

# Synthesis of New Types of Dithiolene Ligands

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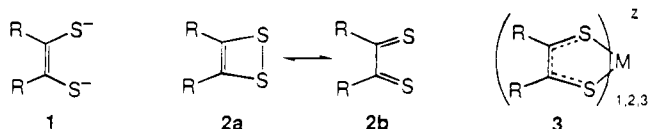
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Three new types of dithiolene ligands have been prepared on the basis of Diels–Alder reactions of the diene 2,3-bis(benzylthio)-1,4-dichloro-5,5-dimethoxy-1,3-cyclopentadiene (**4**), whose structure was established by an X-ray structure determination. Reaction of **4** with excess norbornadiene as the dienophile affords the adduct **5**, S-deprotection and dechlorination of which with sodium in liquid ammonia lead to the ligand salt Na<sub>2</sub>(L-S<sub>2</sub>) (**6**). Treatment of 2 equiv of **4** with 1 equiv of norbornadiene gives the tetraprotected bis(dithiolene) **7**, which is converted to the ligand salt Na<sub>4</sub>(L-S<sub>4</sub>) (**8**) by sodium in liquid ammonia. Reaction of 2-(chloromethyl)-1-(ethoxymethyl)benzimidazole with 1,4-dihydronaphthalen-1,4-imine gives the N-substituted imine dienophile **10**. Reaction of the latter with **4** produces the adduct **11**, which after deprotection affords the ligand salt Na<sub>2</sub>(L-NS<sub>2</sub>) (**12**). The *endo,exo* ligand stereochemical outcome of the Diels–Alder reaction was proven by determination of the structure of [Ni(L-S<sub>2</sub>)<sub>2</sub>] (**13**). This compound crystallizes in monoclinic space group *P*2<sub>1</sub>/*n* with *a* = 7.636(2) Å, *b* = 8.64(4) Å, *c* = 20.962(4) Å, β = 96.57(2)°, and *Z* = 2. The complex is planar and centrosymmetric. The related complex [Ni(L-S<sub>2</sub>)(dppe)]·Et<sub>2</sub>O was isolated in triclinic point group *P*1̄ with *a* = 11.087(5) Å, *b* = 13.173(7) Å, *c* = 15.663(6) Å, α = 90.82(5)°, β = 97.49(3)°, γ = 114.60(3)°, and *Z* = 2. Also prepared were [Pd(L-S<sub>2</sub>)(bpy)] and [Mo(L-S<sub>2</sub>)<sub>3</sub>]. The ligand L-S<sub>2</sub> is the first dithiolene with structure above and below the chelate ring. This feature does not hinder the formation of bis and tris complexes; the collective properties of the four complexes indicate that L-S<sub>2</sub> is a generic dithiolene with electron-releasing substituents. The *endo,exo* stereochemistry of L-S<sub>4</sub> was proven by a crystal structure determination of precursor **7**. This ligand is a bis(dithiolene) capable of forming binuclear complexes with multielectron redox capacity. The *endo,exo* stereochemistry of L-NS<sub>2</sub> was demonstrated by the X-ray structure of the protected form **11**. This species is designed as a facial tridentate ligand; the method of synthesis is such that the benzimidazole ligand should be replaceable by other binding groups. (bpy = 2,2'-bipyridyl, dppe = 1,2-bis(diphenylphosphino)ethane.)

## Introduction

Metal dithiolene complexes<sup>1–7</sup> have provoked considerable interest as solid state electrical conductors, near-infrared absorbers in laser Q-switch dyes, nonlinear optical materials, electron carriers in solution, and, generally, objects for investigation of nonclassical electronic structures. Dithiolene ligands are most frequently isolated in the reduced (enedithiolate) form **1** (R =



H, alkyl, aryl, CN; R<sub>2</sub> = SC(S)S).<sup>8</sup> However, a significant number of known or potential ligands are also available in the

dithiacyclobutene (dithiete, **2a**) and dithione (**2b**) forms,<sup>9</sup> which can occasionally exist in equilibrium.<sup>10</sup> Here the term “dithiolene” refers to a ligand in the enedithiolate, dithione, or intermediate oxidation state. Methods of synthesis of dithiolene ligands have been summarized.<sup>5,6</sup> Complexes of **1** are simply formed by reaction with the appropriate metal ion while those of **2a,b** are most usually produced in oxidative addition reactions with reduced metal sources. The vast majority of dithiolene complexes are of the bis- and tris-chelate types; electronically delocalized chelate rings **3** are the consequence of a (mean) ligand oxidation state between 2– and 0.

We have become interested in dithiolene ligands elaborated to contain a second coordinating functionality. All mono-(dithiolenes) thus far characterized function as bidentate ligands. Those which contain two dithiolene functionalities are largely unknown. The few species that include an additional metal binding site (such as a carboxylate, nitrile, or tertiary amine) are not configured so as to bind to the same metal. We describe here preparations of a bis(dithiolene) ligand and of a tridentate dithiolene. The former has the potential of sustaining binuclear complexes with multielectron redox capacity, while the latter is of a type that is of potential interest with regard to models of the molybdenum cofactor<sup>11,12</sup> of oxotransferases;<sup>12</sup> the cofactor

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contains an enedithiolate group attached to a pterin nucleus and coordinated to molybdenum. Recently, bis(dithiolene) coordination was crystallographically demonstrated in a tungsten-containing aldehyde oxidase.<sup>13</sup> Consequently, biological function must be added to the foregoing aspects of contemporary interest in metal dithiolenes.

### Experimental Section<sup>14</sup>

**Preparation of Compounds.** Solvents were dried by standard methods and were distilled before use. 1,4-Dihydronaphthalen-1,4-imine was prepared from 1-bromo-2-fluorobenzene and *N*-(trimethylsilylpyrrole)<sup>15</sup> by literature procedures.<sup>16</sup>

**2,3-Bis(benzylthio)-1,4-dichloro-5,5-dimethoxy-1,3-cyclopentadiene (4).**  $\alpha$ -Toluenethiol (46 g, 0.37 mol) was stirred with ground potassium hydroxide (54 g, 0.77 mol) in 200 mL of Me<sub>2</sub>SO. The supernatant of the mixture was added dropwise to a stirred solution of 1,2,3,4-tetrachloro-5,5-dimethoxy-1,3-cyclopentadiene (46 g, 0.17 mol, Aldrich 95%) in 200 mL of Me<sub>2</sub>SO over 1 h. The mixture was stirred overnight, and the reaction was quenched by adding cold water (500 mL). The resultant slushy mixture was stirred, and the sticky precipitate formed was collected by filtration. This material was dissolved in ethyl ether (800 mL), and the solution was dried with anhydrous sodium sulfate. After the drying agent was removed by filtration, the solution was concentrated on a rotary evaporator until precipitate started forming. The saturated solution was cooled at -20 °C overnight. A yellow solid was collected by filtration; additional product was obtained by volume reduction of the filtrate. The combined crops were purified by recrystallization from ether to afford the product as a yellow crystalline solid (17.4 g, 23%); mp 107–108 °C. Additional product (about 3%) and other byproducts were obtained by extraction of the aqueous layer of the quenched reaction mixture with ether and separation by column chromatography. Analytical samples were obtained by chromatography on silica gel using 8:1 petroleum ether/ethyl ether (v/v) eluant. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.77 (6), 4.27 (4), 7.20 (t, 2), 7.25 (t, 4), 7.30 (d, 4). Anal. Calcd for C<sub>21</sub>H<sub>20</sub>Cl<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: C, 57.40; H, 4.59; S, 14.51. Found: C, 58.06; H, 4.93; S, 14.69. The compound was further identified by an X-ray structure determination.

