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Synthesis, Structures, and Properties of Mixed Dithiolene-Carbonyl and Dithiolene-Phosphine Complexes of Tungsten

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A new, high yield synthesis of $[Ni(S_2C_2Me_2)_2]$ (**3**) is described using 4,5-dimethyl-1,3-dithiol-2-one, $Me_2C_2S_2C{=}O$ (**1**), as dithiolene ligand precursor. Reaction of $(Me_2C_2S_2)Sn^nBu_2$, **2**, with WCl_6 produces tris(dithiolene) $[W(S_2C_2Me_2)_3]$ (**6**) and demonstrates the potential synthetic utility of this compound in metallodithiolene synthesis. The series of compounds $[W(S_2C_2Me_2)_x(CO)_{6-2x}]$ ($x = 1-3$), obtained as a mixture via the reaction of $[Ni(S_2C_2Me_2)_2]$ with $[W(MeCN)_3(CO)_3]$, has been characterized structurally. A trigonal prismatic geometry is observed for $[W(S_2C_2Me_2)(CO)_4]$ (**4**) and confirmed by a DFT geometry optimization to be lower in energy than an octahedron by 5.1 kcal/mol. The tris(dithiolene) compound $[W(S_2C_2Me_2)_3]$ crystallizes in disordered fashion upon a 2-fold axis in $C2/c$, a different space group than that observed for its molybdenum homologue ($P\bar{1}$), which is attributed to a slightly smaller chelate fold angle, α, in the former. The reactivity of **4** and $[W(S_2C_2Me_2)_2(CO)_2]$ (**5**) toward PMe_3 has been examined. Compound **4** yields only $[W(S_2C_2Me_2)(CO)_2(PMe_3)_2]$ (**7**), while **5** produces either $[W(S_2C_2Me_2)_2(CO)(PMe_3)]$ (**8**) or $[W(S_2C_2Me_2)_2(PMe_3)_2]$ (**9**) depending upon reaction conditions. Crystallographic characterization of **5**, **8**, and **9** reveals a trend toward greater reduction of the dithiolene ligand (i.e., more ene-1,2-dithiolate character) across the series, as manifested by C−C and C−S bond lengths. These structural data indicate a profound effect exerted by the π-acidic CO ligands upon the apparent state of reduction of the dithiolene ligand in compounds with ostensibly the same oxidation state.

Introduction

Heteroleptic tungsten dithiolene complexes have been explored almost exclusively in the context of modeling the structures, spectroscopy, and reactivity of the catalytic sites of tungstoenzymes and molybdenum isosymes. A considerable body of synthesis has now been developed in which a bis(dithiolene) tungsten[1−5] or mono(dithiolene) tungsten unit[6−8] is constant and supporting chalcogenide or chalcogenate coligands are varied. The starting point for much of this work has been the $[W(S_2C_2R_2)_2(CO)_2]$ (R = Me, Ph) complexes originally described by Schrauzer[9] and examined more recently by Holm.[10,11] The reaction types by which $[W(S_2C_2R_2)_2(CO)_2]$ have been converted to biologically relevant catalytic site analogues have been non-redox carbonyl displacement reactions.

The prevalence of dithiolene supporting ligands for molybdo- and tungstoenzyme catalytic sites suggests the possible utility of this ligand type in supporting non-biological redox catalysis. This possibility has not been explored. An

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obstacle to the use of dithiolenes as supporting ligands in homogeneous catalysis is a paucity of starting materials and methods which would lead one to reactive compounds other than coordinatively saturated tris(dithiolene) or, for the Group VIII metals, bis(dithiolene) complexes. For this reason, $[W(S_2C_2Me_2)_2(CO)_2]$ invites further scrutiny of its behavior, for example, toward direct oxidative addition reactions. The preparation of $[W(S_2C_2Me_2)_2(CO)_2]$ is attended by the formation of modest quantities of the unusual mono(dithiolene) compound $[W(S_2C_2Me_2)(CO)_4]$, a species of interest for similar reasons. The following are selected initial results from a broad survey of the reactivity of $[W(S_2C_2Me_2)_x(CO)_{6-2x}]$ ($x = 1$ or 2) with a variety of small molecule substrates under a range of conditions.

Experimental Section

4,5-Dimethyl-1,3-dithiol-2-one (**1**) was prepared by a modified version of a literature procedure.[12] All other reagents were either purchased from commercial sources and used as received (Na metal, $SnCl_2{}^nBu_2$, WCl_6, $NiCl_2$, I_2, 1.0 M PMe_3 in toluene, Me_3NO) or prepared using literature methods ($[W(CO)_3(MeCN)_3]$[13]). Solvents either were dried with a system of drying columns from the Glass Contour Company (CH_2Cl_2, *n*-pentane, hexanes, Et_2O, THF, C_6H_6, toluene) or freshly distilled according to standard procedures[14] (MeOH, CH_3CN). Silica columns were run in the open air using 60−230 μm silica (Dynamic Adsorbents).

Syntheses. 2,2-Di-*n*-butyl-4,5-dimethyl-1,3,2-dithiastannole (2). Pieces of freshly cut sodium metal (1.96 g, 0.085 mol) were added to dry, distilled MeOH (200 mL) under a N_2 atmosphere at 0 °C. The resulting mixture was stirred for 30 min to allow complete consumption of the Na metal. Under an outward nitrogen flow, 4,5-dimethyl-1,3-dithiol-2-one (5.0 g, 0.034 mol) was then added to the NaOMe/MeOH solution. Stirring was continued for 2 h at 25 °C, during which time the homogeneous colorless solution developed a slight yellowish aspect. Under an outward flow of N_2, solid $SnCl_2{}^nBu_2$ (10.4 g, 0.034 mol) was added, which produced the immediate formation of a colorless precipitate. This heterogeneous mixture was stirred overnight at ambient temperature. The precipitate was separated by filtration, and the filtrate was reduced to dryness under reduced pressure. The crude solid was redissolved in a minimal volume of CH_2Cl_2 and evaporated onto ~4 g of SiO_2. This coated silica was loaded as a dry solid onto a silica column packed as a slurry in hexanes. Elution began with *n*-hexanes (100 mL) and was continued with 100 mL portions of a CH_2Cl_2:hexanes mixture that incrementally increased from 1% to 5% CH_2Cl_2 in hexanes (v/v). Compound **2** was collected as the leading fraction from the column. Yield: 4.5 g, 0.013 mol, 38%. $R_f = 0.54$ (2:3 CH_2Cl_2:hexanes). ^{1}H NMR (δ, ppm in $CDCl_3$): 1.99 (s, 6H, dithiolene CH_3), 1.68 (quintet, 4H, -$CH_2CH_2CH_2$-), 1.53 (t, 4H, -SnCH_2-), 1.34 (sextet, 4H, $J = 7.3$ Hz, -$CH_2CH_2CH_3$), 0.90 (t, 6H, $J = 7.3$ Hz, ^{n}Bu CH_3). ^{13}C NMR (δ, ppm in $CDCl_3$): 123.2 (olefinic C), 28.1, 26.9, 22.9, 21.5, 13.8. ESI-MS$^+$: *m/z* 352 ($M + H^+$).

$[Ni(S_2C_2Me_2)_2]$ (3). The following procedure is an alternative to the original preparation described by Schrauzer.[15] Portions of freshly cut Na metal (6.29 g, 0.274 mol) were added to freshly distilled MeOH (300 mL) with rapid stirring at 0 °C under a N_2 atmosphere. Stirring was continued for 2 h to allow for complete reaction. A solution of 4,5-dimethyl-1,3-dithiol-2-one (20.0 g, 0.137 mol) in MeOH (50 mL) was added via cannula to the NaOMe solution, and the resulting mixture was stirred an additional 2 h at ambient temperature. Under nitrogen flow, anhydrous $NiCl_2$ (8.87 g, 0.068 mol) was added as a single portion, producing a change in color to dark brown. After stirring for 6 h, one ½ equiv of solid I_2 (17.4 g, 0.0684 mol) was added under nitrogen flow, and stirring was continued for an additional 6 h. The precipitate that developed in the reaction vessel was collected by vacuum filtration and washed with portions of deionized H_2O (2 × 50 mL) followed by MeOH (2 × 50 mL) and Et_2O (3 × 50 mL). The dark blue solid was dried under vacuum for 24 h to afford pure $[Ni(S_2C_2Me_2)_2]$ (17.5 g, 0.059 mol, 87% yield) that was spectroscopically identical to samples prepared via the method of Schrauzer.[15,16]

$[W(S_2C_2Me_2)(CO)_4]$ (4), $[W(S_2C_2Me_2)_2(CO)_2]$ (5), $[W(S_2C_2Me_2)_3]$ (6) (Method 1). The following procedure is a slight adaptation of the procedure described by Holm and Goddard.[10] A solution of $[Ni(S_2C_2Me_2)_2]$ (1.51 g, 5.12 mmol) and $[W(CO)_3(MeCN)_3]$ (1.00 g, 2.56 mmol) in 250 mL of dry CH_2Cl_2 was stirred overnight under a N_2 atmosphere. The mixture was filtered to remove polymeric $[Ni(S_2C_2Me_2)]_x$, and the dark filtrate was reduced to dryness in vacuo. The dark residual solid was extracted with *n*-pentane (2 × 50 mL). The pentane extracts were filtered, reduced to dryness, and redissolved in a minimal volume of pentane (~30 mL). This solution was directly loaded onto a silica column packed as a slurry in *n*-pentane and eluted with the same solvent. An orange band corresponding to $[W(S_2C_2Me_2)(CO)_4]$ rapidly eluted and was followed by a slower red-violet band corresponding to $[W(S_2C_2Me_2)_2(CO)_2]$. These bands were separately collected and reduced to dryness. The dark solids remaining after the first *n*-pentane extraction were extracted with a minimal portion of 30% C_6H_6 in pentane, and the extracts were directly pipeted onto a column containing the same solvent mixture. Elution brought down a red-violet band of additional $[W(S_2C_2Me_2)_2(CO)_2]$, which was collected and combined with the material obtained from the first silica column, followed by a dark greenish-blue band of $[W(S_2C_2Me_2)_3]$.

