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Article

Preparation and Isolation of Dithiolene Thiophosphoryl Molecules as Stable, Protected Forms of Dithiolene Ligands

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The reaction of P_4S_{10} with acyloins, RC(O)CH(OH)R, in refluxing dioxane, followed by the addition of alkylating agents, forms dithiolene thiophosphoryl thiolate compounds, $(R_2C_2S_2)P(S)(SR')$, which are readily isolated and purified. The compounds that have been prepared and identified spectroscopically are those with R = *p*-anisyl, R′ = Me (**1**); R = *p*-anisyl, R′ = Bz (**2**); R = Ph, R′ = Me (**4**); R = Et, R′ = Bz (**5**). Compounds **1**, **2**, and **4** were structurally characterized by X-ray crystallography and found to possess a tetrahedral coordination geometry about the phosphorus atom, with overall C_s symmetry. In each case, the mirror plane bisects the dithiolene S–P–S chelate and contains the thiophosphoryl bond, which ranges in length from 1.9241(8) to 1.9361(7) Å. The use of 2-(bromomethyl)naphthalene as organic electrophile in the P_4S_{10}/acyloin reaction produced bis(2-methylnaphthalenyl) disulfide as the only identifiable product. The substitution of Lawesson's reagent for P_4S_{10} in reactions with acyloins produced deoxy acyloin rather than products resulting from chalcogen exchange. Compounds **1**–**2** and **4**–**5** are Group 5 analogues of 1,3-dithiol-2-ones, $(R_2C_2S_2)C{=}O$, and undergo a similar hydrolysis in aqueous base to liberate ene-1,2-dithiolate dianions from which corresponding metal dithiolene complexes may be prepared. Deprotection of **1** in MeO^-/MeOH, followed by the addition of $NiCl_2{\cdot}6H_2O$ and then I_2, produces square planar $[Ni(S_2C_2(C_6H_4\text{-}p\text{-}OCH_3)_2)_2]$ (**8**) in 93% yield. A high-resolution structure of **8** ($P\bar{1}$) reveals dithiolene C–C and C–S bond lengths that are clearly indicative of the thionyl radical monoanionic nature of the ligand. The use of isolated $(R_2C_2S_2)P(S)(SR')$ compounds as a dithiolene ligand source for the preparation of metal dithiolene complexes offers the advantages of clean reactivity and high yield.

Introduction

Following the initial flurry of activity that attended their discovery in the 1960s,[1] metal dithiolene complexes have been the subject of continuous investigation due to the numerous applications arising from their interesting physical properties. Among the applications for which they either hold promise or for which they are currently employed are use as superconducting materials,[2] magnets,[3] light harvesting devices,[4] sensing devices,[5] reversibly bleachable dyes in laser systems,[6] and optical data storage systems.[7] Their occurrence at the active sites of mononuclear molybdenum[8,9] and tungsten enzymes[9,10] has further stimulated exploratory synthesis and study of metal dithiolene complexes.

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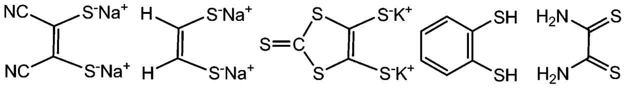

(a) Na_2(mnt) **(b)** Na_2(edt) **(c)** K_2(dmit) **(d)** H_2bdt **(e)** Dithiooxamide

Figure 1. Dithiolene ligands available via preparative scale syntheses or from commercial sources.

Despite 40 years of research and study, one of the persistent hindrances to work in this area is limited synthetic access to certain classes of dithiolene ligands. Although the dicyano substituted ene-1,2-dithiolate ligand (Figure 1, (**a**)),[11] ethylene-1,2-dithiolate (Figure 1, (**b**)),[12] the dimercaptoisotrithione ligand (dmit^{2-}, Figure 1 (**c**)),[13] benzene-1,2-dithiol,[14] dithiooxamide, and various derivatives of the latter three, are either commercially available or easily made, simple dialkyl- and diaryl-substituted dithiolene ligands are considerably more difficult to prepare and isolate in useful multigram quantities. A method for generating dialkyl- and diaryl-substituted dithiolene ligands in situ from P_4S_{10} and α-hydroxy ketones (acyloins) was first described by Schrauzer[15] and still remains a useful method for the generation of metal dithiolene complexes. The chief disadvantages of the P_4S_{10}/acyloin method of Schrauzer are poor-to-modest yields observed with certain acyloin substrates and the inability to deliver well-defined stoichiometric quantities of dithiolene ligand to a metal complex such that anything other than bis- or tris(dithiolene) complexes are obtained. These bis- and tris(dithiolene) metal complexes often are synthetic dead ends because of their very robust nature.

