6 evident by IR spectroscopy, and the relative volatility of MeN≡C collectively recommend 4a for study as a synthon toward heteroleptic nickel dithiolene complexes that are not directly accessible from 1, as shown in Scheme 2. The feasibility of MeN≡C substitution from 4a is demonstrated by its facile and complete conversion to 4e (Scheme 4). Compound 11 is formed from 4a in yields of 67% under conditions that yielded only minor amounts from 1. The identity of 11 was confirmed structurally by X-ray diffraction (Figure 3). Two eq of IPr (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) in reaction with 4a produces mono-carbene, mono-isonitrile complex 12, demonstrating an inability to accommodate two bulky carbene
ligands in a cis arrangement. The MeNC ligand in 12 is modestly bent away from the IPr ligand in response to its steric profile, which opens the C(15)–Ni(1)–C(42) angle to 94.4(2)° from a value of 89.91(5) in 4a. The bis(cyanide) dianion [13]$^{2-}$ is accessible from 4a, albeit via a modified preparation involving polar, non-coordinating CH$_3$NO$_2$ as solvent and the application of reduced pressure to remove displaced MeNC as a competing ligand. The structure of the [13]$^{2-}$ (Figure 3 (d)) is square planar and highly similar to 4a but with Ni–S and Ni–C bond lengths (Table 2) that are longer by ~0.015 Å. These increased bond distances likely arise from charge-repulsion effect from four anionic ligands in the coordination sphere. A related nickel compound in which the dithiolene chelate is incorporated to a tetrathiafulvalene system was prepared from
[Ni(CN)₄]²⁻ and the in situ generated ene-1,2-dithiolate and appears to be the only other Group 10 complex of the type.³⁹,⁴⁰

On the basis of abundant structural and spectroscopic data, the dithiolene ligands in 1 are unequivocally radical monoanions ((b), Scheme 1), while the ligand remaining in [Ni(S₂C₂Ph₂)L₂] following substitution by L is an unambiguous ene-1,2-dithiolate dianion ((a), Scheme 1). Considerations of electron balance support formulating the departing dithiolene ligands as a fully oxidized α-dithione (Scheme 5, (d)), a form of the ligand whose inherent reactivity likely leads to rapid oligomerization ((e), Scheme 5). Reasoning that use of excess C≡N−R ligand under dilute conditions should promote its interception of the liberated dithione, the reaction of 1 with 4 eq of C≡N−Cy at micromolar concentration was indeed found to lead to modest, isolable quantities of 4,5-diphenyl-1,3-dithio-2-cyclohexylimine, which was identified structurally (Figure 4). Since the cycloaddition reaction illustrated in Scheme 5 (d) is the obvious mechanism by which this heterocycle would form, its isolation is strongly, if not definitively, indicative of the formation of dithiobenzil.

In his early exploratory studies, Schrauzer did not consider the fate of the dithiolene ligand displaced from 1 by PR₃. In view of the evidence reported here for the fully oxidized state of the departing dithiolene ligand, it appears appropriate to classify the ligand-substitution reactions of Scheme 2 as, fundamentally, net ligand redox disproportionation reactions. Substitution of dithiolene ligand from [Pt(S₂C₂R₂)₂] (R = Me, p-anisyl) has been shown to proceed via association of phosphine to form six-coordinate bis(dithiolene) bis(phosphine) complexes that are isolable (Scheme 5, (h)).⁴¹ This associative step is an atypical oxidative addition because two
electrons move from the divalent metal ion to the dithiolene ligands, thereby forming ene-dithiolates from radical monoanions, rather than to the ligands that have been added. Reductive elimination leaves a square planar M(II) ion with a fully reduced ene-dithiolate (Scheme 5, (i)) and implicitly expels the second dithiolene ligand in a two-electron oxidized form. Although none has been observed, it is probable that the reactions of 1-3 with isonitriles and dithiooxamides similarly proceed through six-coordinate intermediates (Scheme 5, (b)). It is also likely that irreversible oligomerization of the extruded α-dithione provides the thermodynamic impetus for dithiolene ligand substitution in these reactions.