$[W(S_2C_2Me_2)(CO)_4]$: 0.192 g, 0.46 mmol, 18.1% yield. R_f (*n*-pentane) = 0.91. ^{1}H NMR (δ, ppm in C_6D_6): 2.37 (s, dithiolene CH_3). ^{13}C NMR (δ, ppm in C_6D_6): 216.31 (*C*O), 155.14 (olefinic *C*), 24.79 (dithiolene *C*H_3). Absorption spectrum (CH_2Cl_2): λ_{max} (ε_M) 236 (sh, 35700), 268 (sh, 11300), 316 (7400), 406 (12100). IR (ν, cm^{-1}): 2074 (s, CO), 1987, (s, CO), 1967 (s, CO), 1262 (w), 1094 (w), 1018 (w), 802 (w), 548 (w), 506 (w), 447 (w). Anal. Calcd for $C_8H_6O_4S_2W$: C, 23.20; H, 1.46; O, 15.45. Found: C, 23.41; H, 1.42; O, 15.50.

$[W(S_2C_2Me_2)_2(CO)_2]$: 0.240 g, 0.504 mmol, 19.7% yield. R_f (40% C_6H_6 in *n*-pentane) = 0.78. ^{1}H NMR (δ, ppm in C_6D_6): 2.35 (s, dithiolene CH_3). ^{13}C NMR (δ, ppm in C_6D_6): 219.12 (*C*O), 160.84 (olefinic *C*), 24.53 (dithiolene *C*H_3). Absorption spectrum (CH_2Cl_2): λ_{max} (ε_M) 358 (5820), 508 (17500), 636 (405). IR (ν, cm^{-1}): 2022 (s, CO), 1949 (s, CO), 1475 (m), 1363 (w), 934 (m), 558 (w), 446 (s). Anal. Calcd for $C_{10}H_{12}O_2S_4W$: C, 25.22; H, 2.54; O, 6.72. Found: C, 25.22; H, 2.51; O, 6.82.

$[W(S_2C_2Me_2)_3]$: 0.034 g, 0.063 mmol, 2.5% yield. R_f (40% C_6H_6 in *n*-pentane) = 0.59. ^{1}H NMR (δ, ppm in $CDCl_3$): 2.72 (s, 18H, dithiolene CH_3). ^{1}H NMR (δ, ppm in C_6D_6): 2.25 (s, 18H, dithiolene

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CH_3). ^{13}C NMR (δ, ppm in $CDCl_3$): 167.6 (olefinic *C*), 25.5 (dithiolene CH_3). Absorption spectrum (CH_2Cl_2): 254 (12900), 268 (sh, 4840), 310 (3730), 402 (10800), 508 (4710), 608 (19700).

[W($S_2C_2Me_2$)$_3$] (6) (Method 2). A 50 mL Schlenk flask was charged with a stir bar, ($Me_2C_2S_2$)Sn(^{n}Bu)$_2$ (0.465 g, 1.3 mmol) and WCl_6 (0.175 g, 0.44 mmol). Dry toluene (40 mL) was added via syringe; a dark green color immediately became apparent. The flask septum was exchanged with an oven-dried condenser leading to a Schlenk line equipped with mercury bubbler. The reaction mixture was heated to reflux for 12 h under N_2, whereupon it was cooled to room temperature, and the solvent was removed under reduced pressure. The solid residue was washed with MeOH (3 × 10 mL) to remove the di(*n*-butyl)tin dichloride byproduct and then dried in vacuo. Yield: 0.190 g, 0.35 mmol, 80% yield. ESI-MS$^-$: *m/z* 538 (M$^-$). Anal. Calcd for $C_{12}H_{18}S_6W$: C, 26.76; H, 3.37; S, 35.73. Found: C, 26.97; H, 3.37; S, 35.44.

[W($S_2C_2Me_2$)(CO)$_2$(PMe_3)$_2$] (7). A 50 mL Schlenk flask with stir bar was charged with [W($S_2C_2Me_2$)(CO)$_4$] (0.088 g, 0.214 mmol) under an atmosphere of N_2. Toluene (15 mL) was added via syringe to afford a yellow solution, followed by addition of PMe_3 (1.5 mL of 1.0 M toluene solution, 1.5 mmol). A color change to red developed immediately. After heating to 75 °C with stirring for 8 h, the solvent was removed in vacuo to afford a red solid. Recrystallization was accomplished by slow evaporation of a C_6H_6 solution under nitrogen. Yield: 0.104 g, 0.204 mmol, 95% yield. ^{1}H NMR (δ, ppm in $CDCl_3$): 2.53 (s, 6H, dithiolene CH_3), 1.77 (d, J_{PH} = 10 Hz, 18H, P(CH_3)$_3$). ^{13}C NMR (δ, ppm in $CDCl_3$): 237.33 (t, J_{PC}= 21.8 Hz, *C*O), 145.16 (t, olefinic *C*), 24.52 (t, dithiolene *C*H_3), 20.95 (m, P(*C*H_3)$_3$). ^{31}P NMR (δ, ppm in $CDCl_3$): −4.87 (s, J_{PW} = 171.9 Hz). Absorption spectrum (CH_2Cl_2): 342 (sh, 4410), 372 (7110), 454 (sh, 1200). IR (ν, cm^{-1}): 1910 (vs, CO), 1844 (vs, CO), 1811 (vs, CO), 1415 (m), 1277 (s), 934 (vs), 855 (w), 723 (w), 670 (m), 571 (w), 473 (w). Anal. Calcd for $C_{12}H_{24}O_2P_2S_2W$: C, 28.25; H, 4.74; P, 12.14. Found: C, 28.43; H, 4.62; P, 12.29.

[W($S_2C_2Me_2$)$_2$(CO)(PMe_3)] (8). A solution of [W($S_2C_2Me_2$)$_2$(CO)$_2$] (0.173 g, 0.363 mmol) in toluene (20 mL) was treated with PMe_3 (0.425 mL of 1 M toluene solution, 0.425 mmol) at ambient temperature. An immediate change in color from magenta to intense orange ensued, and the resulting solution was stirred 2 h. The solvent was removed in vacuo to afford an orange solid that was recrystallized by slow evaporation of a C_6H_6 solution. Yield: 0.175 g, 0.333 mmol, 92% yield. ^{1}H NMR (δ, ppm in $CDCl_3$): 2.71 (s, 12H, dithiolene CH_3), 1.65 (d, J_{PH} = 9.6 Hz, 9H, P(CH_3)$_3$). ^{13}C NMR (δ, ppm in $CDCl_3$): 232.65 (s, *C*O), 155.09 (br s, olefinic *C*), 24.04 (s, dithiolene *C*H_3), 21.09 (d, J_{PC} = 35.9 Hz, P(*C*H_3)$_3$). ^{31}P NMR (δ, ppm in $CDCl_3$): 1.95 (s, J_{PW} = 217.6 Hz). Absorption spectrum (CH_2Cl_2) λ_{max} (ε_M): 484 (29000), 358 (15600), 324 (sh, 7900), 276 (sh, 14500). IR (ν, cm^{-1}): 1929 (s, CO), 1501 (w), 1270 (m), 953 (m), 670 (w), 446 (s). Anal. Calcd for $C_{12}H_{21}OPS_4W$: C, 27.49; H, 4.04; P, 5.91. Found: C, 27.65; H, 4.00, P, 5.72.

[W($S_2C_2Me_2$)$_2$(PMe_3)$_2$] (9). A solution of [W($S_2C_2Me_2$)$_2$(CO)$_2$] (0.30 g, 0.630 mmol) in 30 mL of toluene was treated with PMe_3 (2.5 mL of 1 M toluene solution, 2.5 mmol) delivered via syringe. A single portion of freshly sublimed Me_3NO (0.095 g, 1.26 mmol) was added under N_2 flow, and the resulting mixture was stirred for 2 h. A second portion of PMe_3 (2.5 mL of 1 M toluene solution, 2.5 mmol) was added, and the mixture was then heated to reflux for 4 h. During this time period, a yellow precipitate developed. The reaction mixture was cooled to ambient temperature, and the yellow solid was isolated by filter cannulation, washed with *n*-pentane (20 mL) and dried in vacuo. Crystallization of this crude product was accomplished by diffusion of hexanes vapor into a C_6H_6 solution under nitrogen. Yield: 0.270 g, 0.472 mmol, 75% yield. ^{1}H NMR (δ, ppm in $CDCl_3$): 2.63 (s, 12H, dithiolene CH_3), 1.80 (d, J_{PH} = 8.8 Hz, 18H, P(CH_3)$_3$). ^{13}C NMR (δ, ppm in $CDCl_3$): 149.95 (s, olefinic *C*), 23.76 (m, P(*C*H_3)$_3$), 23.0 (s, dithiolene *C*H_3). ^{31}P NMR (δ, ppm in $CDCl_3$): −5.43 (s, J_{PW} = 239.43 Hz). Absorption spectrum (CH_2Cl_2) λ_{max} (ε_M): ~270 (sh, 16500), ~344 (sh, 7800), ~382 (sh, 11800), 410 (13100), ~462 (sh, 7500). IR (ν, cm^{-1}): 2905 (m), 1534 (w), 1408 (m), 1276 (s), 947 (vs), 723 (m), 670 (m). Anal. Calcd for $C_{14}H_{30}P_2S_4W$: C, 29.37; H, 5.28; P, 10.82. Found: C, 29.29; H, 5.14, P, 10.64.