In his early studies of the complex P_4S_{10}/acyloin reaction system, Schrauzer isolated an amber resinous material which he formulated on the basis of spectral, analytical, and reactivity data as a mixture of phosphoryl and thiophosphoryl thioesters.[16] Further characterization of this mixture was not easily done at that time. Although Schrauzer's method is a messy and indeed quite malodorous reaction system, its redeeming aspect is that the P_4S_{10} and acyloins used in the synthesis are inexpensive and available from commercial sources. In view of this point, and as part of an ongoing effort to improve the accessibility of alkyl- and aryl-substituted dithiolene ligands, we determined that a re-examination of Schrauzer's P_4S_{10}/acyloin reaction system would be a worthwhile endeavor. One motivation is a clarification of some aspects of this reaction system. A report in the patent literature[17] describes significantly better yields of metal dithiolene complexes when 1,3-dimethyl-2-imidazolidinone is employed as solvent rather than dioxane, as reported by Schrauzer, but it is unclear whether this alternative solvent has been found to be similarly effective by other researchers. Furthermore, it is uncertain whether the P_4S_{10}/RC(O)CH(OH)R method of dithiolene ligand generation has intrinsic limitations due to the steric bulkiness and/or degree of electron deficiency presented by the R groups of the acyloin substrate. Finally, we reasoned that the introduction of organic electrophiles rather than metal cations into this system would stabilize thiophosphoryl dithiolene species that could then be isolated and stored. These "trapped" thiophosphoryl dithiolene intermediates would then have the obvious advantage of permitting deprotection under cleaner, more controlled conditions and with greater stoichiometric precision.

Chart 1. Numerical Designations for Compounds

$((H_3CO\text{-}p\text{-}C_6H_4)_2C_2S_2)P(S)(SMe)$	**1**
$((H_3CO\text{-}p\text{-}C_6H_4)_2C_2S_2)P(S)(SBz)$	**2**
$(H_3CO\text{-}p\text{-}C_6H_4)_4C_4S$	**3**
$((C_6H_5)_2C_2S_2)P(S)(SMe)$	**4**
$(Et_2C_2S_2)P(S)(SBz)$	**5**
$(C_{10}H_7CH_2S)_2$	**6**
$(H_3CO\text{-}p\text{-}C_6H_4)C(O)CH_2(C_6H_4\text{-}p\text{-}OCH_3)$	**7**
$[Ni(S_2C_2(C_6H_4\text{-}p\text{-}OCH_3)_2)_2]$	**8**

Experimental Section

Materials and Methods. All reactions were conducted under N_2 using standard Schlenk line techniques. Phosphorus sulfide (P_4S_{10}), Lawesson's reagent, $[(CH_3O\text{-}p\text{-}C_6H_4)P(S)(\mu\text{-}S)]_2$, anisoin, benzoin, 4-hydroxy-3-hexanone (propioin), methyl iodide, benzyl bromide, 2-(bromomethyl)naphthalene, Me_3SiCl, dioxane, and 1,3-dimethyl-2-imidazolidinone were purchased from commercial sources and used as received. Mesitoin (2-hydroxy-1,2-bis(2,4,6-trimethylphenyl ethanone) was prepared by the Mg/MgI_2-mediated reductive coupling of mesitoyl chloride followed by an acid-catalyzed rearrangement of the resulting ene-1,2-diol to the corresponding isomeric α-hydroxy ketone.[18] Silica columns were run in the open air using 60−230 μm silica (Dynamic Adsorbents).

Physical Methods. ^1H NMR and ^{31}P NMR spectra were obtained with a Varian UNITY INOVA 400 instrument using $CDCl_3$ as solvent; ^1H NMR and ^{13}C NMR peak positions are referenced against the solvent signals, while ^{31}P NMR signals are relative to the H_3PO_4 signal loaded from a reference file. Cyclic voltammetry measurements were made with a BAS electrochemical analyzer upon analyte solutions in dry CH_2Cl_2. The supporting electrolyte used was Bu_4NPF_6, while Ag/Ag^+ and Pt disk electrodes were employed as reference and working electrodes, respectively. Melting points were determined with a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Canadian Microanalytical Service, Ltd., of Delta, British Columbia.

