Synthesis, Structures, and Reactivity of Bis(dithiolene)molybdenum(IV,VI) Complexes Related to the Active Sites of Molybdoenzymes

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Abstract: The existence of a universal pterin dithiolene cofactor ligand for the molybdenum and tungsten oxotransferases supports a biological significance of the fundamental chemistry of mono- and bis(dithiolene) complexes of these elements. Members of the dimethyl sulfoxide (DMSO) reductase family of enzymes contain two pterin dithiolene ligands; at least one enzyme functions by using the minimal reaction couple Mo^{IV} + $Me_2SO \rightleftarrows Mo^{VI}O + Me_2S$. Accordingly, the synthesis, structures, and reactivity of bis(dithiolene)Mo(IV,VI) complexes of benzene-1,2-dithiolate and related ligands have been investigated. A convenient synthesis of square pyramidal $[Mo^{IV}O(S_2C_2R_2)_2]^{2-}$ complexes is reported. Compounds of the type $[Mo(S_2C_2R_2)_2(R'NC)_2]$, including $[Mo(bdt)_2(MeNC)_2]$ (**13**), were prepared by reacting $Na_2(S_2C_2R_2)$ and R′NC with $[MoCl_4(MeCN)_2]$ and were shown to be identical (R′ = Me) to byproducts in the synthesis of $[Mo^{IV}O(S_2C_2R_2)_2]^{2-}$. In one such reaction, the Fischer carbene complex $[Mo(Me_4bdt)_2(MeNC)(CMe_4bdt)]$ (**16**) was isolated. Silylation of $[Mo^{IV}O(bdt)_2]^{2-}$ affords $[Mo^{IV}(bdt)_2(OSiBu^tPh_2)]^-$ (**8**); an analogous reaction of $[MoO_2(bdt)_2]^{2-}$ yields $[Mo^{VI}O(bdt)_2(OSiBu^tPh_2)]^-$ (**11**). The structures of square pyramidal **8** and cis-octahedral **11** reveal them to be minimal unconstrained representations of the des-oxo $[Mo^{IV}(S_2pd)_2(O{\cdot}Ser)]$ and mono-oxo $[Mo^{VI}O(S_2pd)_2(O{\cdot}Ser)]$ sites, respectively, of *Rhodobacter sphaeroides* DMSO reductase. This description applies in the limit of symmetrical dithiolene coordination; silyloxide is a simulator of serinate binding. Complex **8** shows limited reactivity with sulfoxides, and **11** is unreactive toward sulfides. However, **11** is reduced to **8** by tertiary phosphines; with excess phosphine, $[Mo(bdt)_2(PMePh_2)_2]$ (**17**) was formed. This compound was also prepared independently from $[MoCl_4(MeCN)_2]$ and the phosphine. The compounds **13**, **16**, and **17** form an isoelectronic set with idealized trigonal prismatic (C_{2v}) stereochemistry. These results complement a parallel development of bis(dithiolene)W(IV,VI) complexes as active-site analogues of tungstoenzymes (Lorber, C.; Donahue, J. P.; Goddard, C. G.; Nordlander, E.; Holm, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 8102). Certain comparisons between the properties of molybdenum and tungsten bis(dithiolenes) are offered. (bdt = benzene-1,2-dithiolate(2−), S_2pd = pterin dithiolene(2−).)

Introduction

All molybdenum oxotransferase and hydroxylase enzymes, which catalyze the overall reaction $X + H_2O \rightleftarrows XO + 2H^+ + 2e^-$, are now recognized to contain a universal cofactor (Moco) in which a molybdenum atom is coordinated by one or two pterin dithiolene ligands (S_2pd).[1] Recognition of the cofactor as a pterin dithiolene complex and initial elucidation of nearly all of its structure are derived from the contributions of Rajagopalan and Johnson.[2] The essential Moco structure is set out in Figure 1. The reduced pyrazine ring of the pterin nucleus is fused to a pyran ring that is functionalized as an ene-1,2-dithiolate, affording binding of the molybdenum atom in the familiar dithiolene chelation mode. The existence of the pyran ring (rather than an open chain structure) was first established by the X-ray structure of a tungsten aldehyde oxidoreductase.[3] This ring also carries a phosphate side chain to which a nucleotide (R) is conjugated in enzymes of procaryotic origin.

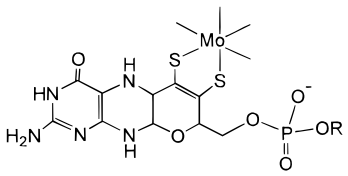

Figure 1. Partial structure of the molybdenum cofactor (R absent or a nucleotide).

The presence or absence of a nucleotide and, if present, its identity are the only known variables in the organic part of the Moco structure. Even more recently, protein crystallography has served to confirm the cofactor structure in *Desulfovibrio gigas* aldehyde oxidoreductase,[4] *Rhodobacter sphaeroides* (*Rs*) dimethyl sulfoxide (DMSO) reductase,[5] *Rhodobacter capsulatus* (*Rc*) DMSO reductase,[6,7] chicken liver sulfite oxidase,[8] and

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Escherichia coli formate dehydrogenase.[9] Crystallographic aspects of Moco have been thoroughly scrutinized.[10]

Synthetic systems that have been developed for examination of molybdenum-mediated oxygen atom transfer have nearly always centered on the minimal reaction paradigm $Mo^{IV}O + XO \rightleftarrows Mo^{VI}O_2 + X$,[11−14] where XO and X are substrate or product. Certain of these systems involve dithiolene complexes.[12c,14] It is probable that this reaction applies to the sulfite oxidase enzyme family.[1] Note, for example, the spectroscopic detection of the indicated oxomolybdenum groups, coordinated by one pterin dithiolene ligand, in chicken liver sulfite oxidase.[15] In the DMSO reductase family,[1,16] a uniform description of oxidized and reduced molybdenum sites has not yet emerged. The aforementioned reaction may also be operative in the *Rc* enzyme, for which one set of crystal structures[7] and extended X-ray absorption fine structure (EXAFS) results[17] have established the coordination units $[Mo^{VI}O_2(S_2pd)_2(O{\cdot}Ser)]$ and $[Mo^{IV}O(S_2pd)_2(O{\cdot}Ser)]$. However, X-ray examination of another crystalline form of the *Rc* enzyme has led to the five-coordinate formulation $[Mo^{VI}O_2(S_2pd)(O{\cdot}Ser)]$ for the oxidized state.[6] The situation with *Rs* DMSO reductase is apparently different. Crystallography[5] and EXAFS[18] have afforded descriptions of the mono-oxo $[Mo^{VI}O(S_2pd)_2(O{\cdot}Ser)]$ and des-oxo $[Mo^{IV}(S_2pd)_2(O{\cdot}Ser)]$ active sites. These imply that the minimal reaction is $Mo^{VI}O + Me_2S \rightleftarrows Mo^{IV} + Me_2SO$, consistent with ^{18}O labeling results[19] and a resonance Raman spectroscopic interrogation of different enzyme states in the catalytic cycle.[20] The mono-oxo Mo(VI) and des-oxo Mo(IV) coordination units were not anticipated in the explicit formulation of the catalytic cycle of any enzyme prior to the crystallographic results for *Rs* DMSO reductase, and in this sense their occurrence may be considered somewhat surprising. Further, the situation is complicated by the asymmetric binding of one pterin dithiolene ligand in the Mo(IV,VI) states, as determined by crystallography,[5] and the tight symmetrical chelation of each dithiolene, as deduced from spectroscopy.[20] The source of structural discrepancies between different samples of the *Rc* enzyme, between the highly homologous *Rc* and *Rs* enzymes, and the apparently variable ligand-binding modes in the *Rs* enzyme is not yet clear.

The foregoing uncertainties notwithstanding, the existence of dithiolene binding in Moco and in all known tungsten enzymes[21] provokes an imperative for synthetic, structural, and reactivity investigations of the dithiolene complexes of these elements that may be related to active sites and their properties. Mono(dithiolene)$Mo^{IV,V}O$,[22] bis(dithiolene)$Mo^{IV,V}O$,[14,23] bis(dithiolene)$Mo^{VI}O_2$,[14] and tris(dithiolene)Mo[23b,g,24] complexes (excluding organometallics) have been prepared. In the development of metal dithiolene chemistry,[25] considerable emphasis has been placed on the tris-complexes and the noninnocence of dithiolene ligands in highly oxidized species. From this previous work, the principal results of interest in the present context are these: (i) X-ray structures of the $Mo^{IV}O$ (square pyramidal) and $Mo^{VI}O_2$ (irregular cis-octahedral) complexes have been determined;[14a,b,d,e,23d,f−i] (ii) oxo-transfer rates from $[Mo^{IV}O_2(mnt)_2]^{2-}$ to tertiary phosphines are dependent on the stereoelectronic properties of the substrates;[14f,26] (iii) oxo transfer to phosphine substrates is faster with the molybdenum complex of the pair $[MO_2(mnt)_2]^{2-}$ (M = Mo, W);[12c] (iv) $[Mo^{IV}O(bdt)_2]^{2-}$ (and ring-substituted versions thereof) is converted to $[Mo^{VI}O_2$-

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(26) Abbreviations: bdt, benzene-1,2-dithiolate(2−); CMe_4bdt, 4,5,6,7-tetramethylbenzene-1,3-dithiol-2-ylidene; edt, *cis*-ethylene-1,2-dithiolate(2−); L−S_2, 10,10-dimethoxy-1,4,4aα,5,8,8aα-hexahydro-1α,4α:5β,8β-dimethanonaphthalene-2,3-dithiolate(2−); Me_4bdt, 3,4,5,6-tetramethylbenzene-1,2-dithiolate(2−); mnt, maleonitriledithiolate(2−); tfd, *cis*-bis(1,2-trifluoromethyl)ethylene-1,2-dithiolate(2−).

$(bdt)_2]^{2-}$ by atom transfer from Me_3NO;[14b,d] and (v) the reactants $[Mo^{VI}O_2(mnt)_2]^{2-}/HSO_3^-$ constitute a functional sulfite oxidase analogue reaction system.[14a] Notably absent from this summary are des-oxo Mo(IV) and mono-oxo Mo(VI) bis(dithiolene) complexes potentially related to the active site of *Rs* DMSO reductase. Availability of such species could provide useful spectroscopic benchmarks, unconstrained structures, and reactivity information. We are currently engaged in an examination of bis(dithiolene) complexes related to the active sites of molybdenum and tungsten enzymes, with the intention of acquiring information relevant to the structure and function of those sites. We have reported certain of our initial results[27] and provided a fuller account of tungsten−dithiolene chemistry.[28] Here we describe an accompanying investigation of the bis(dithiolene)molybdenum systems that both complements and extends research by ourselves and others.

Experimental Section[26]

Preparation of Compounds. Except where otherwise noted, all reactions and manipulations were conducted under a pure dinitrogen atmosphere either in an inert atmosphere box or by using standard Schlenk techniques. Acetonitrile and dichloromethane were freshly distilled from CaH_2, and methanol was distilled from magnesium; CD_3CN (Aldrich) was dried over freshly activated molecular sieves. Diethyl ether and tetrahydrofuran (THF) were distilled from sodium/benzophenone and stored over 4 Å (pore size) molecular sieves. Methylisonitrile was prepared as described in the literature.[29] In the following preparations, all volume reduction and evaporation steps were performed in vacuo.

Li_2(bdt). A 1.6 M solution of *n*-butyllithium in hexane (3.6 mL, 5.76 mmol) was added dropwise to a rapidly stirred solution of 1,2-benzenedithiol[30] (0.50 g, 3.52 mmol) in 30 mL of THF held at 0 °C. The mixture was stirred at 0 °C for 15 min and at ambient temperature for 1 h. Removing the solvent left a sticky residue, which was washed with ether to give a white solid suspension. Removal of the ether and collection of the product yielded a very light, white powder (0.490 g, 90%). ^{1}H NMR (CD_3OD): δ 7.35 (m, 1), 6.55 (m, 1). This compound can also be prepared by the reductive cleavage of 1,2-di-*n*-butylmercaptobenzene[31] with Li/NH_3.