Three other reaction products were isolated. **2-(Benzylthio)-1,3,4-trichloro-5,5-dimethoxy-1,3-cyclopentadiene:** <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.98 (6), 4.18 (2), 7.2–7.3 (m, 5). **1,3-Bis(benzylthio)-2,4-dichloro-5,5-dimethoxy-1,3-cyclopentadiene:** <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.95 (6), 4.08 (2), 4.32 (2), 7.2–7.3 (m, 10). **1,2,3-(or 1,2,4)-Tris(benzylthio)-4-(or 3-)chloro-5,5-dimethoxy-1,3-cyclopentadiene:** <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.75 (6), 4.15 (2), 4.27 (2), 4.32 (2), 7.2–7.3 (m, 15).

**2,3-Bis(benzylthio)-1,4-dichloro-10,10-dimethoxy-1,4,4a,5,8,8a-hexahydro-1 $\alpha$ ,4 $\alpha$ :5 $\beta$ ,8 $\beta$ -dimethanonaphthalene (5).** A solution of 4 (4.63 g, 10.5 mmol) in norbornadiene (25 mL) was deaerated and refluxed (bath temperature 100–110 °C) under a dinitrogen atmosphere for 120 h. The reaction mixture was cooled and the excess norbornadiene removed in vacuo. The crude product was chromatographed on a silica gel column eluted with 7:1 pentane/ether (v/v). The purified product was obtained as a white waxlike solid in >96% yield; further purification can be achieved by recrystallization from hexane. NMR (CDCl<sub>3</sub>):  $\delta$  1.11 (d, 1), 1.73 (d, 1), 2.51 (2), 2.82 (2), 3.59 (3), 3.62 (3), 3.86 (d, 2), 4.15 (d, 2), 6.26 (2), 7.2–7.3 (m, 10). MS (positive ion CI, NH<sub>3</sub>): *m/z* 548 ([M + NH<sub>4</sub>]<sup>+</sup>), 531 ([M + H]<sup>+</sup>). Anal. Calcd for C<sub>28</sub>H<sub>28</sub>Cl<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: C, 63.27; H, 5.31; Cl, 13.34; S, 12.02. Found: C, 63.33; H, 5.36; Cl, 13.37; S, 12.06.

**Disodium 10,10-Dimethoxy-1,4,4a,5,8,8a-hexahydro-1 $\alpha$ ,4 $\alpha$ :5 $\beta$ ,8 $\beta$ -dimethanonaphthalene-2,3-dithiolate (Na<sub>2</sub>(L-S<sub>2</sub>), 6).** Under a dinitrogen atmosphere, 5 (1.31 g, 2.47 mmol) was suspended in liquid ammonia at -78 °C and titrated with sodium metal (0.45 g, 20 mmol) in small portions; at the end point, a blue color persisted for > 15 min. The reaction was quenched with solid NH<sub>4</sub>Cl (0.57 g, 11 mmol) to

give a yellowish solution. Ammonia was allowed to evaporate, and the solid residue was washed with ether. This material was suspended in methanol (10 mL), and the mixture was filtered. Solvent removal afforded the product as a yellow powder in >90% yield. <sup>1</sup>H NMR (CD<sub>3</sub>OD):  $\delta$  0.96 (d, 1), 1.90 (2), 2.03 (d, 1), 2.55 (2), 2.61 (2), 3.08 (3), 3.17 (3), 6.13 (2).

**2,3,6,7-Tetrakis(benzylthio)-1,4,5,8-tetrachloro-12,12,13,13-tetramethoxy-1,4,4a,5,8,8a,9,9a,10,10a-decahydro-1 $\alpha$ ,4 $\alpha$ :5 $\alpha$ ,8 $\alpha$ :9 $\beta$ ,10 $\beta$ -trimethanoanthracene (7).** A mixture of powdered diene 4 (0.92 g, 2.1 mmol) and norbornadiene (0.12 mL, 1.1 mmol) was placed in a medium-walled glass tube with a stirring bar under a dinitrogen atmosphere. The tube was evacuated when immersed in liquid nitrogen and was sealed. After being heated at 135–140 °C for 40 h with stirring, the tube was cooled and opened. The brown solid was dissolved in dichloromethane and chromatographed on a silica gel column eluted with 2:1 pentane/ether (v/v). The product was obtained as a white solid in 85% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.33 (2), 2.43 (4), 2.64 (2), 3.55 (6), 3.66 (6), 3.85 (d, 2), 4.13 (d, 2), 7.23–7.28 (m, 20). FAB-MS (3-nitrobenzyl alcohol): *m/z* 991 ([M + Na]<sup>+</sup>), 968 (M<sup>+</sup>). Anal. Calcd for C<sub>49</sub>H<sub>48</sub>Cl<sub>4</sub>O<sub>4</sub>S<sub>4</sub>: C, 60.61; H, 4.98; Cl, 14.61; S, 13.21. Found: C, 60.69; H, 5.08; Cl, 14.51; S, 13.31. This compound was further identified by an X-ray structure determination.

**Tetrasodium 12,12,13,13-Tetramethoxy-1,4,4a,5,8,8a,9,9a,10,10a-decahydro-1 $\alpha$ ,4 $\alpha$ :5 $\alpha$ ,8 $\alpha$ :9 $\beta$ ,10 $\beta$ -trimethanoanthracene-2,3,6,7-tetrathiolate (Na<sub>4</sub>(L-S<sub>4</sub>), 8).** Under a dinitrogen atmosphere, a suspension of 6 (0.40 g, 0.41 mmol) in 60 mL of liquid ammonia was titrated with small pieces of sodium metal (0.15 g, 6.5 mmol). The end point was determined as the deep blue color that persisted over 20 min. The reaction was quenched by the addition of solid NH<sub>4</sub>-Cl (0.17 g, 3.2 mmol). The bright yellow solution was allowed to warm slowly to room temperature while ammonia was evaporated with dinitrogen stream. The solid residue was stirred with ether for several hours and the mixture filtered through a fine frit. The remaining solid was extracted with methanol; the extract was filtered, and the filtrate was concentrated. Addition of ether resulted in a precipitate, which was collected and washed with copious amounts of ether to give the product as an off-white solid in 80% yield. <sup>1</sup>H NMR (CD<sub>3</sub>OD):  $\delta$  1.27 (2), 1.76 (4), 2.26 (2), 2.62 (4), 3.10 (12).