X-ray Structures. The numbering system by which the compounds are hereafter identified is defined in Chart 1 and Scheme 1. Crystals of **1** (pale yellow needles), **2** (pale yellow blocks), **3** (large white plates), **4** (pale yellow blocks), **6** (thin white plates), **7** (large white plates), and **8** (brown column-shaped crystals) were grown by slow evaporation of eluant obtained directly from the silica columns used to purify the compounds. All crystals were

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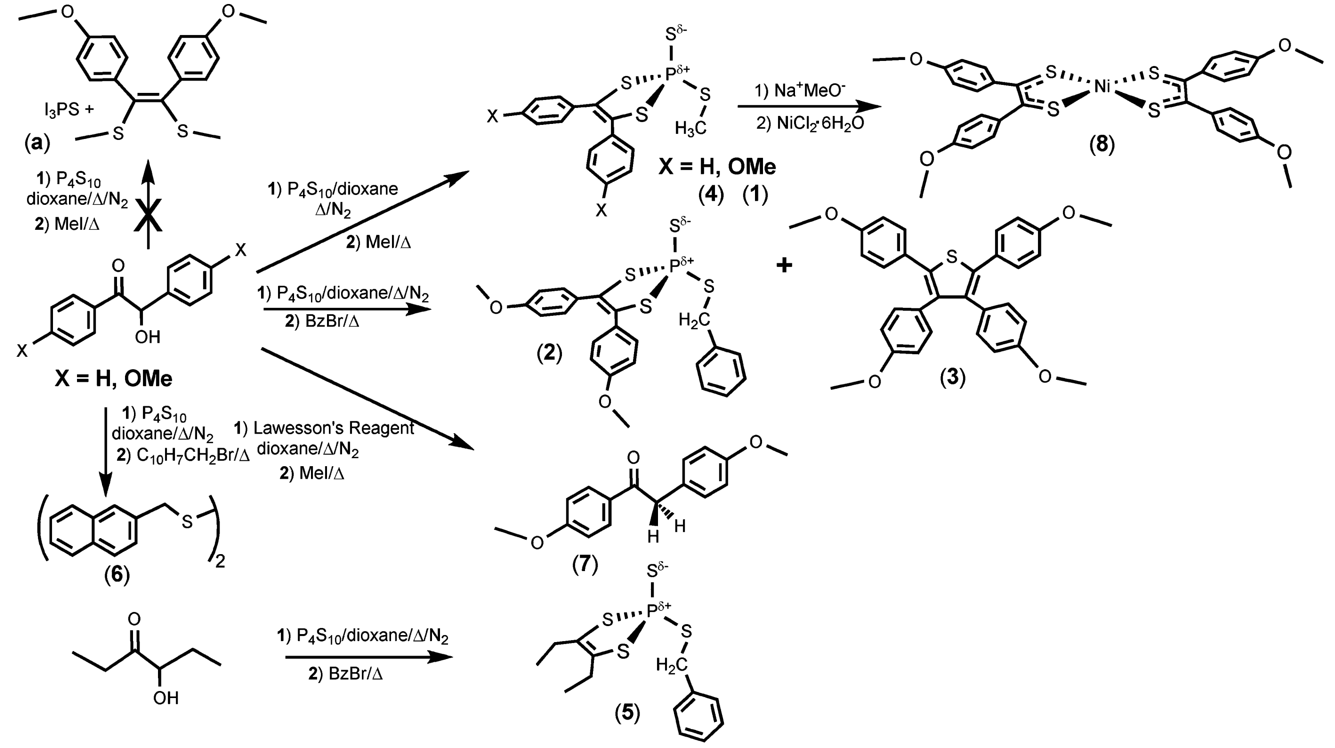
Scheme 1. Summary of Preparations of Thiophosphoryl Dithiolene Compounds



coated in Paratone oil and mounted onto a nylon cryoloop attached to a goniometer. Data were collected with a Bruker APEX CCD diffractometer, which was equipped with a Kryoflex attachment supplying a nitrogen stream at 100 K. Using the SMART software package,[19] full spheres of data were obtained by collecting three sets of 606 frames in ω (0.3°/scan) with φ held constant at 0°, 120°, and then 240°. The raw data were reduced to F^2 values using the SAINT+ software,[20] and a global refinement of unit cell parameters was performed using 2905−9014 selected reflections from the full data set. Multiple measurements of symmetry-equivalent reflections provided the basis for an empirical absorption correction, as well as a correction for any crystal decomposition during the course of the data collection (SADABS[21]). All structure solutions were obtained by direct methods, and refinements were accomplished by full-matrix least-squares procedures using the SHELXTL software suite.[22] 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. Methyl substituents were allowed to refine an orientation around the O−C or S−C bond that optimized the model for electron density for this group.