$(Et_4N)_2[Mo^{IV}O(bdt)_2]$. $[Mo^{IV}OCl(MeNC)_4](PF_6)$[32] (0.171 g, 0.375 mmol) and Et_4NCl (0.190 g, 1.15 mmol) were partially dissolved in 30 mL of acetonitrile; the mixture was cooled to −40 °C. Over 10 min, a solution of Li_2(bdt) (0.115 g, 0.746 mmol) in 15 mL of THF was added. The color changed to a light yellow-brown, and a yellow-orange solid precipitated as the reaction proceeded. The mixture was stirred rapidly for 2 h while it was gradually warmed to room temperature. Removing the solvent yielded a brown solid, which was washed with acetonitrile (2 × 2 mL). (*Caution*: Trapped solvent smells strongly of methylisonitrile.) The orange solid was dissolved in 30 mL of dimethylformamide (DMF), and the solution was filtered through a packed column of Celite. Slow diffusion of Bu^{t}OMe into the filtrate caused the product to crystallize as bright orange needles (0.108 g, 44%). Absorption spectrum (DMF): λ_{max} (ϵ_M) 328 (11 100), 384 (sh), 454 (401) nm. IR (KBr): 1481 (s), 1430 (s), 1173 (s), 903 (vs, ν_{MoO}), 754 (s) cm^{-1}. ^{1}H NMR (anion, CD_3CN): δ 7.51 (m, 1), 6.71 (m, 1); these signals were observed only after stirring the solution with tin powder overnight to reduce traces of paramagnetic $[MoO(bdt)_2]^-$.[23d] FAB MS: *m*/*z* 392 (M^-). Anal. Calcd. for $C_{28}H_{48}MoN_2OS_4$: C, 51.51; H, 7.41; N, 4.29; S, 19.64. Found: C, 51.62; H, 7.36; N, 4.25; S 19.81. This compound has been prepared previously by other methods.[14b,23d]

$(Et_4N)_2[Mo^{IV}O(edt)_2]$. $[Mo^{IV}OCl(MeNC)_4](PF_6)$ (0.517 g, 1.13 mmol) and Et_4NCl (0.418 g, 2.52 mmol) were partially dissolved in 30 mL of acetonitrile, and the mixture was cooled to −30 °C. Over 15 min, a solution of Na_2(edt)[33] (0.309 g, 2.27 mmol) in 30 mL of methanol was added. The color changed from lavender to red-orange, and all undissolved starting material was drawn into solution. After the solution was stirred for 20 min at reduced temperature, it was warmed to room temperature and concentrated to dryness. The resulting red solid was dissolved in acetonitrile and filtered through a packed column of Celite. The filtrate was concentrated to dryness, and the red solid was recrystallized by slow vapor diffusion of 1,2-dimethoxyethane into a DMF solution (10 mL) over a 3-day period. The product initially crystallized as $(Et_4N)_2[MoO(edt)_2]\cdot(Et_4N)(PF_6)$ in the form of large orange-red square plates (0.508 g, 54%). The identity of this material was determined crystallographically.[34] Two subsequent crystallizations from DMF/1,2-dimethoxyethane removed $(Et_4N)(PF_6)$ and yielded the pure product as large red needles (0.239 g, 38%). Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 260 (12 100), 293 (4640), 468 (201), 531 (129) nm. IR (KBr): 1479 (vs), 1452 (s), 1391 (s), 1171 (s), 1001 (s), 904 (vs, ν_{MoO}), 780 (s), 674 (s) cm^{-1}. ^{1}H NMR (anion, CD_3CN): δ 6.61 (s). ^{13}C NMR (anion, CD_3CN): δ 130.48 (s). FAB MS$^-$: *m*/*z* 292 (M^-). Anal. Calcd. for $C_{20}H_{44}MoN_2OS_4$: C, 43.46; H, 8.02; N, 5.07; S, 23.20. Found: C, 43.28; H, 7.70; N, 5.06; S, 23.56. The identity of this compound was confirmed by an X-ray structure determination.

$(Ph_4P)_2[Mo^{IV}O(edt)_2]$. The previous procedure on the same scale was followed except for the use of 3 equiv of Ph_4PCl. After filtration of an acetonitrile solution of the crude product to remove halide salts and concentration of the filtrate, $(Ph_4P)(PF_6)$ was selectively crystallized by slow diffusion (for 3 days) of methanol into a DMF solution. The red filtrate was concentrated to dryness, dissolved in a minimal amount of DMF, and filtered. Slow vapor diffusion (for 3 days) of benzene into the DMF solution gave the product as dark red prisms (0.430 g, 40%). IR (KBr): 1438 (vs), 1107 (vs), 996 (s), 916 (s, ν_{MoO}), 723 (vs), 690 (vs) cm^{-1}. Anal. Calcd. for $C_{52}H_{44}MoOP_2S_4$: C, 64.32; H, 4.57; P, 6.38; S, 13.21. Found: C, 64.45; H, 4.65; P, 6.45; S, 13.36.

$(Et_4N)[Mo^{V}O(edt)_2]$. $[Mo^{IV}OCl(MeNC)_4](PF_6)$ (0.247 g, 0.541 mmol) and Et_4NCl (0.186 g, 1.12 mmol) were partially dissolved in 30 mL of acetonitrile, and the mixture was cooled to −30 °C. To the mixture was added dropwise a solution of Na_2(edt) (0.147 g, 1.08 mmol) in 20 mL of methanol, causing a color change to red-orange. The mixture was stirred at −30 °C for 10 min and then warmed to room temperature. Solid I_2 (0.069 g, 0.272 mmol) was added. The reaction mixture was stirred for 2 h and taken to dryness. The residue was dissolved in a minimum volume of acetonitrile, and the solution was filtered through a column of packed Celite. The filtrate was evaporated to a purple residue, which was twice recrystallized from acetonitrile by slow vapor diffusion of Bu^{t}OMe. The product was obtained as flat violet-black needles (0.104 g, 45%). Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 279 (6200), 362 (sh), 546 (976), 773 (1940) nm. IR (KBr): 1478 (s), 1458 (s), 1183 (s), 917 (vs, ν_{MoO}), 839 (s), 798 (s), 676 (s) cm^{-1}. FAB MS$^-$: *m*/*z* 292 (M^-). Anal. Calcd. for $C_{12}H_{24}MoNOS_4$: C, 34.11; H, 5.73; N, 3.32; S, 30.35. Found: C, 34.03; H, 5.68; N, 3.30; S, 30.43. The identity of this compound was confirmed by an X-ray crystal structure analysis.

$(Et_4N)_2[Mo^{IV}O(mnt)_2]$. A procedure analogous to that for the preparation of $(Et_4N)_2[MoO(edt)_2]$ was followed. In a typical reaction scale, we used 0.201 g (0.440 mmol) of $[Mo^{IV}OCl(MeNC)_4](PF_6)$, 0.165 g (0.886 mmol) of Na_2(mnt),[35] and 0.228 g (1.38 mmol) of Et_4NCl. The product was crystallized in air as dark red-green needles (0.191 g, 67%) by slow vapor diffusion of Bu^{t}OMe into an acetonitrile solution. Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 293 (sh), 331 (5190), 364 (11 900), 491 (161), 601 (80) nm. IR (KBr): 2205 (vs, ν_{CN}), 2194 (vs, ν_{CN}), 1483 (vs), 1438 (s), 1391 (s), 1171 (s), 1114 (s), 998 (s), 932 (vs, ν_{MoO}), 783 (s) cm^{-1}. ^{13}C NMR (anion, CD_3CN): δ 120.15 (s, CN),

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132.03 (s, C═C). FAB MS$^-$: *m*/*z* 392 (M$^-$). Anal. Calcd. for $C_{24}H_{40}MoN_6OS_4$: C, 44.16; H, 6.18; N, 12.87; S, 19.64. Found: C, 43.98; H, 6.14; N, 12.79; S, 19.78. The identity of this compound was confirmed by an X-ray structure determination. $(Bu_4N)_2[MoO(mnt)_2]$ has been prepared previously by other methods.[14a,23ab]

$(Ph_4P)_2[Mo^{IV}O(edt)(mnt)]$. An equimolar mixture of $Na_2(edt)$ (0.070 g, 0.514 mmol) and $Na_2(mnt)$ (0.096 g, 0.516 mmol) was dissolved in 30 mL of methanol and slowly added to a solution of $[Mo^{IV}OCl(MeNC)_4](PF_6)$ (0.235 g, 0.515 mmol) and Ph_4PBr (0.659 g, 1.57 mmol) in 30 mL of acetonitrile maintained at −30 °C. The solution color changed from lavender to a dirty green-brown. The mixture was stirred for 10 min at −30 °C and then for 30 min at ambient temperature. After the solvent was removed, the residue was dissolved in 30 mL of acetonitrile and filtered through a packed column of Celite, and the filtrate was evaporated to give a pea-green solid. This material was dissolved in 20 mL of acetonitrile and the solution was filtered. Introduction of THF by vapor diffusion over 36 h caused separation of $(Ph_4P)(PF_6)$, which was removed by filtration. The filtrate was concentrated to dryness in vacuo. The solid residue was recrystallized from 10 mL of acetonitrile by vapor diffusion of THF over a period of 7 days. The product was obtained as brown diamond-like crystals in two crops (0.082 g, 31%, based on 50% maximum formation of $[MoO(edt)(mnt)]^{2-}$). Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 286 (14 100), 343 (5590), 433 (1110) nm. IR (KBr): 2184 (vs, ν_{CN}), 1483 (s), 1436 (vs), 1108 (s), 919 (vs, ν_{MoO}), 757 (s), 723 (vs), 690 (vs), 527 (vs) cm^{-1}. ^{1}H NMR (anion, DMF-d_7): δ 6.62 (s). ^{13}C NMR (anion, DMF-d_7): δ 121.87 (s, CN), 129.08 (s, edt), 133.55 (s, mnt). FAB MS$^-$: *m*/*z* 342 (M$^-$). Anal. Calcd. for $C_{54}H_{42}MoN_2OP_2S_4$: C, 63.52; H, 4.15; N, 2.74; S, 12.56. Found: C, 63.64; H, 4.12; N, 2.66; S, 12.47. The identity of this compound was confirmed by an X-ray structure determination.

$(Et_4N)[Mo^{IV}(bdt)_2(OSiBu^tPh_2)]$. To a suspension of $(Et_4N)_2[Mo^{IV}O(bdt)_2]$ (0.126 g, 0.193 mmol) in 30 mL of acetonitrile was added Bu^tPh_2SiCl (0.110 mL, 0.224 mmol), inducing a color change from orange to dirty green-brown. The mixture was stirred for 1 h and was concentrated to dryness in vacuo. The brown residue was washed with acetonitrile (3 mL) and recrystallized as dark green-black blocks (0.106 g, 72% yield) by slow vapor diffusion of Bu^tOMe into an acetonitrile solution. Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 301 (10 500), 352 (22 200), 388 (sh), 461 (sh), 570 (265) nm. IR (KBr): 3048 (s), 2953 (s), 2852 (s), 1481 (s), 1437 (s), 1427 (s), 1111 (s), 947 (vs, ν_{SiO}), 751 (s), 708 (s), 506 (s) cm^{-1}. ^{1}H NMR (anion, CD_3CN): δ 7.82 (d, 4), 7.39 (d, 4), 7.24 (t, 2), 7.08 (m, 8), 0.73 (s, 9). FAB MS$^-$: *m*/*z* 633 (M$^-$). Anal. Calcd. for $C_{36}H_{47}MoONS_4Si$: C, 56.74; H, 6.22; N, 1.84; S, 16.83. Found: C, 56.80; H, 6.28; N, 1.88; S, 16.89. The identity of this compound was confirmed by an X-ray structure analysis.

$(Ph_4P)[Mo^{IV}(edt)_2(OSiBu^tPh_2)]\cdot{}^1/_2Et_2O$. To a suspension of $(Ph_4P)_2[Mo^{IV}O(edt)_2]$ (0.322 g, 0.331 mmol) in 10 mL of acetonitrile was added Bu^tPh_2SiCl (0.160 mL, 0.615 mmol), causing a color change from red to deep brown. The mixture was stirred for 30 min, and a brown microcrystalline solid was collected by filtration. This material was recrystallized by vapor diffusion of ether into a DMF solution of the solid, yielding the product as brown-black crystalline blocks (0.184 g, 61%). Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 261 (sh), 268 (12 200), 275 (10 700), 331 (11 800), 384 (2860), 451 (1230), 561 (355) nm. IR (KBr): 1437 (s), 1426 (s), 1111 (s), 945 (vs, ν_{SiO}), 751 (s), 708 (s) cm^{-1}. ^{1}H NMR (anion, CD_3CN): δ 7.48 (d, 4), 7.44 (m, 4), 7.28 (m, ∼6), 0.76 (s, 9). FAB MS$^-$: *m*/*z* 532 (M$^-$). Anal. Calcd. for $C_{46}H_{48}MoO_{1.5}PS_4Si$: C, 60.84; H, 5.33; P, 3.41; S, 14.12. Found: C, 60.86; H, 5.53; P, 3.36; S, 13.64. The identity of this compound was confirmed by an X-ray structure determination.