**2-(Chloromethyl)-1-(ethoxymethyl)benzimidazole (9).** A solution of chloromethyl ethyl ether (1.9 g, 20 mmol) in dry benzene (10 mL) was added to a stirred suspension of 2-(chloromethyl)benzimidazole (3.3 g, 20 mmol) in dry benzene (30 mL) over a period of 2 h, followed by triethylamine (2.8 mL, 20 mmol). The mixture was stirred for another 2 h and filtered; the filtrate was concentrated to a yellow-orange solid (crop 1). The oily solid residue on the filter was removed and stirred with 0.3 M aqueous K<sub>2</sub>CO<sub>3</sub> solution (100 mL). The mixture was extracted with dichloromethane (3  $\times$  50 mL). The extracts were combined, washed with water, filtered through anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated to an oily brown residue (crop 2). The combined crops were extracted with portions of boiling ether, which left behind a colored residue. The ether extracts were combined, concentrated, and maintained overnight at -78 °C to give the product as a white microcrystalline product which was collected by filtration. Additional crops were obtained from the filtrate to give a total of 2.6 g (58%) of product. An analytical sample was obtained by sublimation in vacuo; mp 98.0–98.5 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.18 (t, 3), 3.51 (q, 2), 4.90 (2), 5.65 (2), 7.28–7.35 (m, 2), 7.48 (d, 1), 7.77 (d, 1). MS (EI, 70 eV): *m/z* 224 (M<sup>+</sup>). Anal. Calcd for C<sub>11</sub>H<sub>13</sub>ClN<sub>2</sub>O: C, 58.80; H, 5.83; N, 12.47. Found: C, 58.67; H, 6.00; N, 12.46.

**9-[(1-(Ethoxymethyl)benzimidazol-2-yl)methyl]-1,4-dihydronaphthalen-1,4-imine (10).** A mixture of 1,4-dihydronaphthalen-1,4-imine (0.62 g, 4.3 mmol), triethylamine (0.66 mL, 4.3 mmol), and 2-(chloromethyl)-1-(ethoxymethyl)benzimidazole (9, 0.97 g, 4.3 mmol) in dry acetonitrile (15 mL) was stirred for 14 h under a dinitrogen atmosphere. The mixture was concentrated on a rotary evaporator to about 10 mL and filtered. The filtrate was evaporated in vacuo to give a viscous oil. The crude product was chromatographed on a basic alumina column eluted with 99:1 dichloromethane/methanol (v/v). The product was obtained as an oily solid (1.2 g, 83%). <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra in CDCl<sub>3</sub> show two sets of broad peaks at room temperature, which coalesce at higher temperatures. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 60 °C):  $\delta$  1.06 (t, 3), 3.40 (q, 2), 3.86 (2, br), 4.65 (2, br), 5.67 (2), 6.84 (2), 6.92

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(14) Abbreviations: bpy, 2,2'-bipyridyl; dppe, 1,2-bis(diphenylphosphino)ethane; L-S<sub>2</sub>, dianion 6; L-S<sub>4</sub>, tetraanion 8; L-NS<sub>2</sub>, dianion 12.

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(2), 7.19 (2), 7.23 (m, 2), 7.44 (d, 1), 7.73 (d, 1). FAB-MS (3-nitrobenzyl alcohol + NaI):  $m/z$  354 ( $[M + Na]^+$ ), 332 ( $[M + H]^+$ ).

**11-[(1-(Ethoxymethyl)benzimidazol-2-yl)methyl]-2,3-bis(benzylthio)-1,4-dichloro-12,12-dimethoxy-1,4,4 $\alpha$ ,9,9 $\alpha$ ,10-hexahydro-1 $\alpha$ ,4 $\alpha$ -methanoanthracen-9 $\beta$ ,10 $\beta$ -imine (11).** Diene **4** (12.1 g, 27 mmol) and dienophile **10** (8.4 g, 25 mmol) were dissolved in chlorobenzene (50 mL) with slight heating. The mixture was deaerated and was heated at 110–120 °C for 24 h under a dinitrogen atmosphere. The solvent was removed in vacuo, and the crude product was purified by chromatography on a silica gel column eluted with ether, followed by recrystallization from a slowly evaporating ether solution. The product was obtained as a white crystalline solid (14.5 g, 75%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.02 (t, 3), 2.59 (2), 3.28 (q, 2), 3.34 (2), 3.46 (3), 3.48 (3), 3.76 (2d, 4), 4.50 (2), 5.72 (2), 7.1–7.3 (m, 15), 7.39 (dd, 2), 7.72 (d, 1). FAB-MS (3-nitrobenzyl alcohol matrix + NaI):  $m/z$  792 ( $[M + Na]^+$ ), 770 ( $[M + H]^+$ ). Anal. Calcd for C<sub>42</sub>H<sub>41</sub>Cl<sub>2</sub>N<sub>3</sub>O<sub>3</sub>S<sub>2</sub>: C, 65.44; H, 5.36; Cl, 9.20; N, 5.45; S, 8.32. Found: C, 65.32; H, 5.40; Cl, 9.30; N, 5.42; S, 8.39. This compound was further identified by an X-ray structure determination.