Related Group 10 bis(dithiolene) complexes with electron-deficient substituents such as -CF₃ and -CN have been observed by Dance and Miller to undergo, in the presence of halide anions, amines, and moderate donor solvents, dithiolene displacement reactions mediated by apparent dithiolene-ligand redox disproportionation.⁴² Although none of the putative intermediates was observed, a multi-step mechanism was formulated involving first the substitution of dithiolene ligand and then a set of rapid electron-transfer reactions. Characterization of the process as net ligand redox disproportionation arose from the occurrence of both reduced bis(dithiolene) complex and oxidized free dithiolene ligand (detected spectroscopically) in the overall reaction, typified by Eq 4. Dance and Miller noted the similarity of Eq 5, their proposed first step, to the type of dithiolene ligand substitution reactions shown in Scheme 2 but conceded that “the distribution of charge between the intermediate mixed ligand complex and the displaced dithiolene ligand is uncertain.”⁴² An absence of the insights that are now offered by modern physical methods and DFT computations prevented Dance and Miller from recognizing Eq 5 and reactions of the type in Scheme 2 as ligand redox disproportionation reactions themselves.

In summary, this report maps out more fully the landscape of possible dithiolene ligand substitution reactions from [M(S₂C₂R₂)₂] (M = Ni²⁺, Pd²⁺, Pt²⁺), which until now has been limited only to substitution by phosphines and diimines. Isonitrile ligands of all types effectively displace one of two dithiolene ligands to afford a new group of organometallic dithiolene complexes. Similarly, dithiooxamides such as ‘Pr₂pipdt yield dithiolate-dithione “push-pull” complexes in a direct and efficient manner. The feasibility of these reactions likely arises from
the dithiolene ligand’s capacity to exert its redox non-innocence in supporting formation of the transient intermediates [M^{IV}(^2S2C2Ph2)2(C≡NR)] and [M^{IV}(^2S2C2Ph2)2(Pr2pipdt)] from [M^{II}(S,SC2Ph2)]. Because these putative intermediates entail two-electron redox chemistry between dithiolene ligand and metal in a net non-redox step, the system adheres to the notion that redox non-innocence be a behavior or property involving a combination of both metal and ligand. Ultimately, reductive elimination of α-dithione from [M^{IV}(^2S2C2Ph2)(C≡NR)2] occurs in what amounts to a net dithiolene redox disproportionation. Although proposed decades earlier by Dance to account for the decomposition of electron-deficient bis(dithiolene) complexes in the presence of weak nucleophiles such as nitriles, amines, and halide anions, such redox disproportionation appears not to have been recognized as being pertinent to the dithiolene displacement reactions that yield isolable heteroleptic dithiolene complexes. Importantly, in instances where 1 is not amenable to direct dithiolene substitution, methylisonitrile complex 4a promises to be useful as an entry point to new heteroleptic dithiolene compounds, such as the mono-carbene compound 12 and dicyanide anion [13]^2. Following reports will elaborate upon the syntheses, structures, properties and applications of these new sets of compounds.

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI. X-ray data collection procedures, figures of crystallographically characterized compounds with full atom labeling, complete crystal data (CIF). CCDC deposition codes: [Et4N][1], 1553819; 4a 1547459; 5b, 1547460; 6e, 1547461; 7, 1547462; 11, 1547463; 12·ClCH2CH2Cl, 1547464; [Et4N]2[13], 1553820; 4,5-diphenyl-1,3-dithiol-2-cyclohexylimine, 1547465.