$[Mo(S_2C_2R_2)_2(R'NC)_2]$. Complexes of this type were prepared by the following general procedure. A stirred solution of $[MoCl_4(MeCN)_2]$[36] (0.519 g, 1.62 mmol) in 15 mL of DMF was treated with 13.0 mmol of R′NC. This brown solution was added to a solution of $Li_2(bdt)$ or $Na_2(S_2C_2R_2)$[30,31,33,37] (3.25 mmol) in 10 mL of DMF. The dark brown reaction mixture was stirred vigorously for 30 min and concentrated in vacuo to a dark brown oil. The oil was dissolved in 10 mL of dichloromethane and evaporated onto silica gel (5 g). The loaded silica gel was added to the top of a silica gel column (3 × 30 cm) packed as a slurry in a dichloromethane/ether mixture. Flash chromatography was performed with the dichloromethane/ether solvent mixtures specified in the following paragraphs (v/v). Compounds were recrystallized from the solvents indicated for each case and were obtained in typical yields of 15−25%. As shown for $[Mo(bdt)_2(MeNC)_2]$, stepwise loss of isonitrile was observed in mass spectra. The identities of all compounds except $[Mo(L-S_2)(MeNC)_2]$, which forms an isomeric mixture, were confirmed by X-ray structure determinations.

(i) $[Mo(bdt)_2(MeNC)_2]$. 1:1, second band, deep red; 1,2-$C_2H_4Cl_2$/Bu^tOMe. Absorption spectrum (dichloromethane): λ_{max} (ϵ_M) 320 (4270), 341 (4610), 408 (10 500), 474 (11 100), 535 (sh), 801 (193) nm. IR (KBr): 2193 cm^{-1} (vs, ν_{NC}). ^{1}H NMR ($CDCl_3$): 8.18 (dd, 2), 7.27 (dd, 2), 3.65 (s, 3). FAB MS$^+$: *m*/*z* 458 (M$^+$), 417 (M$^+$ − MeNC), 376 (M$^+$ − 2MeNC). Anal. Calcd. for $C_{16}H_{14}MoN_2S_4$: C, 41.92; H, 3.08; N, 6.11; S, 27.97. Found: C, 41.82; N, 3.15; N, 5.98; S, 27.91.

(ii) $[Mo(Me_4bdt)_2(MeNC)_2]$. 1:1, third band, deep violet; dichloromethane/ether. Absorption spectrum (dichloromethane): λ_{max} (ϵ_M) 330 (sh), 360 (sh), 417 (18 500), 500 (23 700), 715 (2850) nm. IR (KBr): 2178 cm^{-1} (vs, ν_{NC}). ^{1}H NMR ($CDCl_3$): δ 3.69 (s, 1), 2.86 (s, 2), 2.23 (s, 2). FAB MS$^+$: *m*/*z* 571 (M$^+$). Anal. Calcd. for $C_{24}H_{30}MoN_2S_4$: C, 50.51; H, 5.30; N, 4.91; S, 22.47. Found: C, 50.42; H, 5.38; N, 4.86; S, 22.58.

(iii) $[Mo(edt)_2(Bu^tNC)_2]$. 1:3, second band, dark red-brown; 1,2-dichloroethane/methanol. Absorption spectrum (dichloromethane): λ_{max} (ϵ_M) 285 (sh), 397 (7210), 463 (5480), 523 (3680) nm. IR (KBr): 2145 cm^{-1} (vs, ν_{NC}). ^{1}H NMR ($CDCl_3$): δ 8.78 (s, 2), 1.57 (s, 9). FAB MS$^+$: *m*/*z* 443 (M$^+$). Anal. Calcd. for $C_{14}H_{22}MoN_2S_4$: C, 38.00; H, 5.01; N, 6.33; S, 28.98. Found: C, 37.86; H, 5.12; N, 6.19; S, 28.85.

(iv) $[Mo(L-S_2)_2(MeNC)_2]$. 1:2, second band, deep violet; not recrystallized. Absorption spectrum (dichloromethane): λ_{max} (ϵ_M) 376 (2310), 448 (3970), 535 (5080). IR (KBr): 2167 cm^{-1} (s, ν_{CN}). FAB MS$^-$: *m*/*z* 739 (M$^-$). Anal. Calcd. for $C_{32}H_{38}MoN_2O_4S_4$: C, 52.02; H, 5.18; N, 3.79; S, 17.36. Found: C, 52.11; H, 5.20; N, 3.66; S, 17.43.

$[Mo(Me_4bdt)_2(MeNC)(CMe_4bdt)]$. This compound was initially observed as the second band in the chromatographic purification of $[Mo(Me_4bdt)_2(MeCN)_2]$. To a stirred solution of $[MoCl_4(MeCN)_2]$ (0.230 g, 0.719 mmol) in 20 mL of DMF was added MeNC (0.160 mL, 2.95 mmol), causing a slight darkening of the orange-brown solution. To this mixture was slowly added a suspension of $Li_2(Me_4bdt)$ (0.455 g, 2.16 mmol) in DMF (20 mL); by the end of the addition, the mixture was a very dark brown. The mixture was stirred for 30 min and then concentrated to a black solid, which was dissolved in 30 mL of dichloromethane and evaporated onto 2 g of silica gel. Flash chromatography with dichloromethane/ether (1:1 v/v) eluted a small brown fraction (collected separately), followed by a red fraction that was concentrated to a red-black solid. Recrystallization of this latter material by vapor diffusion of pentane into a dichloromethane solution (3 mL) gave the product as black square plates (0.064 g, 12%). Absorption spectrum (dichloromethane): λ_{max} (ϵ_M) 294 (16 600), 325 (sh), 395 (sh), 458 (20 400), 501 (19 400), 748 (627) nm. IR (KBr): 2942 (vs), 2928 (vs), 2920 (vs), 2866 (vs), 2175 (vs, ν_{NC}), 1444 (s), 1411 (s), 1385 (s), 1222 (s), 829 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.59 (s, 1), 2.86 (s, 2), 2.39 (s, 1), 2.37 (s, 2), 2.24 (s, 1). FAB MS$^+$: *m*/*z* 738 (M$^+$), 697 (M$^+$ − MeNC). The identity of this compound was confirmed by an X-ray structure determination.

$(Et_4N)[MoO(bdt)_2(OSiBu^tPh_2)]$. $(Et_4N)_2[Mo^{VI}O_2(bdt)_2]$[14d] (0.150 g, 0.224 mmol) was dissolved in 5 mL of rigorously dried acetonitrile. To the red-brown solution was added Bu^tPh_2SiCl (0.120 mL, 0.462 mmol), causing an immediate brown-black color. The reaction mixture was stirred for 15 min and concentrated in vacuo to a sticky black residue. This material was washed with ether (2 × 10 mL) and then extracted with 6 mL of acetonitrile/THF (1:9 v/v). The extract was filtered, treated with an equal volume of ether, and maintained at 4 °C for 2 days. The mother liquor was decanted; the semicrystalline black solid was washed with THF (1 mL) and ether (2 × 2 mL) and was dried in vacuo. Addition of ether (5 mL) to the decanted solution followed by the same workup yielded a smaller, second crop. Combining the two crops gave 0.077 g (44%) of product, which in

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Table 1. Crystallographic Data[a] for Compounds of the Type $[Mo^{IV,V}O(S_2C_2R_2)_2]^{2-,-}$

	$(Et_4N)_2[Mo^{IV}O(edt)_2]$	$(Et_4N)[Mo^{V}O(edt)_2]$	$(Et_4N)_2[Mo^{IV}O(mnt)_2]$	$(Ph_4P)_2[Mo^{IV}O(edt)(mnt)]$
formula	$C_{20}H_{44}MoN_2OS_4$	$C_{12}H_{24}MoNOS_4$	$C_{24}H_{40}MoN_6OS_4$	$C_{54}H_{42}MoN_2OP_2S_4$
fw	552.75	422.50	652.80	1021.02
crystal system	monoclinic	triclinic	orthorhombic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_12_12$	Pn
Z	8	4	4	2
a, Å	14.966(3)	8.670(2)	14.784(3)	11.732(2)
b, Å	16.770(4)	15.106(3)	29.946(6)	15.899(3)
c, Å	21.188(4)	15.116(3)	7.346(2)	13.317(3)
α, deg		95.77(2)		
β, deg	90.29(2)	106.49(1)		101.66(3)
γ, deg		104.90(1)		
V, Å^3	5318(2)	1802.0(6)	3252(1)	2432.7(8)
T, K	223	213	293	213
θ range, deg	3−45	3−46	3−48	3−52
R_1[b] (wR_2[c])	0.0335 (0.0686)	0.0464 (0.1236)	0.0754 (0.1601)	0.0934 (0.2244)

[a] Obtained with graphite-monochromatized Mo Kα ($\lambda = 0.71073$ Å) radiation. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 2. Crystallographic Data[a] for Compounds of the Type $[Mo(S_2C_2R_2)_2L_2]$ (L = isonitrile, carbene, phosphine)

	$[Mo(edt)_2(Bu^tNC)_2]$	$[Mo(bdt)_2(MeNC)_2]$	$[Mo(Me_4bdt)_2(MeNC)_2]$	$[Mo(Me_4bdt)_2(MeNC)(CMe_4bdt)]\cdot 2CH_2Cl_2$	$[Mo(bdt)_2(PMePh_2)_2]\cdot ClCH_2CH_2Cl$
formula	$C_{14}H_{22}MoN_2S_4$	$C_{16}H_{14}MoN_2S_4$	$C_{24}H_{30}MoN_2S_4$	$C_{35}H_{43}Cl_4MoNS_6$	$C_{40}H_{38}Cl_2MoP_2S_4$
fw	442.52	458.47	570.68	907.80	875.72
crystal system	monoclinic	monoclinic	monoclinic	orthorhombic	triclinic
space group	$P2_1/m$	$P2_1$	$C2/c$	$Cmca$	$P\bar{1}$
Z	2	2	4	8	2
a, Å	9.278(2)	9.6811(5)	20.142(2)	21.9116(4)	9.8258(11)
b, Å	9.879(2)	9.2174(5)	7.7923(6)	24.9138(3)	10.7281(12)
c, Å	11.530(2)	10.8604(6)	17.858(1)	15.7950(3)	20.776(2)
α, deg					95.000(3)
β, deg	95.54(3)	98.971(1)	115.644(1)		95.467(2)
γ, deg					113.830(2)
V, Å^3	1051.9(4)	957.27(9)	2526.9(3)	8622.5(2)	1975.1(4)
T, K	223	213	213	213	213
θ range, deg	3−50	3−56	3−48	3−45	3−56
R_1[b] (wR_2[c])	0.0257 (0.0685)	0.0460 (0.0735)	0.0338 (0.0701)	0.0852 (0.2203)	0.0547 (0.0821)

[a] Obtained with graphite-monochromatized Mo Kα ($\lambda = 0.71073$ Å) radiation. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

anaerobic solution is extremely sensitive to traces of water. Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 305 (sh), 378 (5670), 565 (2190), 717 (1630) nm. IR (KBr): 2920 (s), 2851 (s), 1469 (s), 1105 (s), 921 (vs, ν_{SiO}), 877 (s, ν_{MoO}), 745 (s), 703 (s) cm^{-1}. ^{1}H NMR (anion, CD_3CN): δ 7.92 (m, 4), 7.35 (m, 6), 7.24 (m, 4), 6.96 (m, 4), 1.02 (s, 9). FAB MS$^-$: m/z 649 (M^-). Anal. Calcd. for $C_{36}H_{47}MoNO_2S_4Si$: C, 55.58; H, 6.09; N, 1.80. Found: C, 55.70; H, 6.13; N, 1.82. The identity of this compound was confirmed by an X-ray structure determination.

$[Mo(bdt)_2(PMePh_2)_2]\cdot C_2H_4Cl_2$. A solution of $PMePh_2$ (1.70 mL, 9.14 mmol) in 10 mL of THF was added to a solution of $[MoCl_4(MeCN)_2]$ (0.363 g, 1.13 mmol) in 20 mL of DMF. To this mixture a solution of $Li_2(bdt)$ (0.350 g, 2.27 mmol) in 15 mL of THF was slowly added dropwise over 10 min, resulting in a color change from orange to dark red. The reaction mixture was stirred for 2 h and concentrated in vacuo to a red oil. The oil was dissolved in dichloromethane and evaporated onto 2 g of silica. The loaded silica was added to a silica column packed as a slurry in 2:1 pentane/ether (v/v), which was then eluted with this solvent mixture to remove unreacted phosphine (readily monitored by thin-layer chromatography). The column was next eluted with 1:4 dichloromethane/ether (v/v), which moved an orange band and resolved it from a slower-moving yellow fraction. The orange fraction was collected and concentrated to a red-orange solid (0.212 g, 24%). Absorption spectrum (dichloromethane): λ_{max} (ϵ_M) 361 (8330), 421 (16 400), 510 (sh) nm. ^{1}H NMR (C_6D_6): δ 8.34 (s, br), 7.09 (m), 6.70 (s, v br), 2.88 (s). ^{31}P NMR (C_6D_6): δ 40.11 (s). FAB MS$^+$: m/z 777 (M^+), 577 ($M^+ - PMePh_2$), 377 ($M^+ - 2PMePh_2$). Anal. Calcd. for $C_{40}H_{38}Cl_2MoP_2S_4$: C, 54.86; H, 4.37; P, 7.07; S, 14.64. Found: C, 54.83; H, 4.32; P, 7.04; S, 14.59. The identity of this compound was confirmed by an X-ray structure determination.