**Disodium 11-[(1-(Ethoxymethyl)benzimidazol-2-yl)methyl]-12,12-dimethoxy-1,4,4 $\alpha$ ,9,9 $\alpha$ ,10-hexahydro-1 $\alpha$ ,4 $\alpha$ -methanoanthracen-9 $\beta$ ,10 $\beta$ -imine-2,3-dithiolate (Na<sub>2</sub>(L-NS<sub>2</sub>), 12).** Under a dinitrogen atmosphere, a suspension of the diprotected dithiolene **11** (2.0 g, 2.6 mmol) in liquid ammonia maintained in a dry ice–acetone bath was titrated using small pieces of sodium metal (0.54 g, 23 mmol). The end point was determined as the intense blue color lasting for more than 20 min. The reaction was quenched using solid NH<sub>4</sub>Cl (0.67 g, 12 mmol). After being stirred for 30 min, the bright yellow reaction mixture was allowed to warm at room temperature while the solvent was evaporated. The pale yellow residue was vacuum-dried, washed with dry diethyl ether, and dissolved partially in methanol (about 60 mL). The inorganic salts in the methanol solution were precipitated by addition of ether (about 3 mL) and removed by filtration through a fine frit. The orange filtrate was evaporated to dryness. The resultant orange residue was stirred with 3 mL of methanol plus 60 mL of dry ether, filtered off through a fine frit, washed thoroughly with ether, and dried *in vacuo*. The product was collected as a white powder (1.28 g, 88%). <sup>1</sup>H NMR spectra in CD<sub>3</sub>OD show complex changes from –50 to +65 °C. <sup>1</sup>H NMR (CD<sub>3</sub>OD, –50 °C):  $\delta$  1.01 (t, 3), 2.37 (m, 1), 2.43 (m, 1), 2.57 (m, 1), 2.98 (m, 2), 3.03 (3), 3.17 (m, 1), 3.19 (3), 3.36 (m, 2), 4.54 (dd, 2), 5.23 (d, 1), 5.55 (d, 1), 5.89 (d, 1), 6.47 (m, 1), 6.56 (m, 2), 7.40 (m, 2), 7.49 (m, 2). FAB<sup>+</sup>-MS (3-nitrobenzyl alcohol + NaI):  $m/z$  565 ( $[M + 2Na]^+$ ), 542 ( $[M + Na]^+$ ), 520 ( $[M + H]^+$ ). FAB<sup>–</sup>-MS (glycerol):  $m/z$  519 ( $[M]^-$ ).

**[Ni(L-S<sub>2</sub>)<sub>2</sub>] (13).** Under a dinitrogen atmosphere, a solution of Na<sub>2</sub>(L-S<sub>2</sub>) (0.25 g, 0.77 mmol) in 15 mL of methanol was added dropwise to a stirred solution of [Ni(OH<sub>2</sub>)<sub>6</sub>]Cl<sub>2</sub> (0.092 g, 0.39 mmol) in 15 mL of methanol, resulting in an immediate color change to deep violet. The mixture was stirred for 30 min, and iodine (0.099 g, 0.39 mmol) was added as an oxidant. Stirring was continued for 2 h, during which time a dark solid precipitated. The mixture was evaporated to dryness, and the residue was dissolved in a minimal amount of dichloromethane and was eluted on a silica column using dichloromethane. Collection of the deep purple band followed by solvent removal afforded the product as a dark purple solid (0.17 g, 72%), which was recrystallized from dichloromethane/ether. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  –0.68 (2), 0.60 (2), 2.39 (4), 2.52 (4), 3.06 (6), 3.25 (6), 3.68 (4), 6.15 (4). Absorption spectrum (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\epsilon_M$ ) 300 (55 000), 395 (3800), 448 (sh, 1600), 545 (2200), 806 (40 000) nm. FAB-MS (3-nitrobenzyl alcohol + NaI):  $m/z$  618 (M<sup>+</sup>). Anal. Calcd for C<sub>28</sub>H<sub>32</sub>NiO<sub>4</sub>S<sub>4</sub>: C, 54.28; H, 5.21; Ni, 9.48; S, 20.70. Found: C, 54.22; H, 5.16; Ni, 9.39; S, 20.78. This compound was further identified by an X-ray structure determination.

**[Ni(L-S<sub>2</sub>)(dppe)] (14).** Under a dinitrogen atmosphere, a solution of Na<sub>2</sub>(L-S<sub>2</sub>) (0.099 g, 0.30 mmol) in methanol was added dropwise to a stirred solution of [NiCl<sub>2</sub>(dppe)]<sup>17</sup> (0.12 g, 0.23 mmol) in dichloromethane. An instant color change to dark green occurred. The reaction mixture was stirred for 1 h under dinitrogen and for 10 min under air. Silica (0.5 g) was added, the solvent removed in vacuo, and the residue dry-loaded onto a silica column, which was eluted with 98:2 dichloromethane/Et<sub>3</sub>N (v/v). The leading green fractions were

collected, combined, and evaporated. The residue was recrystallized from dichloromethane/ether to give the product as a dark green crystalline solid (0.14 g, 85%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.76 (d, 1), 0.88 (d, 1), 2.06 (2), 2.28 (d, 4), 2.44 (2), 2.93 (2), 3.12 (6), 6.15 (2), 7.44–7.77 (m, 20). FAB-MS (3-nitrobenzyl alcohol):  $m/z$  736 (M<sup>+</sup>). Absorption spectrum (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\epsilon_M$ ) 357 (2630), 683 (380) nm. Anal. Calcd for C<sub>40</sub>H<sub>40</sub>NiO<sub>2</sub>P<sub>2</sub>S<sub>2</sub>: C, 65.14; H, 5.47; Ni, 7.96; P, 8.40; S, 8.69. Found: C, 65.21; H, 5.53; Ni, 7.89; P, 8.33; S, 8.60. This compound was further identified by an X-ray structure determination.

**[Pd(L-S<sub>2</sub>)(bpy)] (15).** Under a dinitrogen atmosphere, a stirred suspension [Pd(bpy)Cl<sub>2</sub>]<sup>18</sup> (0.27 g, 0.081 mmol) in methanol was treated dropwise with a solution of Na<sub>2</sub>(L-S<sub>2</sub>) (0.23 g, 70 mmol) in methanol. An immediate color change to dark purple ensued. The mixture was stirred for 3 h under dinitrogen and for 10 min under air. Silica (1.0 g) was added, and the product was isolated as in the previous preparation. A faint leading purple band was discarded; the intensely colored blue band was collected and solvent was removed to afford the product as a blue solid (0.13 g, 34%). The compound readily decomposes in THF and is highly soluble but not stable for prolonged periods in dichloromethane. The compound was identified spectroscopically. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.13 (d, 1), 1.52 (d, 1), 2.12 (2), 2.58 (2), 2.72 (2), 3.18 (3), 3.24 (3), 6.21 (2), 7.39 (t, 2), 7.99 (t, 2), 8.07 (d, 2), 8.76 (d, 2). FAB-MS (3-nitrobenzyl alcohol):  $m/z$  543 (M<sup>+</sup>). Absorption spectrum (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\epsilon_M$ ) 290 (15 100), 318 (9850), 632 (2320) nm.