Acknowledgments‡
The Louisiana Board of Regents (grant LEQSF-(2002-03)-ENH-TR-67) and NSF (MRI: 1228232; MRI: 0619770) are thanked for instrumentation support. Tulane University is acknowledged for its support of the X-ray diffraction facility.
References


Expanding the Scope of Ligand Substitution from \([\text{M}(\text{S}_2\text{C}_2\text{Ph}_2)] (\text{M} = \text{Ni}^{2+}, \text{Pd}^{2+}, \text{Pt}^{2+})\) to Afford New Classes of Heteroleptic Dithiolene Complexes


The scope of dithiolene substitution from \([\text{M}(\text{S}_2\text{C}_2\text{Ph}_2)]_2 (\text{M} = \text{Ni}^{2+}, \text{Pd}^{2+}, \text{Pt}^{2+})\) to produce \([\text{M}(\text{S}_2\text{C}_2\text{Ph}_2)\text{L}_n] (n = 1, 2)\) has been broadened to include isonitriles and dithiooxamides in addition to phosphines and dimines, all of them relatively soft \(\sigma\) donors. Substitution of dithiolene is enabled by redox disproportionation of the dithiolene ligands from radical monoanions to ene-dithiolate and dithione, the latter of which is an enhanced leaving group that is subject to further irreversible reactions.
Supporting Information

for

Expanding the Scope of Ligand Substitution from
\([M(S_2C_2Ph_2)_2]\) (\(M = \text{Ni}^{2+}, \text{Pd}^{2+}, \text{Pt}^{2+}\)) to Afford
New Heteroleptic Dithiolene Complexes

Antony Obanda‡ Kristina Martinez,‡ Russell H. Schmehl,‡ Joel T. Mague,‡ Igor V. Rubtsov,‡
Samantha N. MacMillan,£ Kyle M. Lancaster,£ Stephen Sproules§ and James P. Donahue*‡

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Diffraction-quality crystals of most of the compounds identified by X-ray diffraction were obtained by vapor diffusion techniques. The following solvent pairs provide specific combinations successfully implemented as solvent/diffusing vapor for crystal growth: 4a (CH₂Cl₂/Et₂O), 5c (CH₂Cl₂/Et₂O), 6e (CH₂Cl₂/n-pentane), 7 (CH₂Cl₂/Et₂O), 11 (CH₂Cl₂/Et₂O), 12 (ClCH₂CH₂Cl) (ClCH₂CH₂Cl/hexanes), 4,5-diphenyl-1,3-dithiol-2-cyclohexylimine (CH₂Cl₂/hexanes). A layered diffusion of Et₂O onto a MeCN solution was employed for the crystallization of [Et₄N][Ni(S₂C₂Ph₂)(CN)]₂, while slow evaporation of a CH₂Cl₂ solution of [Et₄N][Ni(S₂C₂Ph₂)₂] afforded a crystalline sample suitable for diffraction. The color and morphology of each crystal are presented in Table 1 of the manuscript.

All crystals were coated with paratone oil and mounted on the end of a nylon loop attached to the end of the goniometer. Except for 7, for which data were obtained at 100 K with a Bruker D8 Venture Photon 100 instrument, data were collected with a Bruker Smart APEX CCD diffractometer equipped with a Kryoflex attachment supplying a nitrogen stream at 100 K or 150 K. The radiation source employed by the D8 Venture was a Cu Incoatec I microfocus source generating X-rays with λ = 1.54178 nm, while the Smart APEX operated with a Mo fine-focus sealed tube providing radiation at λ = 0.71073 nm. An assemblage of six sets of ω-scan frames comprising a hemisphere of data were collected for 7 using 10 second frame times. All data sets gathered using the Smart APEX CCD instrument employed a collection routine comprised of three sets of 400 frames in ω (0.5°/scan), collected at φ = 0.00, 90.00 and 180.00° and two sets of 800 frames in φ (0.45°/scan) collected with ω constant at -30.00 and 210.00°. The frame time used for these data sets were as follows: [Et₄N][1] (20 sec), 4a (10 sec), 5c (30 sec), 6e (15 sec), 7 (15 sec), 11 (30 sec), 12 (25 sec), [Et₄N]₂[13] (20 sec), 4,5-diphenyl-1,3-dithiol-2-cyclohexylimine (30 sec).