X-ray Structure Determinations. The 12 compounds listed in Tables 1−3 were structurally characterized by X-ray crystallography and are henceforth referred to by the numerical designations in Chart 1. Crystallizations were carried out anaerobically. Crystals of (Et_4N)[**3**] (flat violet-black needles), $(Et_4N)_2$[**4**] (red-green needles), and (Et_4N)[**8**] (green-black blocks) were obtained by slow vapor diffusion of Bu^tOMe into acetonitrile solutions. The same technique with THF instead of Bu^tOMe produced diffraction-quality crystals of $(Ph_4P)_2$[**5**] as dark brown diamond-shaped crystals. Solutions of $(Et_4N)_2$[**2**] and (Ph_4P)[**9**] in DMF yielded suitable crystals (dark red needles and ether-solvated brown-black blocks, respectively) after slow introduction by vapor diffusion of 1,2-dimethoxyethane and ether, respectively. Vapor diffusion of methanol (**12**, **13**) or acetonitrile (**15**) into 1,2-dichloroethane solutions gave high-quality crystals of the $[Mo(S_2C_2R_2)_2(R'NC)_2]$ complexes as red-black blocks (**12**), red-black rectangular plates (**13**), and small violet-black prisms (**15**). Compound [**16**]$\cdot 2CH_2Cl_2$ was crystallized as large black square plates by *n*-pentane diffusion into a dichloromethane solution held at 4 °C. Small crystals of (Et_4N)[**11**] were obtained from a 1:1 acetonitrile/ether (v/v) solution left standing for several days. Fine red needles of [**17**]$\cdot C_2H_4Cl_2$ were formed by slow diffusion of pentane into a 1,2-dichloroethane solution.

Data for compounds $(Et_4N)_2$[**2**], (Et_4N)[**3**], and **12** were collected on a Nicolet (Bruker) 4-circle P3 diffractometer by using Mo Kα radiation. The crystals were coated in grease, mounted on glass fibers, and maintained at 223 K under a N_2 stream supplied through an LT-2 apparatus fitted to the diffractometer. Data for $(Et_4N)_2$[**4**] were collected at room temperature on a Siemens P3 4-circle instrument. Refined unit-cell parameters were obtained by least-squares fits of 30−50 randomly searched, machine-centered reflections where $10° \le 2\theta \le 30°$. Data were collected with periodic monitoring of two check reflections out to the 2θ limits (Table 1); in no case was significant decay observed. Data reduction and corrections for scan speed, background, and Lorentz

Table 3. Crystallographic Data[a] for Compounds of the Type $[Mo(S_2C_2R_2)_2(OSiBu^tPh)]^-$

	$(Ph_4P)[Mo^{IV}(edt)_2(OSiBu^tPh_2)]\cdot{}^1/_2Et_2O$	$(Et_4N)[Mo^{IV}(bdt)_2(OSiBu^tPh_2)]$	$(Et_4N)[Mo^{VI}O(bdt)_2(OSiBu^tPh_2)]$
formula	$C_{46}H_{48}MoO_{1.5}PS_4Si$	$C_{36}H_{47}MoNOS_4Si$	$C_{36}H_{47}MoNO_2S_4Si$
fw	908.08	762.02	778.02
crystal system	monoclinic	monoclinic	orthorhombic
space group	$P2_1/c$	*Pn*	*Pbca*
Z	4	2	8
a, Å	13.663(3)	10.6776(1)	10.6275(4)
b, Å	16.470(3)	9.9780(1)	22.7953(9)
c, Å	20.340(4)	17.8337(3)	31.4287(12)
α, deg			
β, deg	101.90(3)	96.339(1)	
γ, deg			
V, Å^3	4479(2)	1888.41(4)	7613.8(5)
T, K	213	213	213
θ range, deg	3−56	3−56	3−56
R_1[b] (wR_2[c])	0.0450 (0.0970)	0.0229 (0.0546)	0.0559 (0.0777)

[a] Obtained with graphite-monochromatized Mo Kα ($\lambda = 0.71073$ Å) radiation. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Chart 1. Designation of Molybdenum Dithiolene Complexes

$[Mo^{IV}O(bdt)_2]^{2-}$	**1**	$[Mo^{VI}O_2(bdt)_2]^{2-}$	**10**
$[Mo^{IV}O(edt)_2]^{2-}$	**2**	$[Mo^{VI}O(bdt)_2(OSiBu^tPh_2)]^-$	**11**
$[Mo^{V}O(edt)_2]^-$	**3**	$[Mo(edt)_2(Bu^tNC)_2]$	**12**
$[Mo^{IV}O(mnt)_2]^{2-}$	**4**	$[Mo(bdt)_2(MeNC)_2]$	**13**
$[Mo^{IV}(edt)(mnt)]^{2-}$	**5**	$[Mo(L-S_2)_2(MeNC)_2]$	**14**
$[Mo^{IV}O(tfd)_2]^{2-}$	**6**	$[Mo(Me_4bdt)_2(MeNC)_2]$	**15**
$[Mo^{IV}O(L-S_2)_2]^{2-}$	**7**	$[Mo(Me_4bdt)_2(MeNC)(CMe_4bdt)]$	**16**
$[Mo^{IV}(bdt)_2(OSiBu^tPh_2)]^-$	**8**	$[Mo(bdt)_2(PMePh_2)_2]$	**17**
$[Mo^{IV}(edt)_2(OSiBu^tPh_2)]^-$	**9**		

and polarization effects were applied by the program XDISK of the SHELXTL PLUS program suite. No absorption correction was applied to the data for $(Et_4N)_2$[**4**]. Absorption corrections were applied by the programs XEMP ($(Et_4N)_2$[**2**], (Et_4N)[**3**]) or XPREP (**12**) by using variations in intensity in azimuthal (Ψ) data for 7−10 reflections with values for 2*θ* being evenly spaced between 10° and 45°.

The compounds $(Ph_4P)_2$[**5**], (Ph_4P)[**9**]$\cdot{}^1/_2Et_2O$, (Et_4N)[**8**], (Et_4N)[**11**], **13**, **15**, [**16**]$\cdot 2CH_2Cl_2$, and [**17**]$\cdot C_2H_4Cl_2$ were mounted on a Siemens (Bruker) SMART charge-coupled device (CCD) area detector instrument with Mo Kα radiation, which was operated at 213 K with an LT-2 device. Data were measured with *ω* scans of 0.3° per frame, 30- or 60-s frames, such that 1271 frames were collected for a hemisphere of data. The first 50 frames were recollected at the end of data collection to monitor for decay; no significant decay was observed. Data out to 2*θ* of 56° were used for the compounds (Ph_4P)[**9**]$\cdot{}^1/_2Et_2O$, (Et_4N)[**8**], (Et_4N)[**11**], **13**, [**16**]$\cdot 2CH_2Cl_2$, and [**17**]$\cdot C_2H_4Cl_2$, but for compound [**16**]$\cdot 2CH_2Cl_2$ data were cut at 2*θ* of 45° in the final refinement cycle because of low-quality high-angle data. For the compounds $(Ph_4P)_2$[**5**] and **15**, the 2*θ* ranges extended to 52° and 48°, respectively. Cell parameters were retrieved by using SMART software (SMART V. 4.043, 1995) and refined by using SAINT software (SAINT V. 4.035, 1995) on all observed reflections between 2*θ* of 3° and the upper thresholds indicated. Data reduction was performed with the SAINT software (SAINT V. 4.035, 1995), which corrects for Lorentz polarization and decay. Absorption corrections were applied by using the program SADABS, as described by Blessing.[38]

The space groups for (Et_4N)[**3**] and **17** were assigned on the basis of statistics and successful solution and refinement of the structure, whereas all the other compounds were assigned unambiguous space groups by analysis of symmetry and observed systematic absences determined by the program XPREP. All structures were solved by direct methods with SHELXS (SHELXS-86, SHELXS-97) and subsequently refined against all data by the standard technique of full-matrix least squares on F^2 (SHELXL-93, SHELXL-97). For the compounds $(Et_4N)_2$-[**2**], (Et_4N)[**8**], (Ph_4P)[**9**]$\cdot{}^1/_2Et_2O$, (Et_4N)[**11**], **12**, **13**, and **15**, all nonhydrogen atoms were refined anisotropically. $(Et_4N)_2$[**4**] and (Et_4N)-[**3**] possessed disordered Et_4N^+ cations, the carbon atoms of which (where appropriate) were refined isotropically with site occupancies factors of 0.5. The two solvate molecules of [**16**]$\cdot 2CH_2Cl_2$ were refined isotropically because of disorder and large thermal parameters. In the anion of $(Ph_4P)_2$[**5**], significant electron density was observed above and below the plane of the mnt ligand, which necessitated fixing the carbon−carbon and carbon−sulfur bonds of this ligand to chemically reasonable values (average values of **4** were used) to prevent an inordinate degree of shifting in the final stages of refinement. For **15**, all the hydrogen atoms were visible in the final electron density maps, all were named, and their positions were allowed to refine. Except for the dichloromethane solvates and the disordered cation of (Et_4N)[**3**], hydrogen atoms were added to the compounds at idealized positions and were refined as riding atoms with uniform values of U_{iso}. Final agreement factors are included in Tables 1−3 and reflect the use of all observed data within the indicated *θ* ranges. All refined structures were examined for any overlooked symmetry with the crystallographic checking program PLATON. Selected interatomic distances and angles for the 12 structures are compiled in Tables 4−6.[39]

Other Physical Measurements. Except for the compounds $[Mo(S_2C_2R_2)_2(R'NC)_2]$, all measurements were made under anaerobic conditions. Absorption spectra were recorded with a Perkin-Elmer Lambda 6 or a Varian Cary 3 spectrophotometer. ^{1}H and ^{13}C NMR spectra were obtained with a Bruker AM 400 or AM 500 spectrometer. IR spectra were measured with KBr disks in a Nicolet Impact 400 Fourier transform IR instrument. FAB mass spectra were recorded on a JEOL SX-102 spectrometer with 3-nitrobenzyl alcohol as matrix. Cyclic voltammograms were recorded with a PAR Model 263 potentiostat/galvanostat using a Pt disk working electrode and a 0.1 M solution of Bu_4NPF_6 supporting electrolyte; potentials are referenced to the saturated calomel electrode (SCE).

Results and Discussion

Synthesis and Structures of Molybdenum(IV,VI) Bis(dithiolenes). (a) Mono-oxo Mo(IV). Our starting point for the expansion of molybdenum dithiolene chemistry in the direction of species related to enzymic active sites is bis(dithiolene)-$Mo^{IV}O$ complexes. Species of this type have been previously prepared by a variety of methods, summarized in Figure 2:[40] (1) cyanide substitution of and concomitant elimination of water from the Mo(IV) starting complex in aqueous medium;[23cdi] (2) ligand substitution of tetrakis(arylthiolato)$Mo^{IV}O$ complexes by proton transfer from added ligand;[14b,23d] (3) reaction of coordinated tetrasulfide with suitably activated acetylenes and elimination of sulfur;[14e,23eg] (4) chloride substitution with reduction of Mo(V,VI) by excess ligand;[14f,23fh] (5) oxo substitution by elimination of water in a protic medium and reduction of Mo(VI) by ligand or an added reductant.[14a,23a] In reaction 2

(38) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33.

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

(40) Two other routes to bis(dithiolene)$Mo^{IV}O$ complexes, reduction of an $Mo^{VI}O_2$ species such as **10** with a tertiary phosphine or reaction with benzoin,[14d] are not included because they are indirect, requiring preparation of a Mo-dithiolene precursor.

Table 4. Selected Interatomic Distances (Å) and Angles (deg) for $[MoO(S_2C_2R_2)_2]^{n-}$ Complexes

	2[a]	**3**[a]	**4**	**5**
Distance, Å				
Mo−S(1−4)	2.394(1)−2.406(1)	2.362(3)−2.386(2)	2.376(5)−2.390(6)	2.370(4)−2.413(3)
Mo−O	1.739(2)	1.677(5)	1.67(1)	1.676(8)
$C-S_{mean}$	1.753(5)	1.731(4)	1.75(2)	1.77(2)[b]
$C-C_{mean}$	1.332(6)	1.31(4)	1.35(3)	1.36(2)[b]
Angles, deg				
O−Mo−S	108.4(1)−109.2(1)	107.3(2)−109.9(2)	105.7(5)−110.6(5)	105.9(3)−109.1(3)
$S-Mo-S_{ring}$[c,d]	83.0	84.0	84.2	83.9
$S-Mo-S_{cis}$[d]	85.1	84.3	84.6	85.9
θ_d[e]	129.0	129.2	129.6	132.5
$Mo\cdots S_4$[f]	0.774	0.757	0.749	0.715

[a] Data for one of two anions in the asymmetric unit. [b] Data are for edt ligand only; bond distances were fixed in mnt ligand. [c] Bite angle. [d] Mean values. [e] Dihedral angle between MoS_2 planes. [f] Displacement of Mo atom from S_4 mean plane.