X-ray Structures. The numbering system by which the compounds are hereafter identified is defined in the preceding Experimental Section and in Scheme 1. Colorless plate crystals of **1** were obtained directly from the receiving flask used in the vacuum distillation of **1**,[12] while colorless column-shaped crystals of **2** deposited upon slow evaporation of a hexanes solution. Dark orange-red plate crystals of **4** grew from a concentrated *n*-pentane solution cooled to −20 °C. Slow evaporation of a benzene solution of **5** yielded red-violet block-shaped crystals of **5**. Dark bluish-red block-shaped crystals of **6** grew by the slow diffusion of MeOH vapor into a nitrobenzene solution. Crystals of **7** (red blocks) and **8** (orange blocks) were grown by evaporation of benzene and Et_2O solutions, respectively, while crystals of **9** were grown by diffusion of hexanes vapor into a benzene solution. All crystals were coated in Paratone oil and mounted onto a nylon cryoloop attached to a goniometer.

Data were collected with a Bruker APEX CCD diffractometer equipped with a Kryoflex attachment supplying a nitrogen stream at 100 K. Full spheres of data were obtained by collecting either three sets of 606 frames in ω (0.3°/scan) with φ held constant at 0, 120, and then 240° (for **4** and **8**) or a combination of three sets of 400 scans in ω (0.5°/scan) at $\varphi = 0$, 90, and 180° with two sets of 800 scans in φ (0.45°/scan) at $\omega = -30$ and 210° (for **1**, **2**, **5**−**7** and **9**) under control of either the SMART software package[17a] or the APEX2 program suite.[17b] The crystal of **6** used for data collection proved to be twinned; approximately 95% of the available reflections could be fit to a two-component twin with lattice orientations offset by a 1.2° rotation about the *c* axis as determined by CELL_NOW.[18] The raw data were reduced to F^2 values using the SAINT+ software,[19] and a global refinement of unit cell parameters was performed using 4054−9991 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[20a] for **1**−**2**, **4**−**5**, **7**−**9**; TWINABS[20b] for **6**). Structure solutions were obtained by direct methods (**1**, **4** and **6**−**8**) or by Patterson methods (**2**, **5**, and **9**), and refinements were accomplished by full-matrix least-squares procedures using the SHELXTL software suite.[21] Compound **6** revealed two distinct forms of disorder, one being a whole molecule disorder over two positions, both upon a crystallographic 2-fold axis, which was modeled as a 9:1 distribution. Only the positions

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(17) (a) *SMART*, Version 5.625; Bruker-AXS: Madison, WI, 2000. (b) *APEX2*Version 2.1−4; Bruker-AXS: Madison, WI, 2007.

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Scheme 1. (A) High-Yield Syntheses for [Ni($S_2C_2Me_2$)$_2$] (**3**) and [W($S_2C_2Me_2$)$_3$] (**6**) and (B) Synthesis of Mixed Dithiolene Carbonyl and Dithiolene Phosphine Tungsten Compounds [W($S_2C_2Me_2$)$_x$(CO)$_y$(PMe$_3$)$_z$]

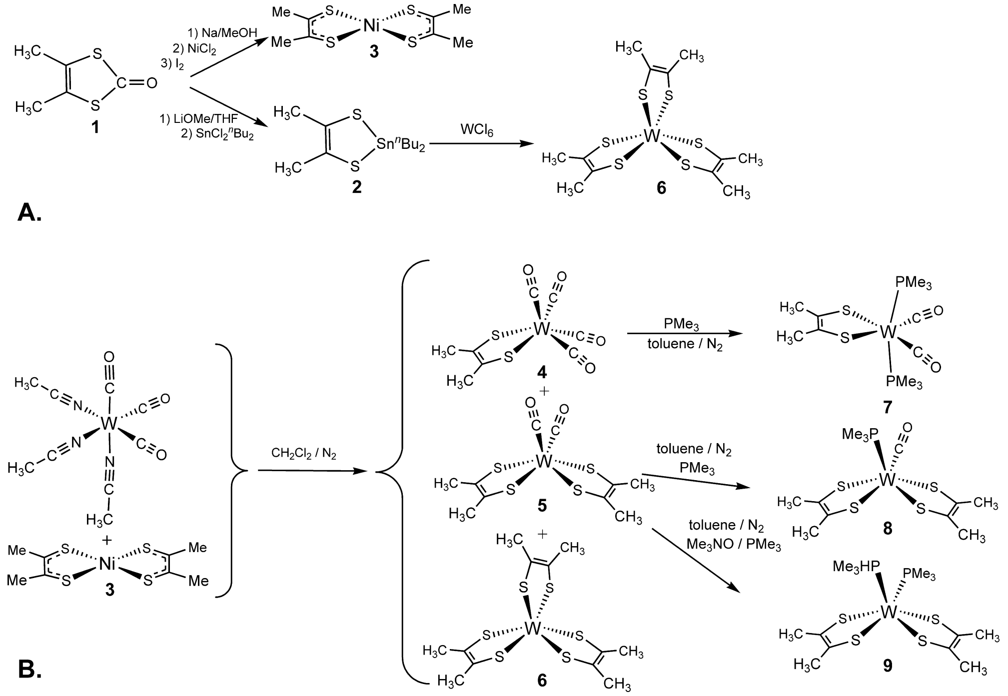

Table 1. Crystal and Refinement Data for Compounds **1**, **2**, and **4**−**9**

	1	**2**	**4**	**5**	**6**	**7**	**8**	**9**
formula	$C_5H_6OS_2$	$C_{12}H_{24}S_2Sn$	$C_8H_6O_4S_2W$	$C_{10}H_{12}O_2S_4W$	$C_{12}H_{18}S_6W$	$C_{12}H_{24}O_2P_2S_2W$	$C_{12}H_{21}OPS_4W$	$C_{14}H_{30}P_2S_4W$
formula wt	146.22	351.12	414.10	476.29	538.47	510.22	524.35	572.41
temperature	100 K	195 K	100 K	100 K	100 K	100 K	100 K	100 K
wavelength, Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
color, habit	white plate	white column	orange plates	red-purple block	blue-red block	red block	orange block	orange column
crystal system	monoclinic	triclinic	triclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)
a, Å	3.9068(3)	10.099(1)	6.878(1)	7.0364(3)	15.344(2)	13.633(4)	8.922(1)	18.384(1)
b, Å	12.1944(8)	10.475(1)	7.600(1)	7.6373(3)	8.918(1)	10.553(3)	9.574(1)	7.4904(5)
c, Å	13.4159(9)	15.224(2)	12.318(2)	13.5606(6)	13.669(2)	13.062(4)	21.246(3)	17.380(2)
α, deg.	90	82.493(2)	94.916(2)	93.506(1)	90	90	90	90
β, deg.	92.044(1)	86.660(2)	97.976(2)	93.891(1)	108.089(2)	105.522(4)	91.982(2)	121.368(1)
γ, deg.	90	77.971(2)	114.880(2)	95.516(1)	90	90	90	90
V, Å^3	638.74(8)	1560.8(3)	571.0(2)	722.01(5)	1778.0(4)	1810.6(9)	1813.8(4)	2043.5(3)
Z	4	4	2	2	4	4	4	4
density, g/cm^3	1.520	1.494	2.408	2.191	2.012	1.872	1.920	1.861
μ, mm^{-1}	0.725	1.878	10.469	8.564	7.186	6.783	6.908	6.211
total reflections	10389	19383	4975	12457	4235	30894	31081	17347
indep. reflections	1566	4942	2603	3434	2206	4497	4513	2546
parameters	75	279	138	157	128	180	179	101
R1[a], wR2[b] (I > 2σ)	0.0281, 0.0696	0.0394, 0.0976	0.0327, 0.0807	0.0175, 0.0393	0.0377, 0.0883	0.0145, 0.0352	0.0148, 0.0342	0.0131, 0.0302
R1[a], wR2[b] (all data)	0.0363, 0.0724	0.0521, 0.1084	0.0363, 0.0824	0.0197, 0.0402	0.0436, 0.0907	0.0153, 0.0355	0.0155, 0.0345	0.0138, 0.0304
GoF	1.356	1.088	1.052	1.055	1.040	1.151	1.128	1.069

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

of the tungsten and sulfur atoms were identified and refined for the minor contributor. The crystallographic 2-fold axis bisects one dithiolene ligand, passes through the tungsten atom, and interrelates the remaining two dithiolene ligands by the 2-fold rotation. Because **6** has only C_{3h} symmetry because of a slight fold of the dithiolene chelate along each intraligand S−S vector, its location on the crystallographic 2-fold axis imposes a second disorder between two highly overlapped rotational variants. This disorder was treated with a ∼1:1 split atom model. Anisotropic refinement of the structure was limited to the tungsten and sulfur atoms only. All 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 have been allowed to refine an orientation around the C−C bond that optimizes the model for electron density for this group. Crystal and refinement data for **1**, **2**, and **4**−**9** are summarized in Table 1.