Syntheses. ((H$_3$CO-*p*-C$_6$H$_4$)$_2$C$_2$S$_2$)P(S)(SCH$_3$), 1. A 100 mL Schlenk flask with stir bar was charged with P_4S_{10} (3.9 g, 7.3 mmol), NH_4Cl, (0.39 g, 7.3 mmol), anisoin (2.0 g, 7.3 mmol), and dry dioxane (50 mL). This heterogeneous mixture was heated at 90 °C for 2 h under a nitrogen atmosphere, during which time the initial pale yellow color was transformed to a dark brown color. The reaction mixture was then cooled to ambient temperature and filtered into a stirred solution of MeI (4.2 g, 29 mmol) in dioxane at 0 °C. The resulting solution was warmed to ambient temperature and then heated to 50 °C for 4 h. The solvent was then removed under reduced pressure, and the solid residue was purified on a silica column eluted with 1:9 Et_2O/hexanes. ((H$_3$CO-*p*-C$_6$H$_4$)$_2$C$_2$S$_2$)P(S)(SCH$_3$) readily crystallized from the eluant as fine, pale yellow, needle crystals. Yield: 0.695 g, 23%. R_f = 0.37 (3:7, Et_2O/hexanes). mp = 140 °C. ^{1}H NMR (ppm in $CDCl_3$) 7.05 (d, 4H, aromatic C−H, J = 8.8 Hz), 6.71 (d, 4H, aromatic C−H, J = 8.8 Hz), 3.75 (s, 6H, $-OCH_3$), 2.62 (d, J_{PH} = 18.8 Hz, 3H, $-SCH_3$); ^{13}C NMR (ppm in $CDCl_3$) 159.8, 131.0, 129.7, 125.9, 114.2, 55.5, 18.5; ^{31}P NMR (ppm in $CDCl_3$) 95.86 (q, J_{PH} = 19 Hz). Anal. Calcd for $C_{17}H_{17}O_2PS_4$: C, 49.50; H, 4.15; S, 31.09. Found: C, 49.57; H, 4.16, S, 31.57.

((H$_3$CO-*p*-C$_6$H$_4$)$_2$C$_2$S$_2$)P(S)(SCH$_2$C$_6$H$_5$), 2. A procedure similar to that described for the preparation of **1** was followed but with BzBr (2.5 g, 15 mmol) as alkylating agent instead of MeI. Yield: 0.750 g of yellow block crystals, 21%. R_f = 0.26 (3:7, Et_2O/hexanes). mp = 110−112 °C. ^{1}H NMR (ppm in $CDCl_3$) 7.40 (d, 2H, aromatic C−H), 7.34−7.28 (m, 3H, aromatic C−H), 7.01 (d, 4H, aromatic C−H, J = 8.6 Hz) 6.69 (d, 4H, aromatic C−H, J = 8.6 Hz), 4.36 (d, 2H, $-SCH_2C_6H_5$, J = 14.8 Hz), 3.73 (s, 6H, $-OCH_3$); ^{13}C NMR (ppm in $CDCl_3$) 159.7, 135.5, 131.1, 129.8, 129.5, 129.1, 128.2, 126.0, 114.2, 55.5, 40.9; ^{31}P NMR ($CDCl_3$) 92.90 (t, J = 14.7 Hz). Anal. Calcd for $C_{23}H_{21}O_2PS_4$: C, 56.54; H, 4.33; S, 26.23. Found: C, 56.76; H, 4.21, S, 26.60.

((H$_3$CO-*p*-C$_6$H$_4$)$_4$C$_4$S, 3. The preparation of **2** yielded trace amounts of white plate crystals of tetra(*p*-anisyl)thiophene, **3**. R_f = 0.36 (3:7, Et_2O/hexanes). ^{1}H NMR (ppm in $CDCl_3$) 7.13 (d, 4H, aromatic C−H, J = 8.8 Hz), 6.85 (d, 4H, aromatic C−H, J = 8.8 Hz), 6.74 (d, 4H, aromatic C−H, J = 8.8 Hz), 6.65 (d, 4H, aromatic C−H, J = 8.8 Hz); ^{13}C NMR (ppm in $CDCl_3$) 158.8, 158.2, 138.5, 137.4, 132.2, 130.5, 129.3, 127.2, 113.9, 113.5, 55.4, 55.2.

((C$_6$H$_5$)$_2$C$_2$S$_2$)P(S)(SCH$_3$), 4. A procedure similar to that described for the preparation of **1** was followed but with benzoin (5.0 g, 11 mmol) in place of anisoin. Yield: 0.830 g of pale yellow

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Table 1. Crystal and Refinement Data for Compounds **1**−**4** and **6**−**8**