Table 5. Selected Interatomic Distances and Angles for Mo Bis(dithiolene) Silyloxide Complexes

	8	**9**	**11**
Distances, Å			
Mo−S1	2.339(1)	2.335(1)	2.492(1)
Mo−S2	2.336(1)	2.335(1)	2.443(1)
Mo−S3	2.338(1)	2.339(1)	2.407(1)
Mo−S4	2.340(1)	2.334(1)	2.427(1)
Mo−O1	1.840(2)	1.838(2)	1.715(2)
Mo−O2			1.932(2)
Angles, deg			
S1−Mo−S2	83.81(2)	83.40(4)	77.55(4)
S3−Mo−S4	83.85(2)	83.53(4)	79.76(3)
O1−Mo−S1	108.47(6)	110.57(8)	143.93(9)
O1−Mo−S2	109.35(6)	107.61(8)	80.60(9)
O1−Mo−S3	108.14(6)	108.86(8)	105.33(9)
O1−Mo−S4	108.48(6)	108.91(8)	104.40(9)
Mo−O1−Si1	175.2(1)	167.8(2)	160.0(2)[b]
C1−C2	1.391(4)	1.331(6)	1.422(5)
C3−C4/C7−C8	1.401(4)	1.307(6)	1.385(5)
$M\cdots S_4$[a]	0.746	0.760	
θ_d[a]	129.2	128.3	

[a] Cf. Table 4. [b] Mo−O2−Si1.

of Figure 2, a several-step preparation[41] proceeding through the $Mo^{V}O$ complex is required to obtain the $Mo^{IV}O$ starting material. Unless stabilization by chelation is highly favorable, the reaction is not likely to proceed if the protonated ligand is substantially less acidic than the arylthiol. Reaction 3 does not take place with weakly activated acetylenes RCCR (e.g., R = Ph, CH_2-OH) or with acetylene itself. Reaction 4 in our hands is not clean and affords low yields, and reaction 5 has been reported only with the mnt ligand. Reaction 1 appears to be the most general. In one example, compound **1** was obtained by reaction of the initial $Mo^{IV}O_2$ complex with the protonated ligand (yield unspecified).[23d] In other preparations, the ligand is generated in the reaction mixture by ring opening of a 2-(*N*,*N*-dimethylimino)-1,3-dithiolium cation or a 1,3-dithiol-2-one. The full details of reaction 1 were published[23i] while the present work was in progress.

We have sought a direct and reasonably general method for preparing bis(dithiolene)$Mo^{IV}O$ complexes. The procedure, summarized in Figure 3, is based on $[Mo^{IV}OCl(MeNC)_4]^+$, which is easily and economically prepared by the reaction of $MoCl_5$ and methylisonitrile in methanol and isolated as the PF_6^- salt.[32a] Halide salts are separated by filtration, and excess isonitrile is readily removed in vacuo. Purified yields in our hands are typically 55%. The method was tested by using ligands with different substituent effects and steric properties. Complexes **1**, **2**, and **4**−**7** are obtained in purified yields of ≳40%; among these is the mixed ligand species **5**. Detailed procedures for **6** and **7** are not given because crystalline salts could not be obtained. Complex **7** was prepared by the method for **2**. In the preparation of **6**, bis(trifluoromethyl)-1,2-dithiete[42] was reduced with sodium acenaphthylenide in THF before reaction with $[Mo^{IV}OCl(MeNC)_4]^+$ in acetonitrile. Complexes **6** and **7** were identified by their mass spectra and electrochemical properties (vide infra). Complexes **1** and, particularly, **2** were prepared because the electronic nature of these ligands more closely approaches that of the pterin dithiolene in Moco (Figure 1).

Structures of complexes **2**, **4**, and **5** are set out in Figure 4; metric parameters are presented in Table 4. All species display a uniform square pyramidal stereochemistry observed previously for related compounds.[23dfghi] For this reason, ranges and mean values, rather than individual values, are given for certain parameters. The molybdenum atom is displaced 0.71−0.77 Å above the mean S_4 plane in the direction of the apical oxo ligand. As a result, MoS_2 planes are canted at the dihedral angles θ_d = 129.0−132.5°; chelate rings are essentially or exactly planar. The Mo−S bond distances exhibit no clear ligand dependence. However, the Mo−O distance in **2** is marginally longer (by 0.07 Å) than in **4** and **5**, presumably reflecting the absence of an electron-withdrawing substituent in the former. Values of ν_{MoO} in KBr follow a similar trend: **2** (904, 916 cm^{-1}) ≲ **5** (919 cm^{-1}) < **4** (932 cm^{-1}). The C−C bond distance in **2** (1.332(6) Å) is consistent with a double bond; that is, the ligand functions as an ene-1,2-dithiolate. Distances in **4** and **5** are less precise but favor the same description. Molybdenum(IV) in these complexes has the $4d_{xy}^2$ configuration. These effects are readily interpreted in terms of substituent properties. Increasing the electron-withdrawing capability of the ring substituents enhances π-bonding of oxo with the Mo d_{xz} and d_{yz} orbitals by decreasing dithiolene electron donation to the metal.

Reaction of **2** with iodine in acetonitrile yields **3** in 45% purified yield as the Et_4N^+ salt. The compound displays an intense violet color typical of the chromophores of $Mo^{V}O$ complexes with thiolate ligands.[43] The structure of **3** (Figure 4, Table 4) has the square pyramidal stereochemistry established for $[MoO(bdt)_2]^-$.[23d] The Mo−S bond distances are marginally shorter than in **2**. One ligand is folded along the S1−S2 vector, forming a dihedral angle of 144° with the MoS(1,2) plane. The other chelate ring is essentially planar. The same effect appears in $(Ph_4P)[MoO(bdt)_2]$, where one ring is depicted as nonplanar.[23d] The origin of this effect in these two compounds, the only bis-

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Table 6. Selected Interatomic Distances and Angles for Mo Bis(dithiolene) Isonitrile, Carbene, and Phosphine Complexes

	12	**13**	**15**	**16**	**17**
Distance, Å					
Mo−S1	2.356(1)	2.356(2)	2.358(1)		2.350(2)
Mo−S2	2.349(1)	2.356(1)	2.358(1)	2.359(3)	2.351(2)
Mo−S3		2.358(1)		2.358(3)	2.355(2)
Mo−S4		2.365(1)			2.347(2)
Mo−X1	2.078(4)	2.093(6)	2.093(4)	2.09(1)[a]	2.541(2)[c]
Mo−X2	2.090(4)	2.109(5)		2.12(2)[b]	2.530(2)[c]
Angles, deg					
X1−Mo−X2	80.3(2)	78.9(2)	77.7(2)	77.0(6)	87.35(6)[c]
S1−Mo−S2	81.45(3)	81.91(5)	81.57(3)	80.58(9)	82.03(6)
S3−Mo−S4		82.04(5)			81.87(6)
θ_d[d]	129.1	127.2	132.7	128.4	124.3
Mo···S_4[d]	0.766	0.791	0.715	0.784	0.802

[a] X1 = carbene carbon. [b] X2 = isonitrile carbon. [c] X1 = X2 = phosphorus. [d] Cf. Table 4.

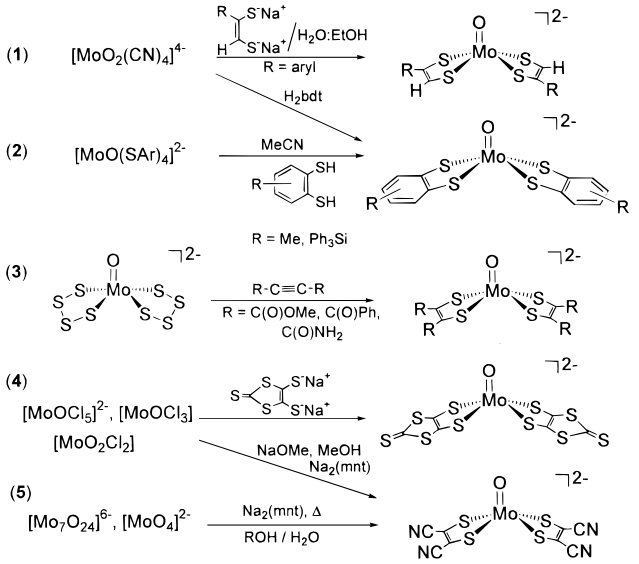

Figure 2. Summary of five reported reactions for the preparation of bis(dithiolene)$Mo^{IV}O$ complexes.

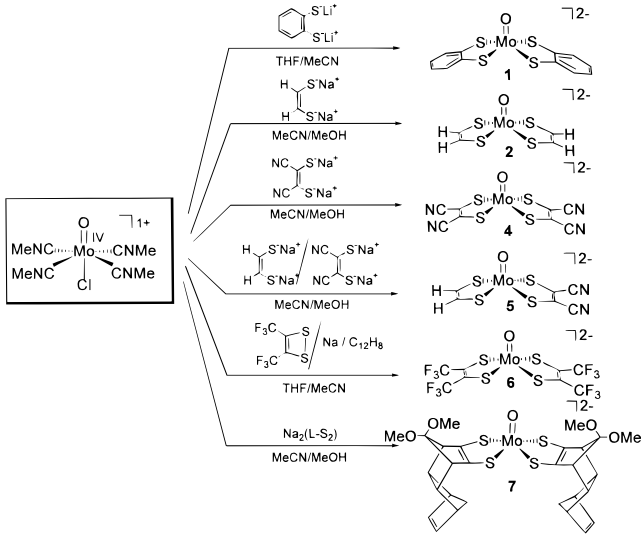

Figure 3. Scheme for the synthesis of bis(dithiolene)$Mo^{IV}O$ complexes **1**, **2**, and **4**−**7** based on the reactivity of $[Mo^{IV}OCl(MeNC)_4]^+$.

(dithiolene)$Mo^{V}O$ complexes for which structural data are available, is obscure. Overall, the structural differences between **2** and **3** are slight, consistent with a difference of one nonbonding electron between the two. Complexes **2** and **3** provide unconstrained structural representations of $Mo^{IV,V}O(S_2$-pd$)_2$ enzyme sites in the limit of tight dithiolene binding.

The $[Mo^{IV}O(S_2C_2R_2)_2]^{2-}$ complexes display a reversible oxidation step to $Mo^{V}O$ species, the potential of which correlates with the properties of the R substitutent. As expected, the most positive value is for mnt complex **4** (+0.48 V) and the most-negative value is for alkyl-substituted $[MoO(L{-}S_2)_2]^{2-}$ (−0.71 V). These and other values are summarized in Table 7, from which it is seen that certain complexes display a $Mo^{V}O/Mo^{VI}O$ couple at much more positive potentials. Voltammograms of two complexes exhibiting the three-member electron-transfer series 1 are presented in Figure 5. Attempts to isolate $Mo^{VI}O$ complexes have failed. The series $[MoO(SR)_4]^{2-,-,0}$ (R = 2,4,6-$Pr^i_3C_6H_2$) has been described, and the Mo(V,VI) members were isolated.[44]

$$[Mo^{IV}O(S_2C_2R_2)_2]^{2-} \leftrightarrow [Mo^{V}O(S_2C_2R_2)_2]^{-} \leftrightarrow [Mo^{VI}O(S_2C_2R_2)_2]^{0} \quad (1)$$

(b) Des-oxo Mo(IV) and Mono-oxo Mo(VI). We have sought analogues of the reduced and oxidized sites of *Rs* DMSO reductase. Noting prior silylation reactions of $Mo^{V}O_2$[45] and $Mo^{VI}O_2$[46] groups, $[MoO_4]^{2-}$,[47] $[Mo_2O_7]^{2-}$,[48] and analogous reactions of oxotungsten dithiolenes,[28] we obtained the desired two types of compounds by the silylation reactions 2−4 depicited in Figure 6. The products (Et_4N)[**8**] (72%) and (Ph_4P)-[**9**] (61%) were isolated in the indicated yields.[49] The product

$$[MoO(bdt)_2]^{2-} + Ph_2Bu^tSiCl \rightarrow [Mo(bdt)_2(OSiBu^tPh_2)]^{-} + Cl^{-} \quad (2)$$

$$[MoO(edt)_2]^{2-} + Ph_2Bu^tSiCl \rightarrow [Mo(edt)_2(OSiBu^tPh_2)]^{-} + Cl^{-} \quad (3)$$

$$[MoO_2(bdt)_2]^{2-} + Ph_2Bu^tSiCl \rightarrow [MoO(bdt)_2(OSiBu^tPh_2)]^{-} + Cl^{-} \quad (4)$$

(44) Soong, S.-L.; Chebolu, V.; Koch, S. A.; O'Sullivan, T.; Millar, M. *Inorg. Chem.* **1986**, *25*, 4067.

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(49) Other silyl chlorides (e.g., Me_2Bu^tSiCl, Ph_3SiCl) may be substituted in reactions 6 and 7; however, the Ph_2Bu^tSiCl gave products more amenable to isolation and crystallization.