Other Physical Methods. UV−vis spectra were obtained at ambient temperature with a Hewlett-Packard 8452A diode array spectrometer, while IR spectra were taken as pressed KBr pellets with a Thermo Nicolet Nexus 670 FTIR instrument in absorption mode. All NMR spectra were recorded at 25 °C with a Varian Unity Inova spectrometer operating at 400, 100.5, or 161.8 MHz for ^{1}H, ^{13}C, and ^{31}P, respectively. Spectra were referenced to the solvent residual (^1H, ^{13}C) or to a value loaded from a reference file (^{31}P). Electrospray ionization mass spectra were obtained either with a Bruker Daltonics or with a PESciex Qstar instrument. 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_4NPF_6 as the supporting electrolyte. Under these conditions, the Cp_2Fe^+/Cp_2Fe couple consistently occurred at +440 mV. Elemental analyses were performed by Canadian Microanalytical of Delta, British Columbia or by Midwest Microlab, LLC of Indianapolis, IN.

Calculations

All calculations were performed using the Gaussian 03 suite of software[22] at the B3LYP[23] (Becke-3 exchange[24] and Lee−Yang−Parr correlation[25] functional) level of theory. Full geometry optimizations were performed in C_{2v} symmetry, and stationary points were characterized via analytical frequency calculations. For the S, O, C, and H atoms, the Pople triple-ζ quality basis set (6−311++G(2d,p))[26] with 1 diffuse and 2 polarization functions (d) on the S, C, and O atoms and 1 diffuse and 1 polarization function (p) on the H atoms was used. For the W atom, the Stuttgart triple-ζ quality basis set (SDD) with an Effective Core Potential (ECP) was used.[27]

Discussion

Syntheses. Reported herein is a new and more efficient synthesis of $[Ni(S_2C_2Me_2)_2]$, which considerably improves access to preparative-scale quantities of this useful compound and thus facilitates further exploration of the reactivity of $[W(S_2C_2Me_2)(CO)_4]$ and $[W(S_2C_2Me_2)_2(CO)_2]$. To the best of our knowledge, the P_4S_{10}/acetoin protocol originally described by Schrauzer has remained until now the exclusive method by which transition metal complexes with the methyl substituted dithiolene ligand have been generated. Although it is reproducible, Schrauzer's method suffers from low yields, is attended by the unpleasant smells invariably associated with phosphorus sulfides, and generally requires a further degree of purification of the metallodithiolene product by Soxhlet extraction. Beginning with 4,5-dimethyl-1,3-dithiol-2-one, a compound whose preparation we have simplified and amplified to a scale of tens of grams,[12] straightforward base hydrolysis liberates the fully reduced ene-1,2-dithiolate. Subsequent addition of $NiCl_2$, followed by iodine to oxidize the resulting dianion, yields $[Ni(S_2C_2Me_2)_2]$ on a preparative scale in a minimal time and without the need for additional purification. This synthetic approach supersedes the method of Schrauzer.[15,28]

An alternative useful form to the methyl-substituted dithiolene ligand is the di-*n*-butyltin compound 2,2-di-*n*-butyl-4,5-dimethyl-1,3,2-dithiastannole, **2**. Compound **2** is readily generated from **1** by treatment of the ene-1,2-dithiolate dianion with di-*n*-butyltin dichloride. A slightly different preparation of **2** has been described earlier,[29] but the utility of this compound as a dithiolene ligand precursor or ligand transfer reagent was not probed. Having noted the use made of other dialkyl tin protected dithiolene-type ligands, particularly in ligand exchange reactions with transition metal chlorides,[30−33] the utility of **2** was tested in the synthesis of another homoleptic metal dithiolene compound, $[W(S_2C_2Me_2)_3]$. For reasons that are unclear, $[W(S_2C_2Me_2)_3]$ could not be isolated by introducing WCl_6 to 3 equiv of in situ generated $Na_2[Me_2C_2S_2]$. However, $[W(S_2C_2Me_2)_3]$ was isolated in 80% yield after treatment of WCl_6 with 3 equiv of **2** (Scheme 1), separation of the $^nBu_2SnCl_2$ byproduct by simple MeOH extraction, and purification of the remaining solid by recrystallization. This procedure is analogous to the use of bis((trialkylsilyl)sulfanyl)alkenes as protected dithiolene ligands[34] in that metallodithiolene complex formation is driven, at least in part, by formation of a strong metallodithiolene chelate.

The mixed dithiolene carbonyl compounds $[M(S_2C_2R_2)_2(CO)_2]$ (M = Mo, W; R = Me, Ph) were first reported by Schrauzer as products arising from dithiolene ligand transfer from $[Ni(S_2C_2Me_2)_2]$ to $M(CO)_6$ under photolytic conditions.[9] The yields and ease of synthesis were considerably improved by Goddard and Holm,[10] who noted that use of $[M(CO)_3(MeCN)_3]$ (M = Mo, W) in lieu of the hexacarbonyl resulted in cleaner reactivity without the need for photolysis. In the tungsten system, modest quantities of $[W(S_2C_2R_2)(CO)_4]$, a moderately stable intermediate appearing in the course of formation of $[W(S_2C_2R_2)_2(CO)_2]$, can be isolated. This mono(dithiolene) intermediate is not observed in the molybdenum system, probably because the

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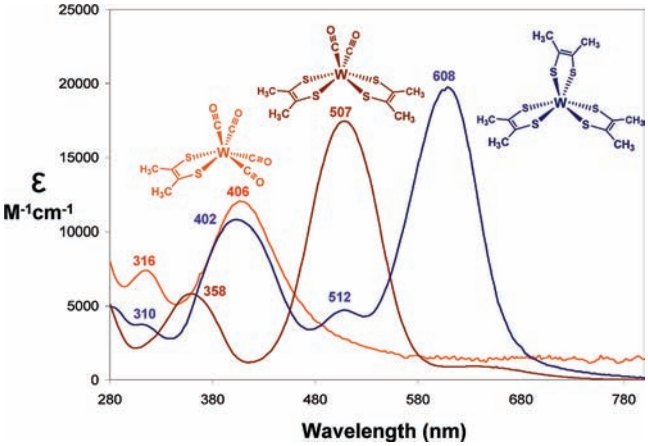

Figure 1. UV−vis spectra (CH_2Cl_2) of the compounds $[W(S_2C_2Me_2)_x(CO)_{6-2x}]$ (x = 1−3). The UV−vis traces are shown with the approximate colors of the compounds.

M−CO bonds in $[M(S_2C_2R_2)(CO)_4]$ are inherently weaker for Mo versus W and render this species unstable against a second dithiolene ligand transfer. Both experiment[35] and theory[36] indicate a ∼5−6 kcal/mol greater M−CO bond strength for W over Mo in the corresponding hexacarbonyls. Mono(dithiolene) complexes of Mo and W are relatively scarce, particularly in compounds bearing other ligands potentially subject to further substitution reactions. For this reason, $[W(S_2C_2Me_2)(CO)_4]$ may have value in the synthesis of tungsten analogues of the catalytic sites of molydoenzymes in the xanthine oxidase family.

The original preparation and isolation of $[W(S_2C_2Me_2)(CO)_4]$ from the reaction of $[W(CO)_6]$ with $[Ni(S_2C_2Me_2)_2]$ as described by Schrauzer was complicated by difficulty in separating it from unreacted $W(CO)_6$ by chromatography and by its intrinsic solution lability, which made recrystallization impractical. Consequently, no yield was determined, and only limited physical data were reported. The reaction of $[W(CO)_3(MeCN)_3]$ with $[Ni(S_2C_2Me_2)_2]$ in CH_2Cl_2 solution according to Goddard and Holm, but with 8−12 h rather than 72 h reaction times, results in modest but consistent 18−20% yields of $[W(S_2C_2Me_2)(CO)_4]$ that are unmixed with residual $[W(CO)_6]$. After separation from $[W(S_2C_2Me_2)_2(CO)_2]$ by elution from a silica column with pure *n*-pentane, recrystallization is readily accomplished from this same solvent at reduced temperature. Under these conditions, $[W(S_2C_2Me_2)_2(CO)_2]$ is produced in similar amounts (∼20% yield), and $[W(S_2C_2Me_2)_3]$ is invariably formed in small quantities (∼2−3%) as well.

The UV−vis spectra of the series $[W(S_2C_2Me_2)_x(CO)_{6-2x}]$ (x = 1−3) are displayed in Figure 1 and reveal a trend toward lower energy absorption and greater intensity as the number of dithiolene ligands is increased. These absorptions are likely transitions involving orbitals that are mixed in composition and are thus not the MLCT or LMCT transitions of more classical inorganic compounds. A more definitive assignment of these transitions will later be made with the use of TD-DFT calculations.