**[Mo(L-S<sub>2</sub>)<sub>2</sub>] (16).** Under a dinitrogen atmosphere, a solution of Na<sub>2</sub>(L-S<sub>2</sub>) (0.36 g, 1.1 mmol) in methanol (25 mL) was added with stirring to a solution of MoCl<sub>5</sub> (0.096 g, 0.36 mmol) in methanol (20 mL). A color change from light yellow to dark brown occurred instantly. The mixture was stirred for 3 h and was refluxed under air for 2.5 h. The dark green solution was cooled and filtered, and the filtrate was concentrated to dryness. The residue was mixed with silica (0.5 g) and dry-loaded onto a silica column, which was eluted with 3:1 pentane/ether (v/v). The leading dark green band was collected; concentration of the eluant solution gave the product (0.10 g, 31%) as a dark green solid. This material was recrystallized by slow diffusion of methanol into a THF solution. The <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub> was consistent with a 1.4(C<sub>3 $\alpha$</sub> ):1(C<sub>7</sub>) mixture of isomers.<sup>19</sup> FAB-MS (3-nitrobenzyl alcohol):  $m/z$  938 (M<sup>+</sup>). Absorption spectrum (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\epsilon_M$ ) 451 (18 000), 641 (18 200) nm. Anal. Calcd for C<sub>42</sub>H<sub>48</sub>MoO<sub>6</sub>S<sub>6</sub>: C, 53.83; H, 5.16; Mo, 10.24; S, 20.53. Found: C, 53.66; H, 5.15; Mo, 10.12; S, 20.39.

**X-ray Structure Determinations.** The structures of the compounds in Table 1 have been determined. Suitable single crystals were obtained by slow evaporation of an ether solution of **4** (tetragonal blocks), vapor diffusion of pentane into ether solutions of **7** (tetragonal blocks) and **11** (parallelepipeds), and vapor diffusion of ether into a dichloromethane solution of **13** (thin plates) and **14** (long needles). Diffraction data were collected using a Nicolet R3m/v diffractometer with graphite-monochromatized Mo K $\alpha$  radiation. Refined unit cell parameters were obtained by least-squares fits of machine-centered reflections with 15° ≤ 2 $\theta$  ≤ 25°. Data sets were processed and corrected for Lorentz and polarization effects with a locally modified version of XDISK (SHELXTL program suite, Siemens XRD Corp., Madison, WI). Empirical absorption corrections (XEMP) were applied to all compounds except **7** using azimuthal  $\psi$ -scan data. Monitored check reflections indicated no significant decay over the course of data collections. Crystallographic data are summarized in Table 1. Structures were solved by direct methods and were refined by means of standard least-squares and Fourier techniques. Nonhydrogen atoms were described anisotropically; hydrogen atoms were assigned idealized locations and given a uniform value for B<sub>iso</sub>. The P $\bar{1}$  space group (**7**, **11**, **14**) was assigned from statistics. All space groups were confirmed by successful refinements of the structures. Final agreement factors are contained in Table 1.<sup>20</sup>

**Other Physical Measurements.** NMR spectra were recorded on a Bruker AM400 or AM500 spectrometer. Absorption spectra were

(18) McCormick, J. B.; Jaynes, E. N., Jr.; Kaplan, R. I. *Inorg. Synth.* **1972**, *13*, 216.

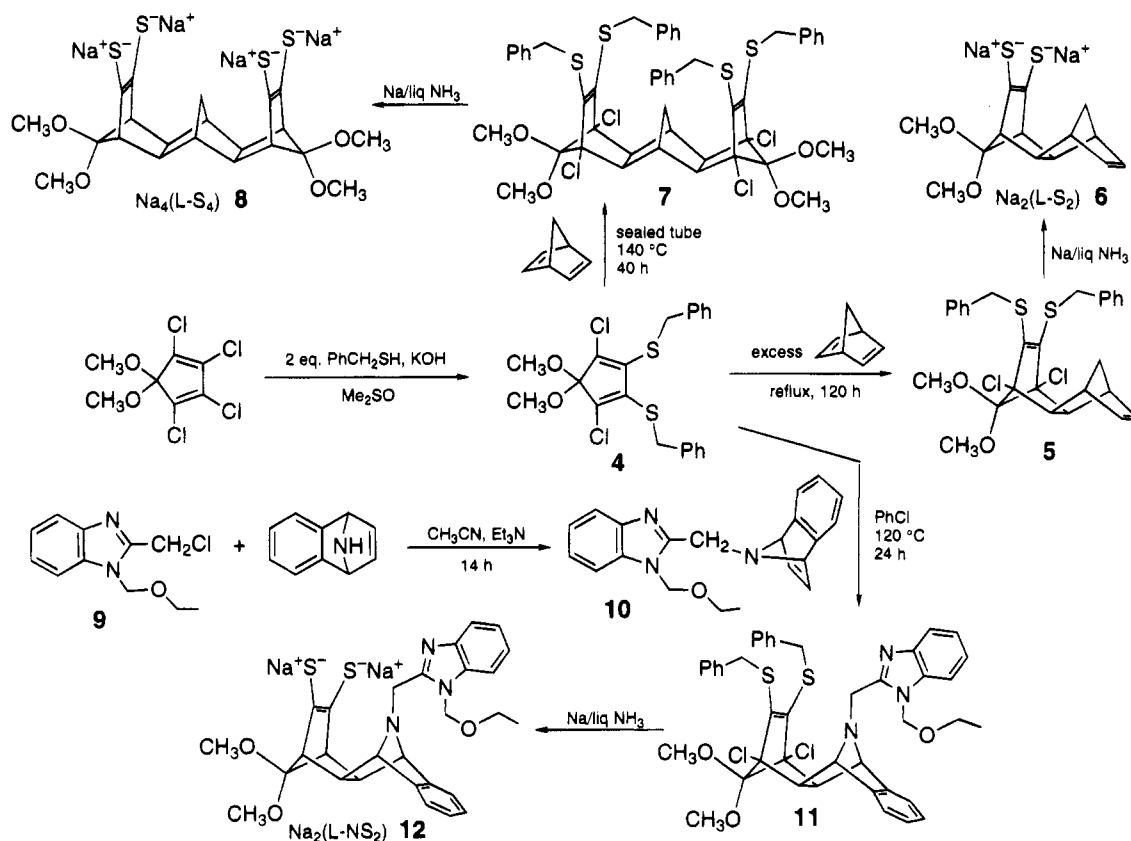
(19) Because of the large number of resonances, many of which overlap, chemical shifts are not included.

(20) See paragraph at the end of this article concerning Supporting Information.