	1	**2**	**3**	**4**	**6**	**7**	**8**
formula	$C_{17}H_{17}O_2PS_4$	$C_{23}H_{21}O_2PS_4$	$C_{32}H_{28}O_4S$	$C_{15}H_{13}PS_4$	$C_{22}H_{18}S_2$	$C_{16}H_{16}O_3$	$C_{32}H_{28}NiO_4S_4$
fw	412.52	488.61	508.60	352.46	346.48	256.30	663.49
space group	$P2_1/n$ (No. 14)	$P2_1$ (No. 4)	$P2_12_12_1$ (No. 19)	$P2_1/n$ (No. 14)	$P2_1$ (No. 4)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	5.8333(8)	7.1334(7)	9.476(3)	6.374(3)	7.596(2)	15.549(4)	9.797(1)
b, Å	16.246(2)	14.442(1)	10.329(3)	23.82(1)	5.863(1)	10.768(3)	12.205(2)
c, Å	19.129(3)	11.290(1)	25.685(7)	10.636(4)	19.351(5)	7.659(2)	14.121(2)
α, deg	90	90	90	90	90	90	105.856(2)
β, deg	92.991(2)	103.833(1)	90	95.981(6)	100.079(4)	93.119(5)	104.118(2)
γ, deg	90	90	90	90	90	90	107.017(2)
V, Å^3	1810.3(4)	1129.3(2)	2514(1)	1606(1)	848.5(3)	1280.4(6)	1453.6(3)
Z	4	2	4	4	2	4	2
ρ_{calcd}, g·cm^{-3}	1.514	1.437	1.344	1.458	1.356	1.330	1.516
μ(Mo Kα) mm^{-1}	0.621	0.510	0.167	0.677	0.313	0.091	0.993
T (K)	100	100	100	100	100	100	100
R1[a]	0.0528	0.0300	0.0703	0.0348	0.0621	0.0528	0.0340
wR2[b]	0.1139	0.0763	0.1752	0.0964	0.1277	0.1394	0.0852

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = \{[\Sigma w(F_o^2 - F_c^2)/\Sigma w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (xP)^2]$, where $P = (F_o^2 + 2F_c^2)/3$.

block crystals, 25%. $R_f = 0.46$ (1:4, Et_2O/hexanes). mp = 111−113 °C. ^1H NMR (ppm in $CDCl_3$) 7.10−7.19 (m, 10H, aromatic C−H), 2.63 (d, 3H, $-SCH_3$, $J_{PH} = 18.4$ Hz); ^{13}C NMR (ppm in $CDCl_3$) 133.6, 130.8, 129.7, 128.9, 128.8, 18.6; ^{31}P NMR (ppm in $CDCl_3$) 97.89 (q, $J_{PH} = 18.8$ Hz). Anal. Calcd for $C_{15}H_{13}PS_4$: C, 51.11; H, 3.72; S, 36.38. Found: C, 51.38; H, 3.94, S, 36.18.

$((C_2H_5)_2C_2S_2)P(S)(SCH_2C_6H_5)$, 5. A procedure similar to that described for the preparation of **1** was followed but with 4-hydroxy-3-hexanone (2.0 g, 17 mmol) in place of anisoin and BzBr (8.8 g, 52 mmol) as alkylating agent instead of MeI. Yield: 0.858 g of yellow oil, 15%. $R_f = 0.41$ (5:95, Et_2O/hexanes). ^1H NMR (ppm in $CDCl_3$) 7.36−7.28 (m, 5H, aromatic C−H), 4.23 (d, 2H, $-SCH_2C_6H_5$, $J = 14.4$ Hz), 2.42 (m, 2H, CH_2CH_3), 2.35 (m, 2H, $-CH_2CH_3$), 1.12 (td, 6H, $-CH_3$). ^{13}C NMR (ppm in $CDCl_3$) 135.6, 132.7, 129.5, 129.0, 128.1, 40.4, 25.0, 14.6. ^{31}P NMR ($CDCl_3$) 98.3 (t, $J_{PH} = 14.7$ Hz). MS (CI): 333.0 (M + H$^+$).

$((H_3CO$-*p*-$C_6H_4)_2C_2S_2)_2Ni$, 8. A solution of **1** (0.30 g, 0.73 mmol) in 2:1 MeOH/THF (30 mL) was treated with 10% LiOMe in MeOH (1.27 mL soln, 0.11 g LiOMe, 2.9 mmol) under a N_2 atmosphere. This homogeneous mixture was stirred 1 h at 25 °C, during which time a gold yellow color developed. To this mixture was added solid $NiCl_2{\cdot}6H_2O$ (0.086 g, 0.36 mmol), which induced an immediate color transformation to dark green. The reaction mixture was stirred several hours at ambient temperature, treated with 2 oxidizing equiv of I_2 (0.091 g, 0.36 mmol), and then stirred an additional 12 h. After removal of the solvent, the solid residue was washed with portions of H_2O followed by MeOH and then dried under vacuum to afford 0.22 g (93% yield) of $[Ni(S_2C_2(C_6H_4\text{-}p\text{-}OCH_3)_2)_2]$, which was identical in every respect to material prepared by Schrauzer's method.[15b] R_f (1:1 CH_2Cl_2/hexanes) = 0.47. Absorption spectrum (CH_2Cl_2) λ_{max} (ϵ_M): 303 (26 700), ~480 (sh, 2100), 927 (9260). ^1H NMR (ppm in $CDCl_3$) 7.33 (d, 8H, aromatic C−H, $J = 8.4$ Hz), 6.81 (d, 8H, aromatic C−H, $J = 8.4$ Hz), 3.82 (s, 12H, $-OCH_3$).