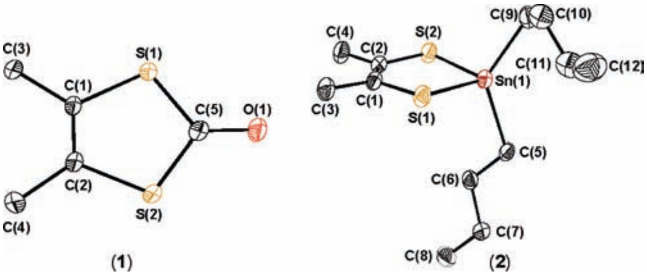

Figure 2. Thermal ellipsoid plot at the 50% probability level for 4,5-dimethyl-1,3-dithiol-2-one (**1**) and 30% level for 2,2-di-*n*-butyl-4,5-dimethyl-1,3,2-dithiastannole (**2**). For **2**, only one of two independent molecules in the asymmetric unit is shown. H atoms are omitted for clarity.

Schrauzer noted the propensity of both $[W(S_2C_2Me_2)(CO)_4]$ and $[W(S_2C_2Me_2)_2(CO)_2]$ to undergo carbonyl displacement reactions by phosphines.[9] As the first part of broad survey of the reactivity of these compounds, we have noted that $[W(S_2C_2Me_2)(CO)_4]$ readily undergoes the displacement of only two CO ligands when introduced to an excess of relatively basic PMe_3 and subjected to vigorous reflux (Scheme 1). Similarly, $[W(S_2C_2Me_2)_2(CO)_2]$ readily undergoes displacement of one CO ligand by PMe_3 to afford the mixed carbonyl phosphine complex **8**. With the use of excess PMe_3, accompanied by Me_3NO to facilitate displacement of CO by its oxidation to CO_2, good yields of $[W(S_2C_2Me_2)_2(PMe_3)_2]$ are obtained. The promotion of CO substitution by phosphine with use of Me_3NO has been previously noted.[37−40] Phosphine basicity appears to be an important factor in enabling the formation of this bis(phosphine) adduct. Reaction of the modestly basic 1,2-bis(diphenylphosphino)ethane ligand with **5** under forcing conditions, despite a chelate effect which would favor CO displacement, produces only trace amounts of $[W(S_2C_2Me_2)_2(dppe)]$. The only other bis(dithiolene) bis(phosphine) complexes of tungsten that are known are $[W(S_2C_2Ph_2)_2(dppe)]$[9] and $[W(bdt)_2(P(OEt)_3)_2]$ (bdt = benzene-1,2-dithiolate), the latter of which is formed in an oxygen atom abstraction reaction between $[WO(bdt)_2Cl]^{1-}$ and excess $P(OEt)_3$.[41]

Structures. The crystal structure of protected ligand **1** has been determined and is presented in Figure 2. This molecule offers baseline C−S single and C═C double bond lengths (Table 2) that are uncomplicated by the potentially "non-innocent" behavior of the dithiolene ligand in its metal complexes. The $C-S_{ave}$ bond length of 1.754[1] Å[42] and the C═C bond length of 1.340(2) Å in **1** agree closely with the typical values of 1.751[17] Å for S−C(sp^2) and 1.331[9] Å

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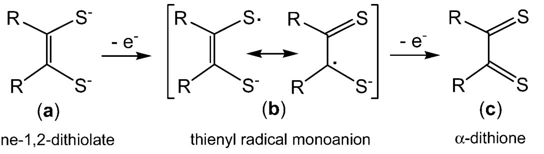
Table 2. Bond Lengths (Å) and Selected Angles (deg) for 4,5-Dimethyl-1,3-dithiol-2-one (**1**) and for 2,2-Di-*n*-butyl-4,5-dimethyl-1,3,2-dithiastannole (**2**)[a]

1				**2**			
S(1)−C(1)	1.755(1)	C(1)−S(1)−C(5)	97.20(7)	Sn(1)−S(1)	2.455(1)	S(1)−Sn(1)−S(2)	88.89(5)
S(2)−C(2)	1.752(2)	C(2)−S(2)−C(5)	97.36(7)	Sn(1)−S(2)	2.408(2)	S(1)−Sn(1)−C(5)	103.8(1)
S(1)−C(5)	1.770(2)	S(1)−C(1)−C(2)	116.9(1)	S(1)−C(1)	1.778(6)	S(1)−Sn(1)−C(9)	106.0(2)
S(2)−C(5)	1.769(2)	S(2)−C(2)−C(1)	116.9(1)	S(2)−C(2)	1.784(6)	S(2)−Sn(1)−C(5)	110.7(2)
C(5)−O(1)	1.211(2)	S(1)−C(5)−S(2)	111.62(8)	C(1)−C(2)	1.338(8)	S(2)−Sn(1)−C(9)	114.3(2)
C(1)−C(2)	1.340(2)	S(1)−C(5)−O(1)	124.3(1)	C(1)−C(3)	1.500(8)	C(5)−Sn(1)−C(9)	125.6(2)
C(1)−C(3)	1.503(2)	S(2)−C(5)−O(1)	124.1(1)	C(2)−C(4)	1.502(8)	C(1)−S(1)−Sn(1)	99.5(2)
C(2)−C(4)	1.506(2)					C(2)−S(2)−Sn(1)	100.4(2)

[a] Data for **2** are for one of two independent molecules in the asymmetric unit.

Scheme 2. Possible Oxidation States of a Dithiolene Ligand



for $(sp^2)C{=}C(sp^2)$ that have been tabulated from a large body of structurally identified compounds.[43] Dithiolene ligand C−S bond lengths that are shorter than 1.751[17] Å by the 3σ criterion that is generally accepted as limiting the confidence of bond length measurements (i.e., C−S bond lengths <1.73 Å) may be taken as indicative of partial thione character to the dithiolene ligand because of some degree of ligand oxidation (b in Scheme 2). Similarly, dithiolene C−C bond lengths longer than the typical C−C olefinic bond length of 1.331[9] Å by the same threshold (i.e., > 1.358 Å) may be interpreted as evidence for some thienyl radical monoanion (b in Scheme 2) involvement, which lowers the carbon−carbon bond order.

Compound **2** was characterized structurally (Figure 2) and found to crystallize in triclinic space group $P\bar{1}$ with two independent molecules in the asymmetric unit, data for only one of which are shown in Table 2. The coordination geometry at Sn in **2** is distorted tetrahedral, the greatest deviation from the idealized value of 109.5° being the S(1)−Sn(1)−S(2) angle (88.89(5)°) because of the constraints of the ligand chelate. The averaged C−S bond length for **2** is 1.776[3] Å, a value somewhat *longer* than those observed in **1**. This difference may be attributable, at least in part, to an absence of a complete set of π bonds around the 1,3,2-dithiastannole ring system, compared to the 1,3-dithiol-2-one ring system, because of the sp^3 hybridization at the tin center. However, the C−C olefinic bond lengths in **2** (1.341[5] Å) are essentially the same as in **1**. Compounds related to **2** that have been structurally identified include $[(\mathrm{mnt})\mathrm{SnR_2}]$ (mnt = maleonitriledithiolate; R = CH_3, ^{n}Bu or Ph)[44] and $[(\mathrm{dmit})\mathrm{SnR_2}]$ (dmit = 1,3-dithiol-2-thione-4,5-dithiolate; R = Me or Et)],[45] although the latter set of molecules are pseudo pentacoordinate owing to intermolecular Sn···S interactions.

Of the three-member series $[\mathrm{W(S_2C_2Me_2)}_x(\mathrm{CO})_{6-2x}]$ (x = 1−3), structural data have only been available for the dicarbonyl compound (x = 2).[10] Reported here are crystal structures of compounds **4** (x = 1) and **6** (x = 3) as well as that of **5** (x = 2) at slightly higher resolution than the previous structural characterization (Figure 3, Tables 1 and 3). The structure of **4** was proposed by Schrauzer to be octahedral[9] but in fact has been found to be a near-perfect trigonal prism (Figure 3) with a Bailar twist angle of 4.0°. This trigonal prismatic coordination geometry is unique among monodithiolene complexes of Mo and W and will later be the subject of a more detailed computational study. Preliminarily, a geometry optimization of trigonal prismatic and octahedral $[\mathrm{W(S_2C_2Me_2)(CO)_4}]$ at the B3LYP level of theory calculates the trigonal prismatic geometry to be 5.12 kcal/mol lower in free energy than the octahedral structure. The calculations also reveal that the octahedral structure is a transition state with one imaginary mode ($34.3i$ cm^{-1}) whose reactant and product are trigonal prismatic structures. A species related to **4** is the dianion $[\mathrm{W(bdt)(CO)_4}]^{2-}$ [46] which crystallography revealed to have an octahedral geometry.

The C−S and C−C (olefinic) bond lengths in **4** are, within the error of the experiment, similar to the corresponding values in **1** and imply a dithiolene ligand in **4** that is closer to a fully reduced ene-1,2-dithiolate description than otherwise. Thus a W(II) oxidation description would appear pertinent to **4**. In contrast, compound **5** reveals C−S and dithiolene C−C bond lengths that are appreciably shorter ($\mathrm{C{-}S_{ave}}$ = 1.722[2] Å) and longer ($\mathrm{C{-}C_{ave}}$ = 1.363[3] Å), respectively, within the resolution limit of the data than those in **1** (1.754[1] Å and 1.340(2) Å, respectively) which strongly points toward the involvement of thienyl radical monoanion character to both dithiolene ligands and consequently a W(II) oxidation state for this compound as well. This W(II) oxidation state formulation for **5** has also been implicated by calculations of the electronic structures of the series $[\mathrm{W(S_2C_2Me_2)_2(CO)_2}]^n$ (n = 0, 1-, 2-).[11]

Tris(dithiolene) compound **6** proved to be surprisingly difficult to crystallize in a diffraction quality form, a stark contrast to its molybdenum homologue, which readily

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(42) Uncertainties for averaged bond lengths were determined using the general formula for uncertainty in a function of multiple variables as described by Taylor, J. R. *An Introduction to Error Analysis*; University Science Books: Sausalito, CA, 1997; pp 73−77.