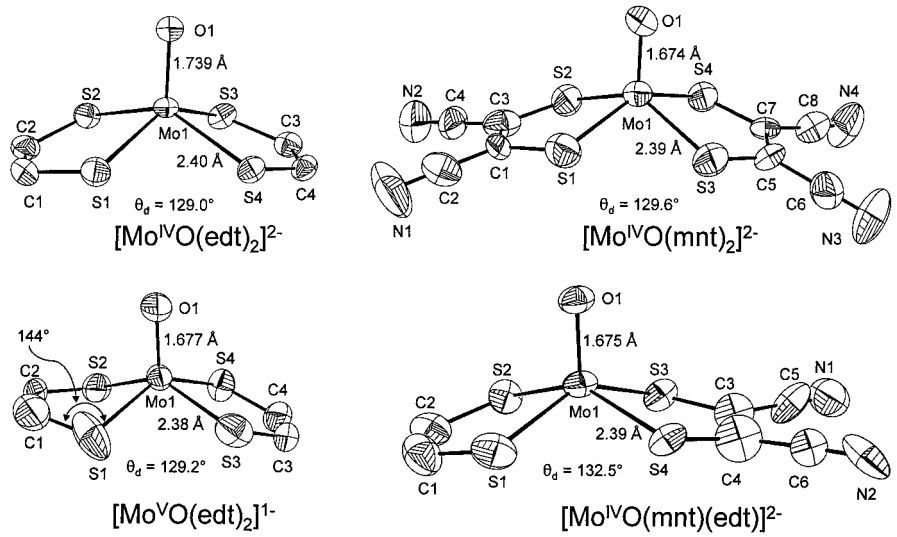

Figure 4. Structures of bis(dithiolene)Mo^{IV,V}O complexes: $[MoO(edt)_2]$,$^{2-,1-}$ $[MoO(mnt)_2]^{2-}$, and $[MoO(edt)(mnt)]^{2-}$. Partial atom labeling schemes and 50% probability ellipsoids are shown. Mo−O and mean Mo−S bond distances and dihedral angles θ_d between MoS_2 coordination planes are indicated.

Table 7. Redox Potentials[a] of $[Mo^{IV}O(S_2C_2R_2)_2]^{2-}$ in Acetonitrile

complex	Mo^V/Mo^{IV}	Mo^{VI}/Mo^V
$[MoO(L-S_2)_2]^{2-}$	−0.71	+0.04
$[MoO(edt)_2]^{2-}$	−0.61	*b*
$[MoO(Me_4bdt)_2]^{2-}$	−0.53	−0.16[c]
$[MoO(sdt)_2]^{2-}$ [d,e]	−0.48	
$[MoO(bdt)_2]^{2-}$	−0.39	+0.56[f]
$[MoO(4\text{-pedt})_2]^{2-}$ [d,g]	−0.35	
$[MoO(S_2C_2(CO_2Me)_2)_2]^{2-}$	−0.09	*b*
$[MoO(edt)(mnt)]^{2-}$	−0.08	+0.54
$[MoO(dmit)_2]^{2-}$ [h]	+0.12	+0.52[c]
$[MoO(tfd)_2]^{2-}$	+0.18	+0.64[c]
$[MoO(mnt)_2]^{2-}$	+0.48	*b*

[a] Cyclic voltammetry (100 mV/s), V vs SCE. [b] Irreversible. [c] Quasireversible. [d] Ref 23i. [e] sdt = $^-$SCH═C(Ph)S$^-$. [f] Measured by differential pulse voltammetry. [g] 4-pedt = $^-$SCH═C(4-pyridyl)S$^-$. [h] dmit = 1,3-dithiole-2-thione-4,5-dithiolate(2−), ref 23f.

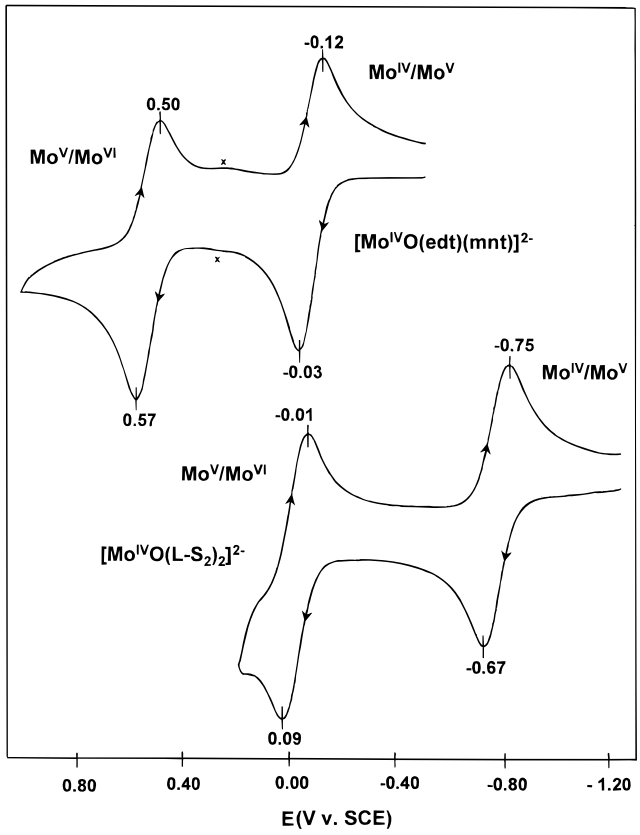

Figure 5. Cyclic voltammograms (100 mV/s) of $[MoO(edt)(mnt)]^{2-}$ and $[MoO(L-S_2)_2]^{2-}$ in acetonitrile solutions illustrating electron-transfer series 1; peak potentials vs SCE are indicated.

of reaction 4,[50] (Et_4N)[**11**], was obtained as a black solid (44%) that is extremely sensitive to traces of water. Even under conditions intended to be rigorously dry, partial decomposition to **8** and the silanol in acetonitrile solution was observed within 2 days. When conditions were not rigorously dry, as in attempted recrystallization from acetonitrile/ether, decomposition of **11** to **1**, $[MoO(bdt)_2]^-$,[51] and silanol occurred over several days. Initial identification of **11** was obtained by the near identity of its ^{1}H NMR spectrum to that of structurally characterized $[WO(bdt)_2(OSiBu^tPh_2)]^-$.[27,28]

The X-ray structures of **8** and **9** in Figure 7 immediately reveal that these are the desired des-oxo Mo(IV) complexes. The two molecules are isostructural; selected bond distances and angles are summarized in Table 5. The complexes exhibit square pyramidal stereochemistry with molybdenum atom displacements from S_4 planes toward the axial silyloxide ligand of ∼0.75 Å and dihedral angles θ_d very similar to the values for bis(dithiolene)Mo^{IV}O complexes. Chelate rings closely approach planarity. There are no significant differences in bond lengths of the same type in the two structures. The Mo−O bonds are 0.10−0.17 Å longer than those in **2**, **4**, and **5**, reflecting the decrease in Mo−O bond order upon silylation. Complexes **8** and **9** are isostructural and nearly isometric with $[W(bdt)_2(OSiBu^tPh_2)]$.[28] Under anaerobic conditions, they are stable indefinitely as solids and for at least 3 days in acetonitrile solution.

The structure of complex **11** is presented in Figure 8; selected dimensional data are included in Table 5. These results confirm the mono-oxo formulation and show the isostructural relation-

(50) An alternative reaction, of **8** and Me_3NO in acetonitrile, proved sluggish and gave a mixture of products (including **11**). In contrast, the reaction of $[W(bdt)_2(OSiBu^tPh_2)]^-$ and Me_3NO proceeded cleanly to afford the W^{VI}O product in 76% yield.

(51) The compound $(Et_4N)[MoO(bdt)_2]$ was isolated, recrystallized from the solvent mixture MeCN/THF/Bu^{t}OMe, and identified by an X-ray structure determination: $P2_1/n$, a = 7.78(2) Å, b = 16.56(3) Å, c = 27.16(4) Å, β = 94.0(1)°, and V = 3489(1) Å^3 (213 K). The anion has been previously characterized structurally as the Ph_4P^+ salt.[23d]

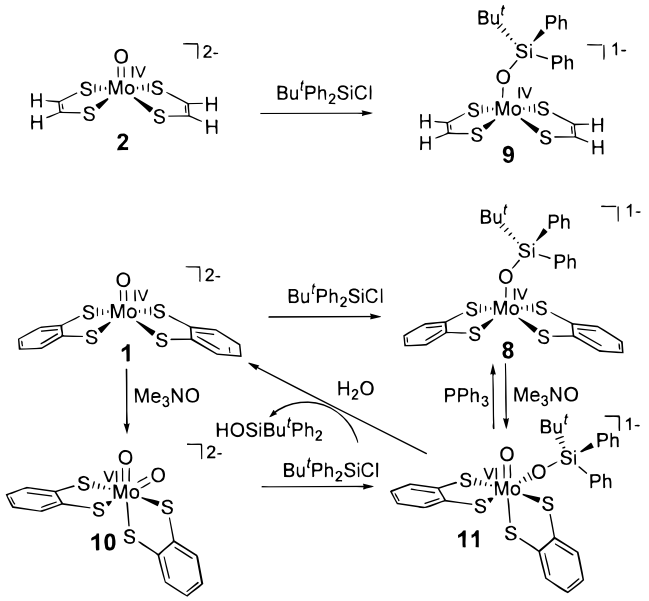

Figure 6. Silylation and oxo-transfer reactions of bis(dithiolene)Mo(IV,VI) complexes in acetonitrile. Note that the oxo-transfer conversions **8** ⇄ **11**, while adequately documented, do not proceed rapidly (Me_3NO) or occur without byproduct formation (PR_3) (see text). The conversion **1** → **10** was first demonstrated by others.[14b]

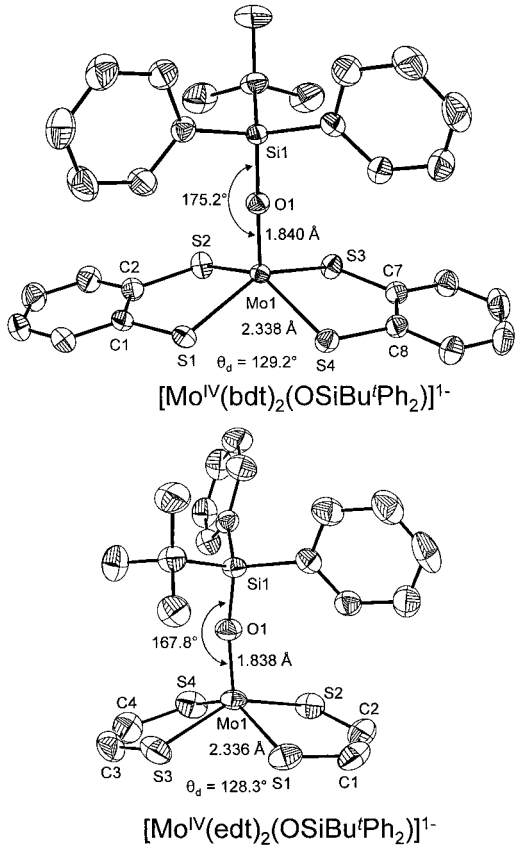

Figure 7. Structures of [Mo(bdt)$_2$(OSiBu^{t}Ph$_2$)]$^-$ (upper) and [Mo(edt)$_2$(OSiBu^{t}Ph$_2$)]$^-$ (lower), showing partial atom-labeling schemes, 50% probability ellipsoids, mean Mo−S bond distances, and dihedral angles θ_d between MoS_2 coordination planes. Also indicated are Mo−O bond lengths and Mo−O−Si bond angles.

ship to [WO(bdt)$_2$(OSiBu^{t}Ph$_2$)]$^-$,[27,28] which is significantly more stable and is readily crystallized.[28] The coordination unit of **11** is irregularly distorted from octahedral, with a normal Mo−O distance (1.715(2) Å), the silyloxide ligand cis to the oxo ligand,

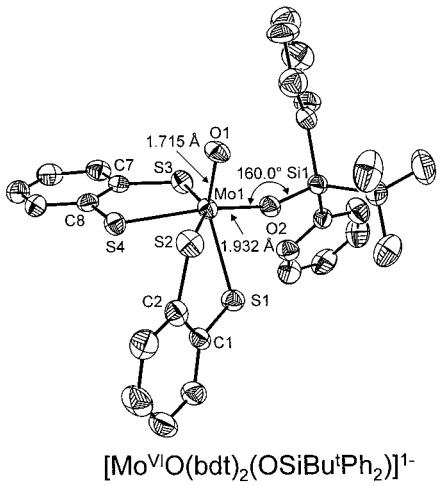

Figure 8. Structure of [MoO(bdt)$_2$(OSiBu^{t}Ph$_2$)]$^-$, showing a partial atom-labeling scheme, 50% probability ellipsoids, and selected bond angles and distances.

and an oxo trans effect on the Mo−S1 bond length of ∼0.05 Å. Other structural features are the same as have been described for the tungsten analogue.[28] Mono-oxo tungsten(VI) complexes are frequently encountered but molecules containing the Mo^{VI}O group are rather uncommon. The few structurally proven five- and six-coordinate examples include [MoOX$_4$] (X = F, Cl),[52] [MoO(O$_2$C$_{10}$H$_6$)(sap)],[53] and [MoO(OC(CF$_3$)$_3$)$_4$].[54]

Complex **11** displays a single reversible reduction step at −0.67 V. In addition, electrochemical solutions of **11** also contain the decomposition product [Mo^{V}O(bdt)$_2$]$^-$, detected by reduction at −0.39 V. After a few scans, the characteristic feature of **11** disappears and the observed voltammogram is that of [Mo^{V}O(bdt)$_2$]$^-$ alone. Thus, **11** is notably unstable under conditions that apparently promote reductive cleavage of silyloxide in the presence of trace proton impurity.