**Table 1.** Crystallographic Data<sup>a</sup> for Compounds **4**, **7**, **11**, **13**, and **14**

	<b>4</b>	<b>7</b>	<b>11</b>	<b>13</b>	<b>14</b>
formula	C <sub>21</sub> H <sub>20</sub> Cl <sub>2</sub> O <sub>2</sub> S <sub>2</sub>	C <sub>49</sub> H <sub>48</sub> Cl <sub>4</sub> O <sub>4</sub> S <sub>4</sub>	C <sub>42</sub> H <sub>41</sub> Cl <sub>2</sub> N <sub>3</sub> O <sub>3</sub> S <sub>2</sub>	C <sub>28</sub> H <sub>32</sub> NiO <sub>4</sub> S <sub>4</sub>	C <sub>40</sub> H <sub>40</sub> NiO <sub>2</sub> P <sub>2</sub> S <sub>2</sub> ·Et <sub>2</sub> O
formula wt	439.44	970.97	770.8	619.50	811.6
crystal system	monoclinic	triclinic	triclinic	monoclinic	triclinic
space group	C2/c	P1	P1	P2 <sub>1</sub>	P1
Z	4	2	2	2	2
a, Å	11.855(5)	11.788(9)	9.080(4)	7.636(2)	11.087(5)
b, Å	12.443(5)	12.737(10)	14.019(4)	8.645(42)	13.173(7)
c, Å	14.196(6)	16.995(13)	15.786(5)	20.962(4)	15.663(6)
α, deg		71.49(2)	76.45(2)		90.82(5)
β, deg	100.91(4)	72.58(2)	75.65(3)	96.57(2)	97.49(3)
γ, deg		78.83(2)	85.02(3)		114.60
V, Å <sup>3</sup>	2056	2295(3)	1891.5(12)	1374.6(6)	2056.4(15)
T, K	223	298	223	223	223
color	light yellow	white	white	purple	green
d <sub>calc</sub> , g/cm <sup>3</sup>	1.42	1.495	1.35	1.486	1.311
μ, mm <sup>-1</sup>	0.53	0.485	0.326	1.043	0.689
R <sup>b</sup> (R <sub>w</sub> <sup>c</sup> ), %	3.38 (3.36)	3.46 (3.83)	5.68 (6.02)	4.49 (3.99)	4.84 (5.21)

<sup>a</sup> All data collected with graphite-monochromated Mo Kα (λ = 0.710 69 Å) radiation using ω scans. <sup>b</sup> R = Σ||F<sub>o</sub>| - |F<sub>c</sub>||/Σ|F<sub>o</sub>|. <sup>c</sup> R<sub>w</sub> = {Σ[w(|F<sub>o</sub>| - |F<sub>c</sub>||)<sup>2</sup>]/Σ[w|F<sub>o</sub>|<sup>2</sup>]}<sup>1/2</sup>, with the weighting scheme provided by a three-term Chebyshev polynomial: Carruthers, J. R.; Watkin, D. J. *Acta Crystallogr.* **1979**, A35, 698.



**Figure 1.** Synthetic routes to the mono(dithiolene) dianion L-S<sub>2</sub> (**6**), the bis(dithiolene) tetraanion L-S<sub>4</sub> (**8**), and the facial tridentate mono(dithiolene) dianion L-NS<sub>2</sub> (**12**).

obtained with a Cary Model 3 spectrophotometer. Mass spectra were recorded on a JEOL AX-505 or a JEOL SX-102 mass spectrometer. Electrochemical determinations were performed with a PAR Model 263 potentiostat/galvanostat using a Pt working electrode and 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> supporting electrolyte; potentials are referenced to an SCE.

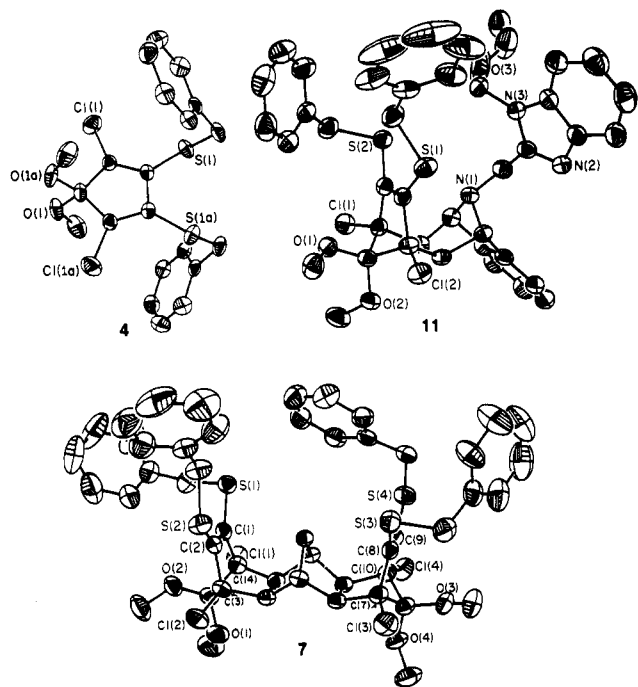
## Results and Discussion

**Ligand Synthesis.** The routes to dithiolene ligands **6**, **8**, and **12** set out in Figure 1 depend on stereospecific Diels–Alder reactions of the diene **4**. Four products were isolated from the reaction of K(SCH<sub>2</sub>Ph) with commercial 1,2,3,4-tetrachloro-

5,5-dimethoxy-1,3-cyclopentadiene, itself a highly reactive diene.<sup>21</sup> Although the 1,3-bis(benzylthio) derivative was formed in higher yield (ca. 40%), the isolation of **4** (23%)<sup>22</sup> was readily achieved by chromatography and crystallization. This compound was definitively identified as the desired 2,3-bis(benzylthio) product by an X-ray structure determination, whose result<sup>20</sup> is shown in Figure 2.

(21) (a) Jung, M. E.; Hudspeth, J. P. *J. Am. Chem. Soc.* **1977**, 99, 5508 and references therein. (b) Lap, B. V.; Paddon-Row, M. N. *J. Org. Chem.* **1979**, 44, 4979.

(22) Although this yield was considered adequate, it may be improved by the use of larger groups (phenoxy, benzyloxy) at the 5-position. Such compounds are available: Shestakova, S. I.; Volodkovich, S. D.; Mel'nikov, N. N. *J. Org. Chem. USSR (Engl. Transl.)* **1970**, 6, 1799.