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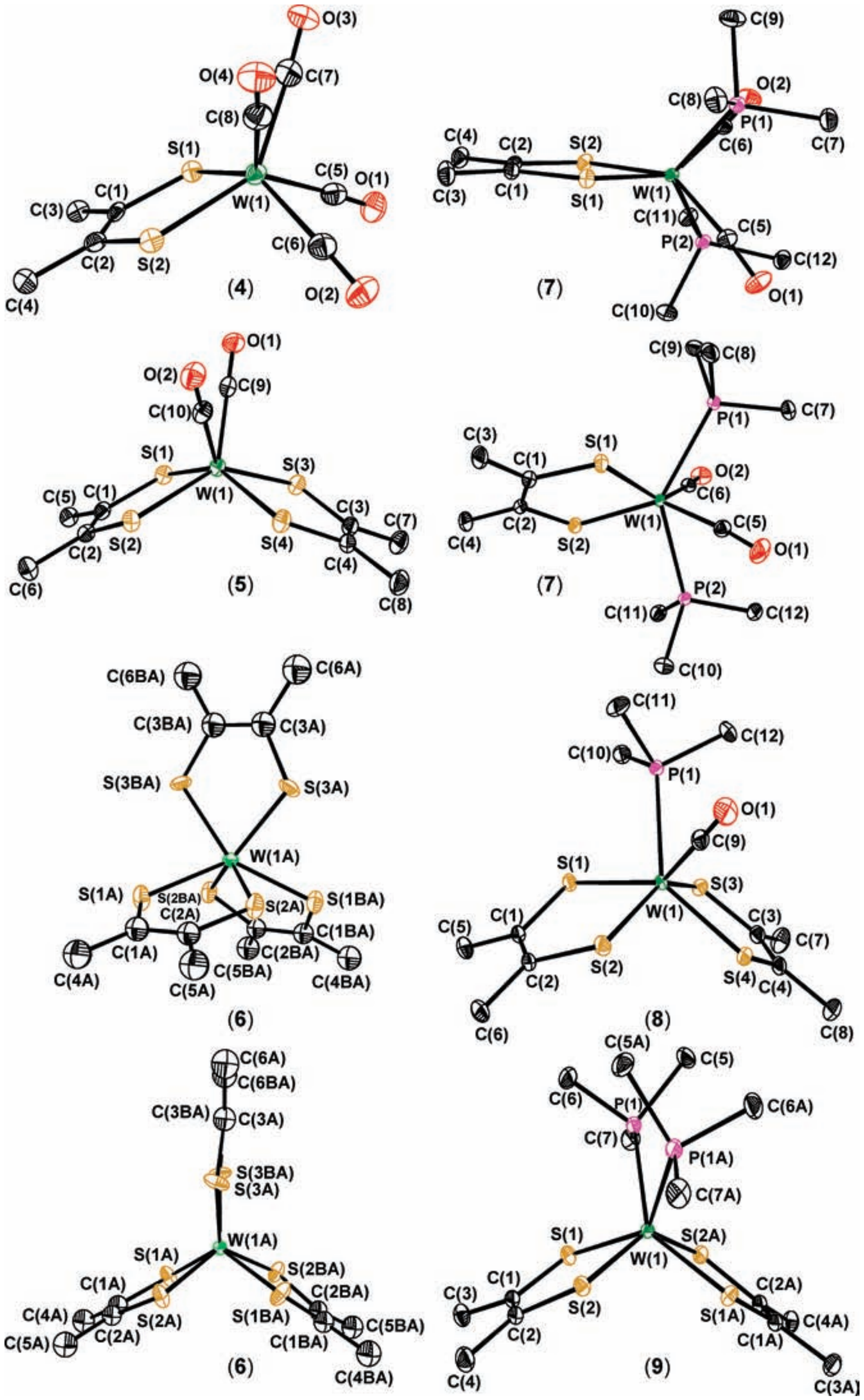

Figure 3. Thermal ellipsoid plots at the 50% (**4**, **5**, **7**−**9**) or 30% (**6**) level. Compounds **6** and **7** are presented in two orientations. For **6**, only the tungsten and sulfur ellipsoids are anisotropic. H atoms are omitted for clarity.

crystallizes by evaporation of benzene solutions.[47] Invariably, crystals of **6** were twinned and demonstrated a high mosaicity. After screening a broad variety of solvents systems and methods, crystals of **6** that showed strong diffraction of X-rays were obtained by the diffusion of MeOH into a nitrobenzene solution. Regrettably, in addition to the twinning complications, the structure of **6** proved to be afflicted with disorder problems which militated against the attainment of low uncertainties in any bond lengths and angles despite an overall acceptably low R factor in the final refinement of the molecule. Consequently, no insight is available into the state of oxidation of the dithiolene ligands in this compound on the basis of C−S and C−C bond lengths (Table 3). Recent XAS and spectroscopic work by Wieghardt and co-workers upon $[W(3,5\text{-}^tBu_2\text{-}C_6H_2S_2)_3]^n$ (n = 0, 1-) have identified W(V) as the metal oxidation occurring in both compounds.[48] However, a sulfur K-edge XAS study and detailed computational analysis of the related $[Mo(S_2C_2Me_2)_3]^{0,1\text{-},2\text{-}}$ series

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compounds **4−6**[a]

[W($S_2C_2Me_2$)(CO)$_4$], **4**		[W($S_2C_2Me_2$)$_2$(CO)$_2$], **5**		[W($S_2C_2Me_2$)$_3$], **6**	
W(1)−S(1)	2.358(2)	W(1)−S(1)	2.3711(7)	W(1A)−S(1A)	2.35(2)
W(1)−S(2)	2.364(2)	W(1)−S(2)	2.3722(7)	W(1A)−S(2A)	2.354(7)
W(1)−C(5)	2.038(7)	W(1)−S(3)	2.3657(7)	W(1A)−S(3A)	2.33(1)
W(1)−C(6)	2.043(6)	W(1)−S(4)	2.3699(7)	W(1A)−S(1BA)	2.38(1)
W(1)−C(7)	2.035(6)	W(1)−C(9)	2.019(3)	W(1A)−S(2BA)	2.381(5)
W(1)−C(8)	2.038(7)	W(1)−C(10)	2.020(3)	W(1A)−S(3BA)	2.381(9)
S(1)−C(1)	1.739(6)	S(1)−C(1)	1.720(3)	S(1A)−C(1A)	1.73(2)
S(2)−C(2)	1.749(6)	S(2)−C(2)	1.722(3)	S(2A)−C(2A)	1.73(2)
S−C$_{\mathrm{ave}}$[b]	**1.744[4]**	S(3)−C(3)	1.721(3)	S(3A)−C(3A)	1.75(2)
C(1)−C(2)	1.351(8)	S(4)−C(4)	1.726(3)	C(1A)−C(2A)	1.36(2)
C(5)−O(1)	1.137(8)	**S−C$_{\mathrm{ave}}$**[b]	**1.722[2]**	C(3A)−C(3BA)	1.387
C(6)−O(2)	1.126(8)	C(1)−C(2)	1.365(4)	S(1A)−W(1A)−S(2A)	81.8(4)
C(7)−O(3)	1.137(8)	C(3)−C(4)	1.361(4)	S(1A)−W(1A)−S(3A)	136.4(4)
C(8)−O(4)	1.142(8)	**olefinic C−C$_{\mathrm{ave}}$**[b]	**1.363[3]**	S(1A)−W(1A)−S(1BA)	132.9(2)
C(1)−C(3)	1.507(8)	C(9)−O(1)	1.142(4)	S(1A)−W(1A)−S(2BA)	82.1(4)
C(2)−C(4)	1.494(8)	C(10)−O(2)	1.141(3)	S(1A)−W(1A)−S(3BA)	83.9(4)
S(1)−W(1)−S(2)	82.38(5)	S(1)−W(1)−S(2)	81.05(2)	S(2A)−W(1A)−S(3A)	81.9(3)
S(1)−W(1)−C(5)	84.7(2)	S(1)−W(1)−S(3)	88.34(3)	S(2A)−W(1A)−S(1BA)	79.5(3)
S(1)−W(1)−C(6)	142.3(2)	S(1)−W(1)−S(4)	148.03(3)	S(2A)−W(1A)−S(2BA)	134.5(2)
S(1)−W(1)−C(7)	86.9(2)	S(1)−W(1)−C(9)	76.77(9)	S(2A)−W(1A)−S(3BA)	137.6(2)
S(1)−W(1)−C(8)	137.5(2)	S(1)−W(1)−C(10)	129.44(9)	S(3A)−W(1A)−S(1BA)	82.7(4)
S(2)−W(1)−C(5)	137.5(2)	S(2)−W(1)−S(3)	141.56(3)	S(3A)−W(1A)−S(2BA)	135.4(2)
S(2)−W(1)−C(6)	88.0(2)	S(2)−W(1)−S(4)	88.80(2)	S(3A)−W(1A)−S(3BA)	81.6(1)
S(2)−W(1)−C(7)	141.7(2)	S(2)−W(1)−C(9)	133.22(8)	S(1BA)−W(1A)−S(2BA)	81.1(3)
S(2)−W(1)−C(8)	85.5(2)	S(2)−W(1)−C(10)	79.01(8)	S(1BA)−W(1A)−S(3BA)	136.0(3)
C(5)−W(1)−C(6)	78.1(8)	S(3)−W(1)−S(4)	80.96(2)	S(2BA)−W(1A)−S(3BA)	81.9(2)
C(5)−W(1)−C(7)	77.2(2)	S(3)−W(1)−C(9)	78.49(8)	W(1A)−S(1A)−C(1A)	109.4(9)
C(5)−W(1)−C(8)	128.7(2)	S(3)−W(1)−C(10)	133.05(8)	W(1A)−S(2A)−C(2A)	108.6(5)
C(6)−W(1)−C(7)	120.7(2)	S(4)−W(1)−C(9)	129.32(9)	W(1A)−S(3A)−C(3A)	107.7(8)
C(6)−W(1)−C(8)	77.3(2)	S(4)−W(1)−C(10)	77.15(9)	S(1A)−C(1A)−C(2A)	119(1)
C(7)−W(1)−C(8)	78.0(2)	C(9)−W(1)−C(10)	84.2(1)	S(2A)−C(2A)−C(1A)	120(1)
W(1)−S(1)−C(1)	108.6(2)	W(1)−S(1)−C(1)	109.7(1)	S(3A)−C(3A)−C(3BA)	120.4
W(1)−S(2)−C(2)	108.5(2)	W(1)−S(2)−C(2)	109.3(1)	S(1A)−C(1A)−C(4A)	118(1)
W(1)−C(5)−O(1)	177.1(5)	W(1)−S(3)−C(3)	109.6(1)	S(2A)−C(2A)−C(5A)	115(1)
W(1)−C(6)−O(2)	177.7(6)	W(1)−S(4)−C(4)	109.7(1)	S(3A)−C(3A)−C(6A)	116(1)
W(1)−C(7)−O(3)	176.8(6)	W(1)−C(9)−O(1)	178.7(3)	θ[c]	0.7°[e]
W(1)−C(8)−O(4)	177.2(6)	W(1)−C(10)−O(2)	178.6(3)	α[d]	7.8°
θ[c]	4.0°	θ[c]	3.4°		
α[d]	0.7°	α[d]	2.7°		