All data were collected under control of either the APEX2¹ or APEX3² software package. Raw data were reduced to F² values using SAINT³, and a global refinement of unit cell parameters was performed using ~8000–10,000 selected reflections from the full data set. In the case of 7, a somewhat smaller set of 6802 reflections was used for the unit cell refinement. Data were corrected for absorption on the basis of multiple measurements of symmetry equivalent reflections with the use of SADABS⁴. All structure solutions were obtained by direct methods.
using SHELXT,\textsuperscript{5} while refinements were accomplished by full-matrix least-squares procedures using SHELXL.\textsuperscript{6} Both the SHELXS and SHELXL programs are incorporated into the SHELXTL\textsuperscript{7} and APEX2\textsuperscript{1}, APEX3\textsuperscript{2} software suites.

All structure refinements were routine and required no special treatment. Hydrogen atoms were added in calculated positions and included as riding contributions with isotropic displacement parameters tied to those of the carbon atoms to which they were attached. Thermal ellipsoid images have been created with the use of XP, which also is part of the SHELXTL package. All structures were checked for overlooked symmetry and other errors by the checkCIF service provided by the International Union of Crystallography.\textsuperscript{8} Final unit cell data and refinement statistics are collected in Table 1 of the manuscript.

References

(7) (a) SHELXTL, Bruker-AXS, Madison, WI, 2015. (b) SHELXTL, Bruker-AXS, Madison, WI, 2016.
(8) See http://checkcif.iucr.org/
Figure S1. Full atom labeling for the [Et$_4$N][Ni(S$_2$C$_2$Ph$_2$)$_2$]. [Et$_4$N][1]. The thermal ellipsoid plot is drawn at the 50% level. Hydrogen atoms are omitted for clarity.

Figure S2. Full atom labeling for the two independent molecules of [(Ph$_2$C$_2$S$_2$)Ni(C=NMMe)$_2$]. 4a. The thermal ellipsoid plot is drawn at the 50% level. Hydrogen atoms are omitted for clarity.
Figure S3. Atom labeling for [(Ph₂C₂S₂)Pd(C≡N'Bu)₂], 5c. The thermal ellipsoid plot is shown at the 50% probability level, and all hydrogen atoms are omitted for clarity.

Figure S4. Atom labeling for [(Ph₂C₂S₂)Pt(C≡NPh)₂], 6e. The thermal ellipsoid plot is shown at the 50% probability level, and all hydrogen atoms are omitted for clarity.
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Figure S6. Complete atom labeling for \([\text{Ni}(S_2C_2\text{Ph}_2)(\text{MeC}^\text{DAD}^\text{Mes})], 11\). The thermal ellipsoid plot is presented at the 50% probability level, and all hydrogen atoms are omitted for clarity.
Figure S7. Complete atom labeling for [Ni(S₂C₂Ph₂)(IPr)(C≡NMe)]·12. The thermal ellipsoid plot is drawn at the 50% probability level, and all hydrogen atoms have been omitted for greater clarity.

Figure S8. Complete atom labeling for the 1,2-dichloroethane interstitial solvent in [Ni(S₂C₂Ph₂)(IPr)(C≡NMe)]·ClCH₂CH₂Cl. The thermal ellipsoid plot is drawn at the 50% probability level.
**Figure S9.** Complete atom labeling for \([\text{Et}_4\text{N}]_2\text{Ni}(\text{S}_2\text{C}_2\text{Ph}_2)(\text{CN})_2\text{].} \) \([\text{Et}_4\text{N}]_2[13]. \) The thermal ellipsoid plot is drawn at the 50% probability level. All hydrogen atoms are omitted for clarity.

**Figure S10.** Complete atom labeling for 4.5-dimethyl-1,3-dithiol-2-cyclohexylimine. The thermal ellipsoid plot is drawn at the 50% level.