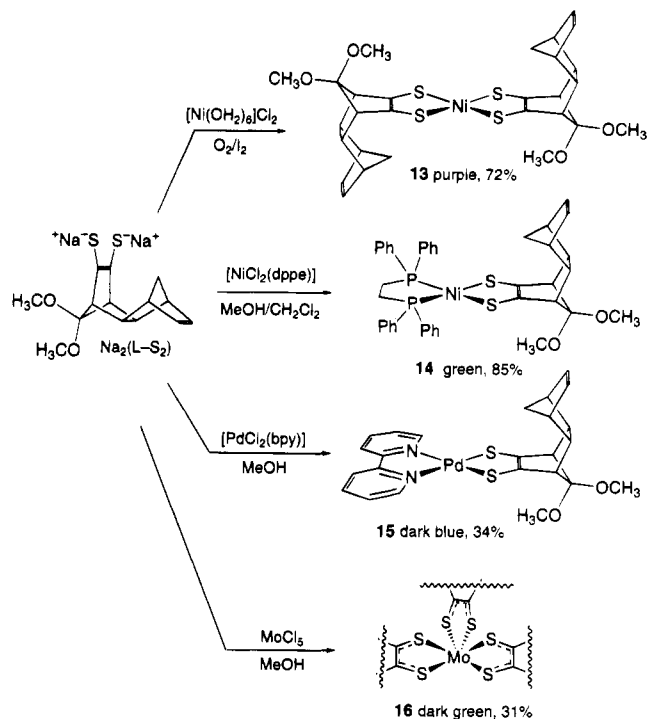


**Figure 2.** Structures of diene **4**, tetraprotected bis(dithiolene) **7**, and diprotected dithiolene **11** showing 50% probability ellipsoids and the atom labels of non-carbon atoms. Compound **4** has an imposed  $C_2$  axis bisecting one C–C bond and containing the tetrahedral carbon atom of the cyclopentadiene ring. Metric parameters are unexceptional and are available elsewhere.<sup>20</sup>

(a) **Mono- and Bis(dithiolenes).** The reaction of **4** with excess norbornadiene affords the Diels–Alder adduct **5** (>96%). Reaction with sodium in liquid ammonia results in S-deprotection and removal of bridgehead chlorine atoms to give the disodium salt **6** ( $Na_2(L-S_2)$ , >90%). The *endo,exo* stereochemistry of **5** and **6** was demonstrated by the structure of  $[Ni(L-S_2)_2]$  (vide infra), whose depiction in Figure 4 makes evident the cisoid arrangement of the enedithiolate and the bridging methylene.

With this stereochemical result in hand, the reaction of 2 equiv of **4** and 1 equiv of norbornadiene was carried out at 140 °C for 40 h in a sealed tube. The anticipated tetraprotected bis(dithiolene) adduct **7** was isolated in good yield (85%). A temperature above 135 °C is required for the reaction to proceed to a satisfactory extent in a reasonable period of time. When a reaction mixture of the same stoichiometry was maintained at 110 °C for 130 h, the result was a mixture of unreacted diene **4**, mono-adduct **5**, and bis-adduct **7** in a 1.5:2:1 mole ratio. Heating the same mixture above 150 °C caused the formation of tarry products. The bis(*endo,exo*) stereochemistry of **7** was demonstrated by the X-ray structure<sup>20</sup> shown in Figure 2, which reveals that the two protected dithiolene units and the bridging methylene are positioned on the same side of the molecule. S-Deprotection and dechlorination of **7** with sodium in liquid ammonia leads to the tetrasodium salt **8** ( $Na_4(L-S_4)$ , 80%).

(b) **Tridentate Dithiolene.** The synthesis of ligand **12** is based on the Diels–Alder reaction of the N-substituted 1,4-dihydronaphthalen-1,4-imine **10** with diene **4** (Figure 1). Treatment of the N-protected 2-(chloromethyl)benzimidazole **9** with an equimolar amount of the imine in acetonitrile in the presence of triethylamine gave the dienophile **10** (83%). The <sup>1</sup>H NMR spectrum of this compound is consistent with slow inversion at the bridging nitrogen atom and a coalescence temperature near



**Figure 3.** Preparation of nickel, palladium, and molybdenum complexes derived from the dithiolene ligand  $L-S_2$  (**6**).

room temperature.<sup>23</sup> Reaction of **4** and **10** in chlorobenzene at 120 °C for 24 h affords the protected dithiolene **11** (75%). Increased reaction time did not appreciably improve the yield. The X-ray structure of this compound,<sup>20</sup> presented in Figure 2, demonstrates the *endo,exo* stereochemistry. The compound was S-deprotected with sodium in liquid ammonia to give the disodium salt  $Na_2(L-NS_2)$  (**12**, 88%). Its <sup>1</sup>H NMR spectrum is indicative of fluxionality. At –50 °C in methanol, the spectrum suggests a departure from averaged mirror symmetry; above 30 °C, the spectrum indicates the onset of inversion of the bridging nitrogen atom.

The synthesis of **12** makes effective use of a substituted 1,4-dihydronaphthalen-1,4-imine as a dienophile, a property that is precedented.<sup>24</sup> The desired *endo,exo* configuration of **11** and **12**, as well as of **5–8**, is predicted by orbital and steric arguments<sup>25</sup> and by the stereochemical outcome of similar Diels–Alder reactions.<sup>24</sup>

**Metal Complexes.** Because some aspects of complexes of  $L-S_4$  and  $L-NS_2$  will depart from those of complexes of the generic dithiolene ligand **1**, a brief investigation of certain complexes of the mono(dithiolene)  $L-S_2$  was conducted for the purpose of later comparison. This is one of the very few ligands **1** with R = alkyl that has been isolated in substance. Precursors to ligands of this type have been generated by reaction of acyloins with  $P_2S_5$ , and the dithiolene deprotected and trapped by coordination.<sup>26</sup> Complexation reactions are collected in Figure 3.

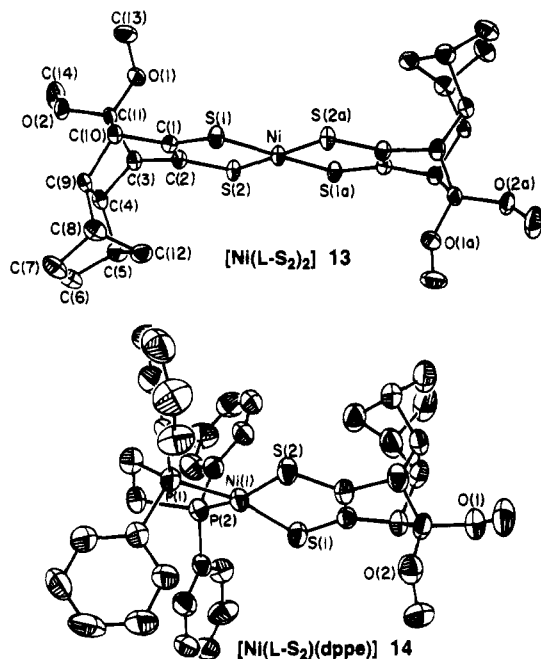
The bis(dithiolene)nickel complex **13** was isolated as a purple crystalline material after oxidation of the initial dianion reaction product. As shown in Figure 4,  $[Ni(L-S_2)_2]$  is planar and centrosymmetric, with the bridging groups in a transoid ar-

(23) Certain related bicyclic amines have high nitrogen inversion barriers, and several have coalescence temperatures near room temperature: Deloughry, W. J.; Sutherland, I. O. *Chem. Commun.* **1971**, 1104.

(24) Sasaki, T.; Manabe, T.; Nishida, S. *J. Org. Chem.* **1980**, *45*, 476.