[a] Averaged bond lengths are in bold faced type. [b] See footnote of reference 42. [c] Bailar twist angle, defined as the twist angle between triangular faces of the trigonal prism. [d] Chelate fold angle, defined as the angle between the WS_2 and S_2C_2 planes. For **5** and **6**, these are averaged values. [e] See text for discussion.

by Solomon and co-workers concluded that the both redox processes in this series are ligand-based and that the metal center is Mo(IV) throughout.[49] While it is unclear what formulation is best suited to describe the oxidation state of tungsten in [W($S_2C_2Me_2$)$_3$], the foregoing studies indicate that fully reduced ene-1,2-dithiolate ligands are not pertinent here and that some degree of partial ligand oxidation is operative.

Figure 4 illustrates the disorder occurring in **6** as a consequence of its location on a crystallographic 2-fold axis (vertical and in the plane of the paper) in space group *C*2/*c*. Despite this disorder, it appears that the true Bailar twist angle, defined as the twist angle between triangular faces in the trigonal prism, is 1.8°. This number is close to the value of 2.4° observed in [Mo($S_2C_2Me_2$)$_3$].[47,49] Other, slightly different, split atom models that could be devised to model the disorder in **6** lead to larger Bailar twist angles but also lead to dithiolene C−C and C−S bond distances that are not chemically reasonable. Also of interest is the dithiolene chelate fold angle, α, the angle between the WS_2 and S_2C_2 mean planes. The dithiolene C−S and C−C bond lengths are somewhat less decisive in pointing toward one value or another for α among the possibilities that exist depending on how the ligand disorder is partitioned, but the smaller of the possible values for α, 7.8°, also appears to be most likely. Another point suggesting the smallest possible value for α is the consideration that this molecule is more likely to crystallize on a 2-fold axis if the compound is closer to true D_{3h} symmetry, which has 2-fold symmetry, rather than further from D_{3h} symmetry, with a larger α value. In fact, it

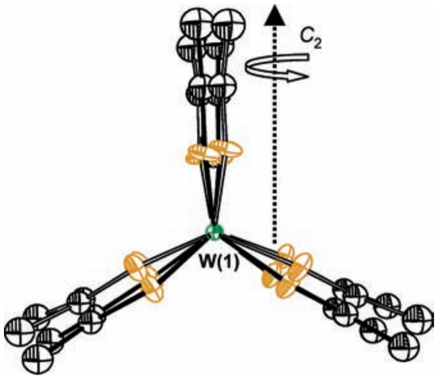

Figure 4. Illustration of the disorder in tris(dithiolene) compound **6** about a crystallographic 2-fold axis.

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Table 4. Selected Bond Lengths (Å) and Angles (deg) for Compounds **7**−**9**[a]

[W($S_2C_2Me_2$)(CO)$_2$(PMe$_3$)$_2$], **7**		[W($S_2C_2Me_2$)$_2$(CO)(PMe$_3$)], **8**		[W($S_2C_2Me_2$)$_2$(PMe$_3$)$_2$], **9**	
W(1)−S(1)	2.3775(7)	W(1)−S(1)	2.3588(6)	W(1)−S(1)	2.3627(5)
W(1)−S(2)	2.3841(7)	W(1)−S(2)	2.3550(5)	W(1)−S(2)	2.3506(5)
W(1)−P(1)	2.4794(8)	W(1)−S(3)	2.3626(6)	W(1)−P(1)	2.4949(5)
W(1)−P(2)	2.4628(8)	W(1)−S(4)	2.3514(5)	S(1)−C(1)	1.741(2)
W(1)−C(5)	1.970(2)	W(1)−P(1)	2.4762(6)	S(2)−C(2)	1.745(2)
W(1)−C(6)	1.979(2)	W(1)−C(9)	2.000(2)	**S−C$_{ave}$**[b]	**1.743[1]**
S(1)−C(1)	1.750(2)	S(1)−C(1)	1.735(2)	C(1)−C(2)	1.346(3)
S(2)−C(2)	1.758(2)	S(2)−C(2)	1.736(2)	S(1)−W(1)−S(2)	80.27(2)
S−C$_{ave}$[b]	**1.754[1]**	S(3)−C(3)	1.730(2)	S(1)−W(1)−S(1A)	137.93(2)
C(1)−C(2)	1.349(3)	S(4)−C(4)	1.730(2)	S(1)−W(1)−S(2A)	86.64(2)
C(5)−O(1)	1.164(2)	**S−C$_{ave}$**[b]	**1.733[1]**	S(1)−W(1)−P(1)	76.89(2)
C(6)−O(2)	1.159(3)	C(1)−C(2)	1.353(3)	S(1)−W(1)−P(1A)	137.93(2)
C(1)−C(3)	1.509(3)	C(3)−C(4)	1.354(3)	S(2)−W(1)−S(1A)	86.64(2)
C(2)−C(4)	1.505(3)	**olefinic C−C$_{ave}$**[b]	**1.354[2]**	S(2)−W(1)−S(2A)	143.02(2)
S(1)−W(1)−S(2)	81.44(2)	C(9)−O(1)	1.153(3)	S(2)−W(1)−P(1)	129.48(2)
S(1)−W(1)−P(1)	85.77(2)	S(1)−W(1)−S(2)	81.02(2)	S(2)−W(1)−P(1A)	79.61(2)
S(1)−W(1)−P(2)	134.40(2)	S(1)−W(1)−S(3)	86.89(2)	S(1A)-W(1)-S(2A)	80.27(2)
S(1)−W(1)−C(5)	91.92(6)	S(1)−W(1)−S(4)	139.80(2)	S(1A)-W(1)−P(1)	137.93(2)
S(1)−W(1)−C(6)	148.41(6)	S(1)−W(1)−P(1)	80.64(2)	S(1A)-W(1)-P(1A)	76.89(2)
S(2)−W(1)−P(1)	135.84(2)	S(1)−W(1)−C(9)	136.27(6)	S(2A)-W(1)−P(1)	79.61(2)
S(2)−W(1)−P(2)	83.51(2)	S(2)−W(1)−S(3)	144.93(2)	S(2A)-W(1)-P(1A)	129.48(2)
S(2)−W(1)−C(5)	144.67(6)	S(2)−W(1)−S(4)	87.73(2)	P(1)−W(1)−P(1A)	88.22(2)
S(2)−W(1)−C(6)	92.89(6)	S(2)−W(1)−P(1)	130.62(2)	W(1)−S(1)−C(1)	110.72(7)
P(1)−W(1)−P(2)	132.11(2)	S(2)−W(1)−C(9)	80.06(6)	W(1)−S(2)−C(2)	110.83(7)
P(1)−W(1)−C(5)	77.45(6)	S(3)−W(1)−S(4)	80.56(2)	S(1)−C(1)−C(2)	118.9(1)
P(1)−W(1)−C(6)	76.78(6)	S(3)−W(1)−P(1)	78.73(2)	S(2)−C(2)−C(1)	119.2(1)
P(2)−W(1)−C(5)	76.60(6)	S(3)−W(1)−C(9)	128.52(6)	θ[c]	5.1°
P(2)−W(1)−C(6)	74.89(6)	S(4)−W(1)−P(1)	132.72(2)	α[d]	2.8°
C(5)−W(1)−C(6)	109.32(8)	S(4)−W(1)−C(9)	78.12(6)		
W(1)−S(1)−C(1)	109.34(7)	P(1)−W(1)−C(9)	82.49(6)		
W(1)−S(2)−C(2)	109.07(7)	W(1)−S(1)−C(1)	109.30(7)		
W(1)−C(5)−O(1)	174.7(2)	W(1)−S(2)−C(2)	109.67(7)		
W(1)−C(6)−O(2)	176.2(2)	W(1)−S(3)−C(3)	110.19(8)		
θ[c]	9.8°	W(1)−S(4)−C(4)	110.64(7)		
α[d]	0.9°	W(1)−C(9)−O(1)	179.0(2)		
		θ[c]	3.7°		
		α[d]	4.5°		