Results and Discussion

The P_4S_{10}/acyloin reaction mixture, after removal of unreacted phosphorus sulfide, was treated with excess (4−6 equiv) of alkyl halide with the intent of liberating cis dialkyl vinyl dithioether ((**a**) in Scheme 1), which then could be subjected to a Na/NH_3 or Na^+EtO^- deprotection protocol. Instead, the principal species identified and isolated in each case was a dithiolene thiophosphoryl thiolate compound in which the thiolate group originated from alkylating agent. The reaction appears to work more or less equally well with either diaryl or dialkyl α-hydroxy ketones, although the use of propioin and benzyl bromide resulted in an oil rather than a crystalline solid (**5**). The use of mesitoin in reactions with P_4S_{10} did not result in identifiable species other than unreacted starting material. The inability to retrieve products analogous to **1**, **2**, **4**, and **5** probably reflects a prohibitive degree of steric crowding such that the chalcogen exchange process that converts α-hydroxy ketone to dithiolene is thwarted. The patent literature, however, does describe a report of the synthesis of $[Ni(S_2C_2(C_6H_2\text{-}2,4,6\text{-}(CH_3)_3)_2)_2]$ but with little characterization data.[17]

All of these new compounds which were solids were characterized by X-ray crystallography; crystal and refinement data are summarized in Table 1. The compounds prepared are identified and referred to hereafter according to the numerical designations shown in Chart 1. Figure 2 presents thermal ellipsoid plots at the 50% probability level for **1**, **2**, **4**, and **8**, while Table 2 presents corresponding selected metric parameters. Crystallographic data for the other compounds that were structurally characterized are available as Supporting Information.

For the P_4S_{10}/anisoin system, a detailed chromatographic analysis of the product mixture also identified tetra(4-methoxyphenyl)thiophene and *trans*-4,4′-dimethoxystilbene as products, the former of which was identified by X-ray diffraction. These thiophene and stilbene byproducts, as well as the appreciable quantities of insoluble, uncharacterized organic material accompanying these reactions, indicate that the vigorous conditions needed to effect oxygen-for-sulfur exchange in the acyloin starting material are leading to competitive decomposition reactions.

The use of Lawesson's reagent in lieu of P_4S_{10} as chalcogen exchange reagent resulted in deoxyanisoin (4-methoxybenzyl 4-methoxyphenyl ketone) as the only identifiable species. This product was identified by X-ray crystallography and found to crystallize with different cell parameters than those found in a previous structural study.[23] The oxygen atom abstraction reaction was unexpected since

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[23] Norment, H. G.; Karle, I. L. *Acta Crystallogr.* **1962**, *15*, 873.

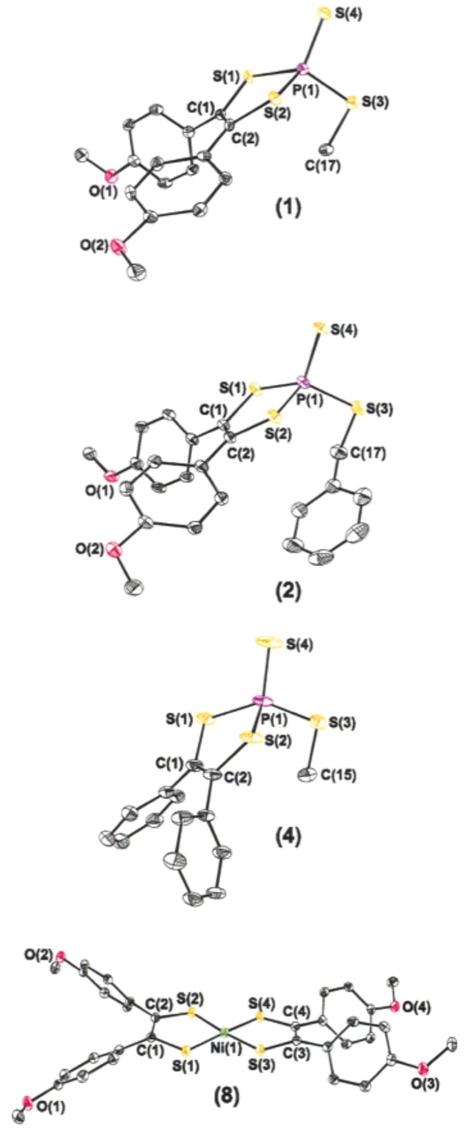

Figure 2. Thermal ellipsoid plots at the 50% probability level for compounds **1**, **2**, **4**, and **8**. Hydrogen atoms are omitted for clarity.