Absorption spectra of **8**, **11**, and their tungsten analogues[27,28] are compared in Figure 9. The occurrence of the same number of features with similar intensities and the red-shifted spectra of the molybdenum complexes are entirely consistent with isostructural M^{IV} and M^{VI}O molecules (M = Mo, W). Similarly, the spectrum of **8**, with features at 460 (sh), 570, and 660 nm, appears related to that of dithionite-reduced *Rs* DMSO reductase, which shows a shoulder at 430 nm and a broad band centered at 640 nm.[55] Likewise, the bands of **11** at 565 and 717 nm are nearly coincident with the maxima at 550 and 720 nm in the oxidized enzyme.[55] We conclude that **8** and **11** are electronically related to, and provide unconstrained structural representations of, the [Mo^{IV}(S$_2$pd)$_2$(O·Ser)] and [Mo^{VI}O(S$_2$pd)$_2$(O·Ser)] sites of *Rs* DMSO reductase. This statement applies in the limit of tight dithiolene chelation, with Mo−S bond lengths of 2.33−2.34 Å in **8**/**9**, and 2.41−2.49 Å in **11**. It is apparently more appropriate to the enzyme preparations examined by EXAFS[18] and resonance Raman spectroscopy[20] than to the crystalline forms used in protein crystallography.[5] In the latter, one dithiolene moiety is not coordinated in the reduced form, and

(52) (a) Edwards, A. J.; Steventon, B. R.; *J. Chem. Soc.* (A) **1968**, 2503. (b) Taylor, J. C.; Waugh, A. B. *J. Chem. Soc., Dalton Trans.* **1980**, 2006. (c) Nielson, A. J. *Inorg. Synth.* **1985**, *23*, 195.

(53) Mondal, J. U.; Schultz, F. A.; Brennan, T. D.; Scheidt, W. R. *Inorg. Chem.* **1988**, *27*, 3950. sap = tridentate Schiff base. A related Mo^{VI}O structure is also described.

(54) Johnson, D. A.; Taylor, J. C.; Waugh, A. B. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1271.

(55) (a) Gruber, S.; Kilpatrick, L.; Bastian, N. R.; Rajagopalan, K. V.; Spiro, T. G. *J. Am. Chem. Soc.* **1990**, *112*, 8179. (b) Bastian, N. R.; Kay, C. J.; Barber, M. J.; Rajagopalan, K. V. *J. Biol. Chem.* **1991**, *266*, 45.

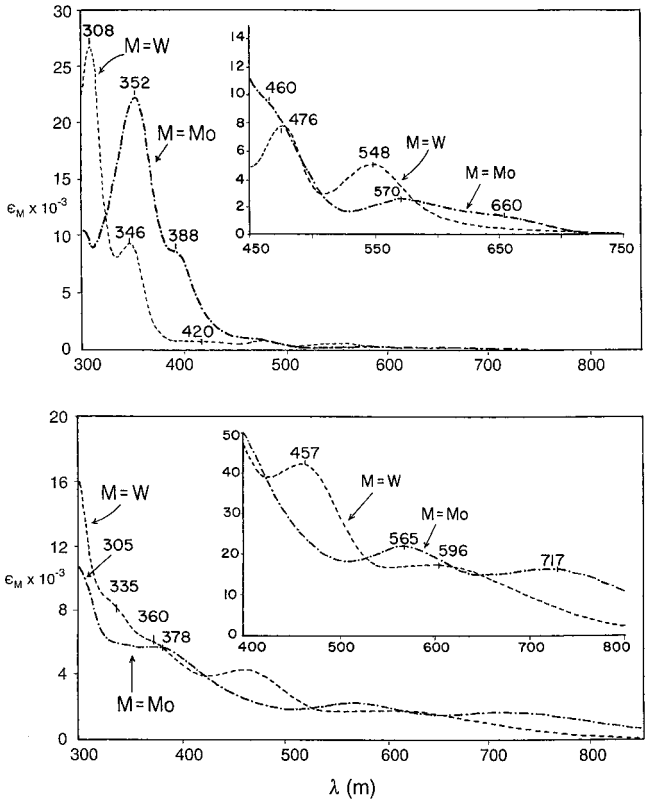

Figure 9. UV/visible spectra of $[M^{IV}(bdt)_2(OSiBu^tPh_2)]^-$ (upper) and $[M^{VI}O(bdt)_2(OSiBu^tPh_2)]^-$ (lower), where M = Mo, W; band maxima are indicated. The upper spectra display five corresponding features and the lower spectra four such features. In the latter, the weak shoulder near ~360 nm (M = W) apparently corresponds to the 378 band (M = Mo).

one dithiolene ligand is asymmetrically coordinated in the oxidized form with Mo−S distances of 2.4 and 3.1 Å.[5] While in the oxidized enzyme the serinate and oxo ligands are cis, the site geometries are otherwise not profitably compared with **8/9** and **11** because of differences in Mo−S coordination. The silyloxide ligand is a simulator of serinate binding.

(c) Isonitrile and Carbene Complexes. In the course of investigating the reactions of Figure 3, small quantities of darkly colored, air-stable byproducts were observed. One of these was isolated and identified as **13** by an X-ray structure determination. Thereafter, a deliberate route to these new compounds was established, and is shown in Figure 10. These reactions were conducted with an 8-fold excess of isonitrile. By this means, complexes **12**−**15** were obtained and shown by absorption spectra to be identical to byproducts in bis(dithiolene)$Mo^{IV}O$ preparations. Because reaction systems lead to more than one product, chromatographic separation was required, leading to modest yields (15−25%). Structures of **12** and **13** are shown in Figure 11 and that of **15** is included in Figure 12. Selected structural data are listed in Table 6. The three complexes are isostructural and present a slightly distorted trigonal prismatic geometry. Given the similarity in molybdenum atom displacements from the S_4 planes (0.72−0.79 Å) and close θ_d values (127.2−132.7°), these species have bis(dithiolene)Mo fragments that approach congruency with those of **1**, **2**, **4**, and **5**. Thus, they represent a conceptual transition from a square pyramid to the C_{2v} form of a trigonal prism. Structurally, the three complexes closely resemble isoelectronic $[W(Se_2C_6H_4)_2(CO)_2]$[56] and $[M(S_2C_2R_2)_2(CO)_2]$ (M = Mo, W)[57] and, like them, pose

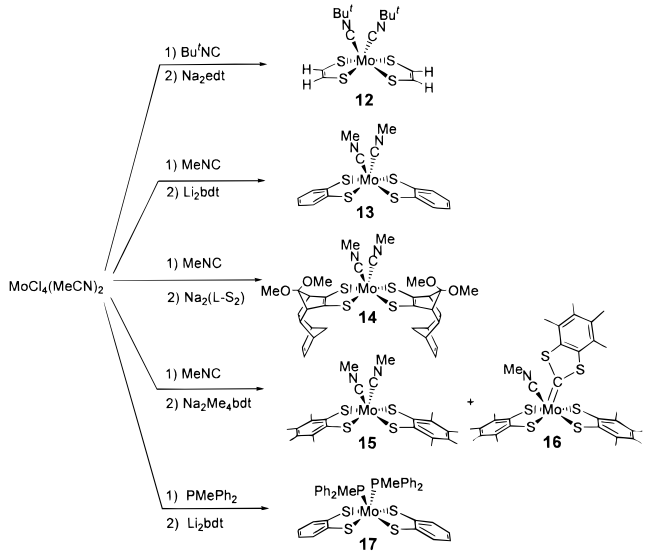

Figure 10. Scheme depicting the synthesis of bis(dithiolene)Mo isonitrile (**12**−**15**), carbene (**16**), and phosphine (**17**) complexes.

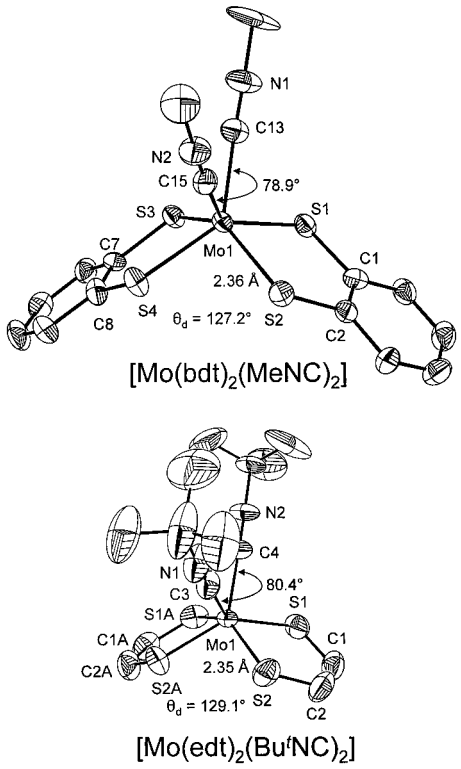

Figure 11. Structures of $[Mo(bdt)_2(MeNC)_2]$ (upper) and $[Mo(edt)_2(Bu^tNC)_2]$ (lower), showing partial atom-labeling schemes, 50% probability ellipsoids, mean Mo−S distances, and dihedral angles θ_d between MoS_2 coordination planes.

the problem of ambiguous oxidation states. The C−C distance of 1.324(5) Å in **12** favors the ene-1,2-dithiolate ligand description and therewith the Mo(IV) oxidation state for the isonitrile complexes.

In the preparation of **15**, an additional product was isolated from chromatography of the reaction system. It was identified by an X-ray structure determination to be the unexpected Fischer carbene complex, **16**. The structure (Figure 12, Table 6), is very closely related to that of **15**, with one isonitrile replaced by the

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(57) (a) Schrauzer, G. N.; Mayweg, V. P.; Heinrich, W. *J. Am. Chem. Soc.* **1966**, *88*, 5174. (b) Kusters, W.; de Mayo, P. *J. Am. Chem. Soc.* **1974**, *96*, 3502. (c) Goddard, C. A.; Holm, R. H., results to be published.

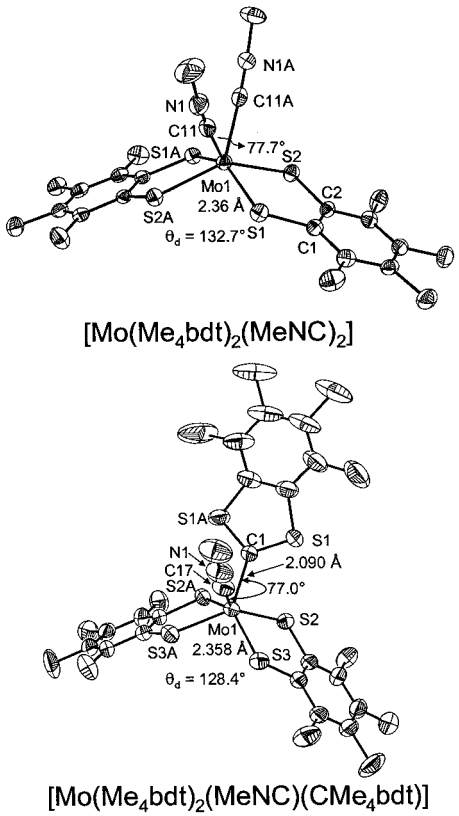

Figure 12. Structures of $[Mo(Me_4bdt)_2(MeNC)_2]$ (upper) and $[Mo(Me_4bdt)_2(MeNC)(CMe_4bdt)]$ (lower), showing partial atom-labeling schemes, 50% probability ellipsoids, mean Mo−S bond lengths, C−Mo−C bond angles, the Mo−C1 bond distance (lower), and dihedral angles θ_d between MoS_2 coordination planes.