(25) (a) Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779. (b) Ginsburg, D. *Tetrahedron* **1983**, *39*, 2095.

(26) (a) Schrauzer, G. N.; Mayweg, V. P. *J. Am. Chem. Soc.* **1965**, *87*, 1483. See also: (b) Schrauzer, G. N.; Mayweg, V. P.; Heinrich, W. *Inorg. Chem.* **1965**, *4*, 1615.



**Figure 4.** Structures of  $[\text{Ni}(\text{L-S}_2)_2]$  (upper) and  $[\text{Ni}(\text{L-S}_2)(\text{dppe})]$  (lower) showing 50% probability ellipsoids and the atom labeling schemes.  $[\text{Ni}(\text{L-S}_2)_2]$  has an imposed symmetry center. Selected bond distances (Å) and angles (deg):  $[\text{Ni}(\text{L-S}_2)_2]$ —Ni—S(1) 2.156(1), Ni—S(2) 2.144(1), S(1)—C(1) 1.682(4), S(2)—C(2) 1.678(4), C(1)—C(2) 1.400(6), S(1)—Ni—S(2) 93.4(1), S(2)—Ni—S(1a) 86.6(1);  $[\text{Ni}(\text{L-S}_2)(\text{dppe})]$ —Ni—S(1) 2.176(3), Ni—S(2) 2.175(3), Ni—P(1) 2.158(3), Ni—P(2) 2.152(3), S(1)—C(1) 1.733(9), S(2)—C(2) 1.752(8), C(1)—C(2) 1.33(2), S(1)—Ni—S(2) 94.0(1), P(1)—Ni—P(2) 86.3(1).

range in  $C_{2h}$  symmetry. Only this isomer was detected by chromatography on silica. Metric parameters are comparable to those of other  $[\text{Ni}(\text{S}_2\text{C}_2\text{R}_2)_2]$  neutral complexes.<sup>27</sup> The complex forms a reversible three-member electron transfer series; in dichloromethane solution  $E_{1/2}(0/-1) = -0.33$  V and  $E_{1/2}(-1/-2) = -1.13$  V. These potentials compare closely with those for  $[\text{Ni}(\text{S}_2\text{C}_2\text{R}_2)_2]^{0.1-2-}$  series with R = alkyl<sup>1,26a</sup> and are otherwise consistent with facile oxidation of an initially generated dianion complex to the neutral form by either dioxygen or iodine.<sup>8c</sup> An intense near-IR band occurs at 806 nm in dichloromethane. It follows that  $[\text{Ni}(\text{L-S}_2)_2]$  displays the essential properties of a bis(dithiolene)nickel complex. Further, the bridging methylene protons of this complex (at C(12), Figure 4) occur as two doublets at  $\delta$  0.60 and  $-0.68$  in  $\text{CDCl}_3$  solution. Compared to those of doubly protected **5** as a reference in the same solvent, these signals have been shifted *upfield* by 1.13 and 1.79 ppm, respectively. These large shifts can only arise from the presence of a ring current in the dithiolene chelate ring. In addition,  $[\text{Ni}(\text{L-S}_2)(\text{dppe})]$  (**14**) was prepared and shown to have a planar structure (Figure 4); bond distances and angles are normal. The complex undergoes two chemically reversible redox reactions in propylene carbonate solution, an oxidation at  $E_{1/2} = +0.21$  V and a reduction at  $-1.54$  V. Several related compounds with the same redox capacity have been prepared,<sup>28</sup> but no structure of a bis(phosphine)(dithiolene) nickel complex

has been previously reported.<sup>29</sup> As noted above, the structures of **13** and **14** establish the stereochemistry of addition between diene **4** and norbornadiene, which was used in devising the syntheses of ligands **8** and **12**.

Two additional complexes were prepared. Dark blue  $[\text{Pd}(\text{L-S}_2)(\text{bpy})]$  (**15**) is related to the mono(dithiolene)  $\alpha, \alpha'$ -diimine complexes of Ni,<sup>30a-c</sup> Pd,<sup>30c</sup> and Pt,<sup>30c,d</sup> which exhibit intense visible absorption bands with pronounced solvatochromism. This complex displays an analogous band at 632 nm in dichloromethane. Lastly, the tris-chelate species  $[\text{Mo}(\text{L-S}_2)_3]$  was prepared. A trigonal prismatic structure analogous to that of  $[\text{Mo}(\text{S}_2\text{C}_2\text{H}_2)_3]$ <sup>31</sup> was established.<sup>32</sup> Chromatography of the dark green reaction product on silica produced a mixture of two isomers whose <sup>1</sup>H NMR spectrum indicated the mole ratio 1.4- $(C_{3h})$ :1- $(C_s)$ . Evidently the bridgehead methylene groups somewhat disfavor but do not prevent the formation of the less symmetric (and more hindered) isomer. The complex exhibits two one-electron reductions at  $E_{1/2} = -0.62$  and  $-1.09$  V in dichloromethane; three-member electron transfer series are typical of tris(dithiolene)molybdenum complexes.<sup>1</sup>

**Summary.** Three new types of dithiolene ligands with *endo*-, *exo* stereochemistry have been prepared using Diels–Alder reactions of the diene **4** and norbornadiene and **10** as dienophiles, followed by deprotection reactions. The ligand L-S<sub>2</sub> is the first example of a dithiolene with structure significantly protruding above and below the plane of the chelate ring. This feature offers no impediment to metal binding, and the ligand behaves as a generic dithiolene with electron-releasing substituents. The bis(dithiolene) L-S<sub>4</sub> has the capability of binding two metals to the same backbone and sustaining the formation of two further chelate rings with individual ligands **1** or with another equivalent of L-S<sub>4</sub>. In this way, molecules capable of storing and releasing up to four electrons and binding substrates between the two metal centers may be developed. The ligand L-NS<sub>2</sub> has been designed to function as a facial tridentate. In the formation of a dienophile based on 1,4-dihydronaphthalen-1,4-imine, the benzimidazole derivative **9** should be replaceable by chloromethyl compounds containing other (suitably protected) binding groups such as pyridyl, thioether, thiolate, and carboxylate. This route would then provide a general entry to *fac*-dithiolenes. In current work, we are extending our investigation of the metal binding features of, and the properties of metal complexes derived from, these new types of dithiolenes.

**Acknowledgment.** We thank Dr. M. J. Scott for experimental assistance and useful discussions. This work was supported by NSF Grant CHE 92-08387. J.P.D. held a National Defense Science and Education Predoctoral Fellowship, 1991–1994.

**Supporting Information Available:** For the compounds in Table 1, tables of crystal data, details of data collections, thermal and positional parameters, bond distances and angles, and calculated hydrogen atom positions (34 pages). Ordering information is given on any current masthead page.

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