Lawesson's reagent has generally superseded P_4S_{10} as a more general and versatile sulfur-for-oxygen exchange reagent.[24] Lawesson's Reagent, however, has found application as a deoxygenating agent, notable examples being the reduction of halo-benzyl alcohols[25] and sulfoxides[26] to the corresponding deoxy species.

Methyl iodide and benzyl bromide alkylate with similar efficacy to form $(R_2C_2S_2)P(S)(SR')$ products. When 2-(bromomethyl)naphthalene was employed as alkylating agent, the only organic product identified from column chromatography was bis(2-methylnaphthalenyl) disulfide (**6**). This compound was found to crystallize (Table 1) in the noncentric space group $P2_1$ with a quasi-helical packing arrangement of disulfide-linked naphthalenyl units. It is unclear whether this product arises from initial formation of $(R_2C_2S_2)P(S)(SCH_2C_{10}H_7)$ by alkylation and subsequent decomposition or whether direct reaction of P_4S_{10} with 2-(bromomethyl)naphthalene affords thiol or thiolate that oxidatively couples with itself upon workup of the reaction. The use of Me_3SiCl as organic electrophile in the P_4S_{10}/acyloin reaction did not appear to produce *S*-silylated analogues of compounds **1**, **2**, **4**, or **5**.

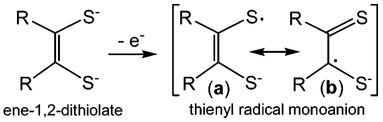

Figure 3. Possible oxidation states of a dithiolene ligand.

When dioxane was employed as solvent, yields of **1**, **2**, **4**, and **5** were consistently near 20%. A recent patent application[17] has described dramatically improved yields (90%) from Schrauzer's P_4S_{10}/acyloin reaction when 1,3-dimethyl-2-imidazolidinone was employed as reaction solvent in place of dioxane. This solvent, however, did not result is visible improvement in the yield of **1** when used as the reaction medium. In view of its expense and the additional inconveniences associated with fully removing this high-boiling solvent in the reaction workup, 1,3-dimethyl-2-imidazolidinone does not offer any practical advantage over dioxane for the preparation of dithiolene thiophosphoryl thiolate compounds from P_4S_{10}/acyloin reaction mixtures.

The reaction of **1** with 4 equiv of Na^+MeO^- in MeOH followed by $NiCl_2{\cdot}6H_2O$ produced the known[15b] nickel bis(dithiolene) complex $Ni(S_2C_2(C_6H_4\text{-}p\text{-}OCH_3)_2)_2$, **8**, in 93% isolated yield. This compound was identified both spectroscopically and structurally by X-ray crystallography. The high yield observed in this reaction suggests that these dithiolene thiophosphoryl molecules may generally lead to high yields of metal complexes if they are used as protected forms of dithiolene ligands. In this connection, the dithiolene thiophosphoryl compounds reported here are highly analogous to 1,3-dithiol-2-ones, which liberate ene-1,2-dithiolate salts when subjected to base hydrolysis.[27] The possibilities for using these dithiolene thiophosphoryl compounds as immediate dithiolene ligand precursors renders them viable alternatives to the several-step syntheses through which 1,3-dithiol-2-ones are typically synthesized.

Compounds **1**, **2**, and **4** (Figure 2) have an approximate tetrahedral configuration around the central phosphorus atom and pseudo-C_s symmetry, with the mirror plane coincident with the S(4)−P(1)−S(3) plane and bisecting the dithiolene chelate. The thiophosphoryl bond distances (P(1)−S(4)) are in the range 1.9241(8)−1.9361(7) Å, values that are within the range observed for similar bond lengths in other structurally characterized thiophosphoryl molecules (1.899(1) Å in $(PhS)_3PS$;[28] 1.893(2)−1.907(2) Å in P_4S_{10};[29] 1.920-

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compounds **1**, **2**, **4**, and **8**