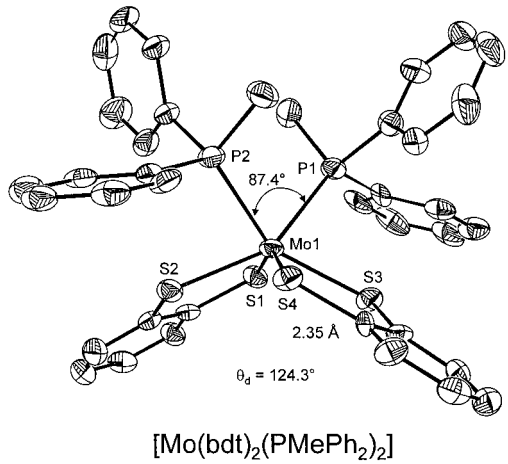

Figure 13. Structure of $[Mo(bdt)_2(PMePh_2)_2]$, showing partial atom-labeling scheme, 50% probability ellipsoids, mean Mo−S distance, and dihedral angle θ_d between MoS_2 coordination planes.

carbene CMe_4bdt. The probable source of the carbenoid carbon is methylisonitrile. The Mo−C1 distance of 2.09(1) Å is consistent with other values for carbene complexes having apparent oxidation states in the Mo(II−IV) range.[58] Analogous carbene complexes are likely to have been formed in the other reactions in Figure 9, inasmuch as chromatography of each system revealed one or more products in addition to **12**−**15**.

Oxygen Atom Transfer Reactivity. Having established complexes **8** and **11** as minimal site representations for reduced and oxidized *Rs* DMSO reductase, we have examined their oxo-transfer propensities in the intended reaction couple Mo^{IV} + XO → $Mo^{VI}O$ + X in acetonitrile solution. Because most reactions are slow, they were conducted at high temperatures. Reactions were monitored by ^1H NMR and by electron ionization and FAB MS. Results are briefly summarized in Figure 6.

(a) Mo^{IV} → $Mo^{VI}O$. Although complex **8** can be partially converted to **11** with Me_3NO, the reaction is not clean and complete even in the presence of several equivalents of the oxo donor. This has led to silylation reaction 4 as the method of choice for the synthesis of **11**. When **8** was treated with 5 equiv of $(p\text{-}FC_6H_4)_2SO$ and the system monitored by ^{19}F NMR as in previous work,[59] 20−25% formation of $(p\text{-}FC_6H_4)_2S$ based on **8** was observed after 24 h at 60 °C. However, the putative product **11** was not detected, apparently because of its instability under these conditions. In the system **8**/50 equiv $(CH_2)_4SO$ at 50 °C for 5 h, no appreciable reaction was observed.

(b) $Mo^{VI}O$ → Mo^{IV}. With *Rc* DMSO reductase, a reduced Me_2SO-bound form of the enzyme can be generated by treating the oxidized form of the enzyme with Me_2S, implying a reversible reaction that depends on the ratio $[Me_2SO]/[Me_2S]$.[7b] While this enzyme is of the $Mo^{VI}O_2/Mo^{IV}O$ type, we did examine the behavior of **11** with two sulfides. No reaction was observed in the system **11**/50 equiv $(CH_2)_4S$ at 50 °C for 5 h. Similarly, no reaction was found in a system containing 5 equiv of $(p\text{-}FC_6H_4)_2S$ for 6 h at room temperature and then after 18 h at 50 °C. Substantial decomposition of **11** was evident at the end of this reaction period.

In further attempts to establish reduction of **11** by oxo transfer, the reaction of the complex with tertiary phosphines was examined. The latter are substantially stronger acceptors in the thermodynamic oxo-transfer scale than are sulfides.[60] We wished to examine the kinetics and mechanism and compare the results with the $Mo^{VI}O_2$ → $Mo^{IV}O$ reduction of bis(dithiolene) complexes by similar substrates.[12c,14f] Treatment of **11** with 2 equiv of PPh_3 at 50 °C for 2 h caused substantial formation of **8** and Ph_3PO. However, when the system was examined spectrophotometrically, clean isosbestic points were not observed, indicating the formation of more than one chromophore. Recourse was taken to the more-basic phosphine $PMePh_2$, which proved reactive at ambient temperature. On treatment with **11** and 1 equiv of phosphine, spectral features clearly indicative of the formation of **8** (Figure 9, upper) were observed, but again isosbestic points did not emerge. With excess phosphine up to 100 equiv, the absorption spectrum that developed was not that of desired product **8** but of an unknown chromophore that gave an orange color to the reaction mixture. Given the existence of $[W(bdt)_2(P(OEt)_3)_2]$,[28] we suspected the formation of an analogous complex in the present system. Using the method in Figure 10, we prepared the orange bis(phosphine) complex **17** independently; it had been previously obtained by a different method.[61] This species is isoelectronic with isonitrile complexes **12**−**15**. Consequently, it is isostructural with them, having distorted trigonal prismatic stereochemistry (Figure 13, Table 6). The molybdenum atom is situated 0.80 Å above the S_4 basal plane, leading to a somewhat tighter angle θ_d (124.3°). From these parameters, the structure of **13** most closely approaches

(58) (a) Bailey, N. A.; Chell, P. L.; Manuel, C. P.; Mukhopadhyay, A.; Rogers, D.; Tabbron, H. E.; Winter, M. J. *J. Chem. Soc., Dalton Trans.* **1983**, 2397. (b) Bailey, N. A.; Dunn, D. A.; Foxcroft, C. N.; Harrison, G. R.; Winter, M. J.; Woodward, S. *J. Chem. Soc., Dalton Trans.* **1988**, 1449. (c) Gunnoe, T. B.; White, P. S.; Templeton, J. L. *Organometallics* **1997**, *16*, 370.

(59) Caradonna, J. P.; Reddy, P. R.; Holm, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 2139.

(60) Holm, R. H.; Donahue, J. P. *Polyhedron* **1993**, *12*, 571.

(61) Lazarowych, N. J.; Morris, R. H. *Can. J. Chem.* **1990**, *68*, 558.

that of **17**. Spectral features nearly the same as those of **17** (λ_{max} 361, 421, 510 (sh) nm) were observed in the system **11**/100 equiv $PMePh_2$. Further, the ^{31}P NMR spectrum of the system **11**/20 equiv $PMePh_2$ in acetonitrile contained, in addition to the phosphine resonance at 20.34 ppm, signals at 34.41 (Ph_2MePO) and 43.63 ppm (**17**). The phosphine oxide was also detected by mass spectrometry. We conclude that **17** is the principal reaction product; other reaction products, if any, were not identified.

Summary

The following are the principal results and conclusions of this investigation.

1. The complexes $[Mo^{IV}O(S_2C_2R_2)_2]^{2-}$, which are the starting points for the synthesis of active site bis(dithiolene) analogues, are conveniently prepared in 40−70% yields by the reaction of 1,2-ene-dithiolate salts with $[MoOCl(MeNC)_4]^+$. All complexes show a reversible $Mo^VO/Mo^{IV}O$ redox step with potentials that exhibit a standard dependence on ligand substituent R. In addition, several are reversibly oxidized to the $Mo^{VI}O$ state.

2. Silylation of $[MoO(bdt)_2]^{2-}$, $[MoO(edt)_2]^{2-}$, and $[MoO_2(bdt)_2]^{2-}$ affords des-oxo $[Mo^{IV}(bdt)_2(OSiBu^tPh_2)]^-$ (72%) and $[Mo^{IV}(edt)_2(OSiBu^tPh_2)]^-$ (61%) and mono-oxo $[Mo^{VI}O(bdt)_2(OSiBu^tPh_2)]^-$ (44%), respectively, in the indicated yields as Et_4N^+ or Ph_4P^+ salts.

3. The X-ray structures of square pyramidal $[Mo^{IV}(bdt)_2(OSiBu^tPh_2)]^-$ and cis-octahedral $[Mo^{VI}O(bdt)_2(OSiBu^tPh_2)]^-$ reveal them to be minimal unconstrained representations of the active sites of *Rs* DMSO reductase in the fully reduced and oxidized forms in the limit of tight, symmetrical dithiolene chelation. Silyloxide is a simulator of serinate coordination. The relation of these complexes to enzyme sites is further strengthened by similarities in absorption spectra.

4. Oxo-transfer propensities of $[Mo^{IV}(bdt)_2(OSiBu^tPh_2)]^-$ and $[Mo^{VI}O(bdt)_2(OSiBu^tPh_2)]^-$ in the reaction couple $Mo^{IV} + XO \rightleftarrows Mo^{VI}O + X$ proved to be limited even under forcing conditions. Oxidation with XO = Me_3NO was sluggish and incomplete; reactions with XO = sulfoxide proceeded to a limited extent or not at all. No appreciable reaction was observed with X = $(CH_2)_4S$ or $(p\text{-}FC_6H_4)_2S$, whereas with X = PPh_3 and $PMePh_2$, oxo transfer did occur but with formation of at least one product in addition to $[Mo^{IV}(bdt)_2(OSiBu^tPh_2)]^-$. The principal product in the reaction system with a large excess of $PMePh_2$ was established to be $[Mo(bdt)_2(PMePh_2)_2]$.

5. The reaction systems in Figure 3 yielded the byproducts $[Mo(S_2C_2R_2)_2(MeNC)_2]$, which have been identified by independent synthesis. In one such synthesis, the carbene complex $[Mo(Me_4bdt)_2(MeNC)(CMe_4bdt)]$ was also isolated. These molecules and $[Mo(bdt)_2(PMePh_2)_2]$ form a coherent set whose members are isoelectronic and isostructural, possessing idealized trigonal prismatic C_{2v} stereochemistry. The chelate C−C bond length in $[Mo(edt)_2(Bu^tNC)_2]$ indicates ene−dithiolate ligation and implies the Mo(IV) oxidation state for this set of complexes. A prominent feature of all molecules (except octahedral $[Mo^{VI}O(bdt)_2(OSiBu^tPh_2)]^-$) is the narrow range for the dihedral angle (124.3−132.7°) between MoS_2 coordination planes. This feature emphasizes the trigonal prismatic stereochemical parentage of both five- and six-coordinate bis(dithiolene) molecules.

6. Of the eight molybdenum compound types in Chart 1, all except the carbene compound have been prepared by us and others[62] in a parallel development of bis(dithiolene)tungsten chemistry.[27,28] Certain property comparisons emerge: (a) complexes of the same type are isostructural and isometric, including the site analogues $[M^{IV}(bdt)_2(OSiBu^tPh_2)]^-$ and $[M^{VI}O(bdt)_2(OSiBu^tPh_2)]^-$; (b) for a given redox couple involving identical ligands, the potential order is $E_W < E_{Mo}$, a periodic property with no exceptions;[12c] (c) where observed qualitatively, stabilities are comparable except for $[M^{VI}O(bdt)_2(OSiBu^tPh_2)]^-$, where the M = Mo complex is generally less stable, especially in the presence of water and other protic impurities; (d) $[W^{IV}(bdt)_2(OSiBu^tPh_2)]^-$ reacts rapidly and completely with certain oxo donors (Me_3NO, Ph_2SeO) but slowly and incompletely with sulfoxides, in contrast to the sluggish reactions, or no reaction, of $[Mo^{IV}(bdt)_2(OSiBu^tPh_2)]^-$. Properties (c) and (d) derive from the greater oxophilicity of tungsten and the attendant relative stabilities of molybdenum- and tungsten-oxo bonds.[63]

Given the generally rapid and complete reaction of Mo(IV) complexes—especially those coordinated in part with thiolate ligands—to reduce sulfoxides to sulfides,[11a−c,12,13a] the lethargic reaction or lack of reaction of **8** with sulfoxides was not anticipated. Further, because this complex appears to be a structurally reasonable site analogue and because resonance Raman results support symmetrical dithiolene chelation during the catalytic cycle of *Rs* DMSO reductase,[20] reaction of **8** with sulfoxides or of **11** with sulfides may be anticipated. The difficulty may in part reside in the stabilities of these compounds under the forcing conditions usually employed. However, that the reactions are slow or do not proceed suggests that one or both of the complexes intrinsically lack one or more essential elements of reactivity. Elucidation of the factors required for a functional bis(dithiolene) reaction couple $Mo^{VI}O + R_2S \rightleftarrows Mo^{IV} + R_2SO$ should be illuminating. Research addressing this point and other aspects of the reactivity of molybdenum and tungsten bis(dithiolenes) is in progress.

Acknowledgment. This research was supported by NSF grant CHE 95-23830. X-ray diffraction equipment was obtained by NIH grant 1 S10 RR 02247. We thank Dr. R. J. Staples for assistance in crystallography.

Supporting Information Available: Crystallographic data for the 12 compounds in Tables 1−3, including intensity collections, positional and thermal parameters, interatomic distances and angles, and calculated hydrogen atom positions (92 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

JA982914F

(62) (a) Ueyama, N.; Oku, H.; Nakamura, A. *J. Am. Chem. Soc.* **1992**, *114*, 7310. (b) Das, S. K.; Biswas, D.; Maiti, R.; Sarkar, S. *J. Am. Chem. Soc.* **1996**, *118*, 1387.

(63) As one example, in the compounds $[(MeCp)_2M^{IV}O]$, the W=O bond enthalpy is ∼20 kcal/mol larger than the Mo=O value: Luo, L.; Lanza, G.; Fragalà, I. L.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 3111.