[a] Averaged bond lengths are in bold faced type. [b] See footnote reference 42. [c] Bailar twist angle, defined as the twist angle between triangular faces of the trigonal prism. [d] Chelate fold angle, defined as the angle between the WS_2 and S_2C_2 planes. The value for compound **8** is an average of two values.

is a slight difference in α which appears to be the principal distinction between the structures of **6** and [Mo($S_2C_2Me_2$)$_3$], for which α = 15.8°.[47,49] Modest though the difference may be, a larger chelate fold for [Mo($S_2C_2Me_2$)$_3$] apparently leads it to crystallize on a general position in $P\bar{1}$ without disorder, while a smaller chelate fold for **6** brings it close enough to idealized D_{3h} symmetry that it can crystallize, albeit with disorder, in the higher symmetry of monoclinic $C2/c$. This divergence in crystal behavior between homologous molybdenum and tungsten compound is unusual. Almost invariably, homologous Mo and W compounds (provided counterions and molecules of solvation are the same) crystallize in the same space group with nearly isometric unit cell parameters. Examples include, to name a select few, [Et$_4$N][M($S_2C_2Me_2$)$_3$] (M = Mo,[47] W[11]), [Et$_4$N]$_2$[M($S_2C_2Me_2$)$_3$] (M = Mo,[11] W[11]), [Et$_4$N][M(O)(OSi^{t}BuPh$_2$)(bdt)$_2$] (M = Mo,[50] W[41]), [M(bdt)$_3$] (M = Mo,[51] W[52]), [M$_2$(DAniF)$_4$] (DAniF = *N*,*N′*-di-*p*-anisylformamidinate; M = Mo,[53] W[54]), and [M(CO)$_6$] (M = Mo,[55] W[56]). The chelate fold angle, α, in trigonal prismatic tris(dithiolene) complexes has been identified as arising from configuration interaction between the metal d$_{z^2}$ orbital, which is doubly occupied, and a ligand-based MO constituted of an interligand antibonding combination of the three dithiolene π-systems.[49,57] As such, the degree of configuration interaction, and hence the magnitude of the ligand chelate fold, might be expected to differ between the Mo and W systems because of an intrinsic difference in energy between the 4d$_{z^2}$ and 5d$_{z^2}$ orbitals in these molecules.

The mixed dithiolene phosphine compounds **7**, **8**, and **9** have all been characterized structurally as well (Figure 3, Table 4). The preparation and structures of several compounds similar to **7** have been previously described, although their synthesis proceeded by displacement of iodide and CO from [WI$_2$(CO)$_3$(PR$_3$)$_2$] (R = Et, Ph) by reduced dithiolene ligand.[58] The coordination geometry of **7** is distorted trigonal prismatic, with a twist angle of 9.8° between triangular faces.

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This distortion is appreciably less than that observed in related structurally characterized compounds (θ = 12−23°).[58] Compounds **8** and **9** adopt the nearly perfect trigonal prismatic coordination geometry that is by now well precedented for bis(dithiolene) complexes of tungsten and molybdenum.[1] The C−S and C−C bond lengths in the series **5**, **8**, and **9** (Tables 3 and 4) reveal a definite trend toward longer (1.722[2] Å → 1.733[1] Å → 1.743[1] Å) and shorter (1.363[3] Å → 1.354[2] Å → 1.346(3) Å) values, respectively. These trends imply that the presence of the strongly π-acidic CO ligands stabilizes the thienyl radical monoanionic form of the dithiolene ligand (Scheme 2), while their removal forces more electron density back upon the dithiolene ligands and causes the ene-1,2-dithiolate description to become operative. These trends are currently being probed by sulfur K-edge XAS spectroscopy, the results of which will be published in a forthcoming study.

Electrochemistry. Compounds **5** and **6** have previously been examined by cyclic voltammetry and found to undergo two highly reversible reductions.[11] Spectroscopic, structural, and computational data indicate that these processes are ligand based for **5**. A similar situation may pertain for **6** inasmuch as the two reversible reductions observed for its molybdenum counterpart, $[Mo(S_2C_2Me_2)_3]$, have also been assigned as ligand-based events. Compound **4** does not display any reversible reduction in either MeCN or CH_2Cl_2, a somewhat surprising observation in view of the presence of four CO ligands that might be expected to accept some amount of charge density. Considering the existence of the related octahedral dianion $[W(S_2C_6H_4)(CO)_4]^{2-}$,[46] one possible explanation for this lack of reversibility is a facile structural reorganization to an octahedral geometry, with a consequent change in the compound's redox potentials.

Compound **8** displays one reversible reduction at a fairly reducing potential of −1.04 V (vs Ag/AgCl), while **7** and **9** reveal only irreversible behavior in both the oxidizing and the reducing directions (see Supporting Information). No improvement in the behavior of **9** is observed upon performing the scan in the presence of excess PMe_3, indicating that dissociation of phosphine upon reduction is not the reason for the observed irreversibility, as has been noted in related iron and cobalt dithiolene systems.[59] Thus, electrochemical reversibility in the series $[W(S_2C_2Me_2)_2(CO)_{2-x}(PMe_3)_x]$ (x = 0, 1, 2) correlates directly with the presence of CO ligand. While this trend may be rationalized simply as the ability to absorb additional charge with a π-acid ligand, the structural data suggest a different nuance in which CO ligand(s) supports some oxidized character to the dithiolene ligands, which are themselves the principal sites of reduction.

Conclusions

This work describes the use of two protected forms of the dimethyl-substituted dithiolene ligand for much improved syntheses of the classical compounds $[Ni(S_2C_2Me_2)_2]$ (**3**) and $[W(S_2C_2Me_2)_3]$ (**6**), previously only available via the P_4S_{10}/acetoin method. The former is prepared via base hydrolysis of $Me_2C_2S_2C{=}O$, followed by addition of $NiCl_2$ and I_2, while the latter is formed in the reaction between WCl_6 and $(Me_2C_2S_2)Sn^nBu_2$.

Improved access to $[Ni(S_2C_2Me_2)_2]$ has enabled further study of the series $[W(S_2C_2Me_2)_x(CO)_{6-2x}]$ (x = 1 (**4**), x = 2, (**5**), x = 3 (**6**)), which is formed as a mixture in reactions between $[W(MeCN)_3(CO)_3]$ and **3**. This series has been fully characterized here for the first time, both structurally and spectroscopically. Near perfect trigonal prismatic coordination geometries are observed for all three compounds. Compound **4** is a rare, if not unique, instance of a mono(dithiolene) compound in this coordination geometry. Compound **6** crystallizes in disordered fashion upon a 2-fold axis and appears to differ from its molybdenum homologue by having a smaller dithiolene chelate fold angle (α).

Mono(dithiolene) compound $[W(S_2C_2Me_2)(CO)_4]$ is subject to carbonyl displacement by PMe_3, affording distorted trigonal prismatic $[W(S_2C_2Me_2)(CO)_2(PMe_3)_2]$. Similarly, treatment of $[W(S_2C_2Me_2)_2(CO)_2]$ with PMe_3 or PMe_3/Me_3NO produces $[W(S_2C_2Me_2)_2(CO)(PMe_3)]$ or $[W(S_2C_2Me_2)_2(PMe_3)_2]$, respectively. Structural data for these compounds identify a correlation between the presence of CO ligand and partially oxidized (thienyl radical monoanion) dithiolene ligand, as manifested by C−S and C−C bond lengths. Of this set of mixed dithiolene-phosphine compounds **7**−**9**, only **8** displays any reversible electrochemistry, a reduction at −1.04 V (vs Ag/AgCl).

With $[W(S_2C_2Me_2)(CO)_4]$ and $[W(S_2C_2Me_2)_2(CO)_2]$ now more available because of the improved access to the key $[Ni(S_2C_2Me_2)_2]$ synthon, an exploration of their reactivity in direct oxidative addition reactions toward a variety of small organic molecules is being probed.

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Supporting Information Available: X-ray crystallographic files in CIF format and thermal ellipsoid plots with full atom labeling for **1**, **2** and **4**−**9**. Selected spectroscopic and electrochemical data for **1**, **2** and **4**−**9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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