	1	**2**	**4**		**8**
P(1)−S(1)	2.098(1)	2.0950(7)	2.1006(9)	Ni(1)−S(1)	2.1221(6)
P(1)−S(2)	2.088(1)	2.0884(7)	2.100(1)	Ni(1)−S(2)	2.1218(6)
P(1)−S(3)	2.068(1)	2.0694(7)	2.0652(8)	Ni(1)−S(3)	2.1342(5)
P(1)−S(4)	1.928(1)	1.9361(7)	1.9241(8)	Ni(1)−S(4)	2.1183(6)
C(1)−C(2)	1.346(4)	1.335(3)	1.347(2)	C(1)−C(2)	1.393(3)
C(1)−S(1)	1.776(3)	1.780(2)	1.771(2)	C(3)−C(4)	1.391(3)
C(2)−S(2)	1.777(3)	1.766(2)	1.767(2)	S(1)−C(1)	1.717(2)
S(4)−P(1)−S(1)	117.66(5)	119.06(3)	115.98(3)	S(2)−C(2)	1.703(2)
S(4)−P(1)−S(2)	114.62(5)	113.36(3)	116.04(4)	S(3)−C(3)	1.717(2)
S(4)−P(1)−S(3)	107.91(5)	105.73(3)	109.19(3)	S(4)−C(4)	1.710(2)
P(1)−S(3)−C(17)/C(15)	101.9(1)	104.63(8)	102.61(7)	S(1)−Ni(1)−S(2)	90.91(2)
P(1)−S(1)−C(1)	98.8(1)	99.35(7)	97.81(6)	S(3)−Ni(1)−S(4)	91.25(2)
P(1)−S(2)−C(2)	99.7(1)	99.91(7)	97.78(6)		

(2) Å in [PhSP(S)(μ-S)];[30] 1.91(1) Å in [BzSP(S)(μ-S)]$_2$;[31] (1.910(2) and 1.912(2) Å in [(C_6H_{11})SP(S)(μ-S)]$_2$;[31] 1.948(2) Å in ($Me_3SnS)_3PS$;[32]).

The structure of **8** (Figure 2) is completely typical of neutral nickel bis(dithiolene) complexes.[33] Surprisingly, the only anisyl-substituted metal dithiolene compound that has been previously characterized by X-ray crystallography is the square planar complex [Pt($S_2C_2(C_6H_4$-*p*-$OCH_3)_2)_2$].[34] Although **8** has inversion symmetry, it rests on a general position in the space group $P\bar{1}$ such that all interatomic distances are independent. The high resolution of the structure reveals the Ni(1)−S(3) distance to be modestly longer than the others, but the difference is still significant statistically. The metal atom deviates 0.02 Å from the mean plane defined by the four sulfur atoms. The C(1)−C(2) and C(3)−C(4) bond distances (1.393(3) and 1.391(3) Å) of the dithiolene chelates are appreciably longer than would be expected for pure olefinic bonds (∼1.35 Å), while the S−C bond distances (1.703(2)−1.717(2) Å) are shorter than bona fide S−C single bonds (∼1.77 Å). Collectively, these metric parameters clearly reveal the π-radical monoanion nature of the ligand, which confers partial thione character to the S−C bonds and some degree of single bond character to the carbon−carbon bonds (Figure 3, resonance structure (**b**)).

Compounds **1**, **2**, and **4** were examined electrochemically for any reversible redox processes. Within the approximately 2 V window permitted by CH_2Cl_2, no reversible feature was observed for any of these compounds. This result is unsurprising since the main group elements do not have empty or partially filled d orbitals at an appropriate energy with which the dithiolene ligand can form delocalized bonding interactions.

Compounds **1**, **2**, **4**, and **5** have all been interrogated by NMR spectroscopy. The ^{31}P NMR spectra reveal P−H coupling on the order of 18−19 Hz to the α-protons of the thiolate group. Thus, the ^{31}P signals in **1**, **2**, **4**, and **5** appear as as quartets and doublets due to P−H coupling to $-SCH_3$ and $-SCH_2C_6H_5$, respectively. In turn, the $-SCH_3$ and $-SCH_2C_6H_5$ ^1H NMR signals all appear as doublets. The magnitude of this P−H coupling is similar to the $J = 16.5$ Hz observed in a thiophosphoryl tris(thiolate) complex $C_{10}H_{15}S_3PS$ derived from reaction of tetrabutylammonium camphor sulfonate with P_4S_{10}.[35] In compound **5**, the coupling pattern for the $-CH_2-$ groups of the ethyl substituents is more complex than expected, consisting of at least 12 lines, but it integrates to the proper signal intensity.

Conclusion

A series of new thiophosphoryl dithiolene molecules has been isolated by treating P_4S_{10}/acyloin reaction mixtures with a variety of organic electrophiles. This procedure works equally well with alkyl- and aryl-substituted acyloins. These thiophosphoryl dithiolene species are undoubtedly the in situ generated species which produce metal dithiolene complexes when transition metal salts are added to the reaction mixture. The ability to "trap" and isolate these molecules in *S*-alkylated forms ($R_2C_2S_2$)P(S)(SR′) enables the preparation of metal complexes, demonstrated here in the case of nickel, in a subsequent step with much higher yields and under milder conditions. This modification of Schrauzer's original reaction protocol may prove useful in instances when noble metal dithiolene complexes are targeted and a premium is placed upon high yields.

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Supporting Information Available: Thermal ellipsoid drawings at the 50% probability levels with complete atomic labeling in PDF and complete X-ray data (atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates) in CIF format for **1**−**4** and **6**−**8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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