1082 *Inorg. Chem.* **2010**, *49*, 1082–1089
DOI: 10.1021/ic902066m

Inorganic Chemistry
Article

Reactions of Monodithiolene Tungsten(VI) Sulfido Complexes with Copper(I) in Relation to the Structure of the Active Site of Carbon Monoxide Dehydrogenase

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Received October 19, 2009

Reactions directed at the synthesis of structural analogues of the active site of molybdenum-containing carbon monoxide dehydrogenase have been investigated utilizing $[WO_2S(bdt)]^{2-}$ (**1**) and $[WOS_2(bdt)]^{2-}$ (**2**) and sterically hindered [Cu(R)L] or $[Cu(SSiR'_3)_2]^-$ as reactants. All successful reactions of **2** afford the binuclear W^{VI}/Cu^I products $[WO(bdt)(\mu_2\text{-}S)_2Cu(L)]^{2-/-}$ with L = carbene (**3**), Ar*S (**4**), Ar* (**7**), $SSiR_3$ (R = Ph (**5**), Pr^i (**6**)). Similarly, $[W(bdt)(OSiPh_3)S_2]^-$ leads to $[W(bdt)(OSiPh_3)(\mu_2\text{-}S)_2Cu(SAr^*)]^-$ (**8**). These complexes, with apical oxo and basal dithiolato and sulfido coordination (excluding **8**), terminal thiolate ligation at Cu^I (**4**−**6**, **8**), and W-(μ_2-S)-Cu bridging, bear a structural resemblance to the enzyme site. Differences include two bridges instead of one and the absence of basal oxo/hydroxo ligation. Complex **8** differs from the others by utilizing apical and basal sulfido ligands in bridge formation. Related reaction systems based on **1** gave **4** in small yield or product mixtures in which the desired monobridged complex $[WO_2(bdt)(\mu_2\text{-}S)Cu(R)]^{2-}$ was not detected. Mass spectrometric analysis of the reaction system with L = carbene suggests that any monobridged species forms may converted to the dibridged form by disproportionation. In these experiments, the use of W^{VI} preserves the structural integrity of Mo^{VI}, whose analogues of **1** and **2** have not been isolated. (Ar* = 2,6-bis(2,4,6-triisopropylphenyl)phenyl, bdt = benzene-1,2-dithiolate(2-)).

Introduction

The single-atom unsupported bridge M−S−M′ between heterometals is an uncommon structural element in synthetic molecules and metalloprotein sites, and has been recognized in only one enzyme type. Carbon monoxide dehydrogenases in aerobic carboxidotrophic bacteria are Mo−Cu−Fe−S enzymes that utilize carbon monoxide as the sole source of carbon and energy and catalyze the reaction $CO + H_2O \rightleftharpoons CO_2 + 2H^+ + 2e^-$. The most thoroughly studied Mo−CODH[1] is that from *O. carboxidovorans*. Crystallographic results at 1.1 Å resolution for the oxidized form of the enzyme disclose the active site structure in Figure 1.[2] Here the Mo^{VI} atom is coordinated in an approximate square pyramidal configuration with axial oxo and basal dithiolene, hydroxo, and sulfido ligation. A nearly linear Mo−S−Cu bridge is evident, terminated by cysteinate binding to two-coordinate Cu^I. Crystallographic bond lengths are in good agreement with EXAFS results.[3] These enzymes are to be distinguished from Ni−Fe−S CODHs of anaerobic organisms whose catalytic site consists of a $NiFe_3S_4$ cuboidal cluster to which is linked an exo Fe^{II} atom.[4−6] The latter is bound to the cluster by one μ_3-S atom which, however, is part of a Fe−S−Fe−S−Ni bond sequence with four bonds intervening between the nickel and external iron atom.

Mo−CODH is classified in the xanthine oxidoreductase family,[7,8] all members of which manifest one pyranopterindithiolene, two oxo/hydroxo, and one sulfido ligand(s), with the latter in the equatorial plane of an idealized square pyramid. The structures and dimensions of quinoline 2-oxidoreductase[9] and bovine xanthine oxidoreductase[10] and its reaction intermediates with substrates,[11,12] among other information, substantiate this arrangement. Mo−CODH is a derivative of this structure motif, the essential features of which have been reproduced in the structural analogue $[WO_2S(bdt)]^{2-}$.[13,14]

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(1) Abbreviations are given in Chart 1.

(2) Dobbek, H.; Gremer, L.; Kiefersauer, R.; Huber, R.; Meyer, O. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 15971–15976.

(3) Gnida, M.; Ferner, R.; Gremer, L.; Meyer, O.; Meyer-Klaucke, W. *Biochemistry* **2003**, *42*, 222–230.

(4) Jeoung, J.-H.; Dobbek, H. *Science* **2007**, *318*, 1461–1464.

(5) Gong, W.; Hao, B.; Wei, Z.; Ferguson, D. J.; Tallant, T.; Krzycki, J. A.; Chan, M. K. *Proc. Natl.Acad. Sci. U.S.A.* **2008**, *105*, 9558–9563.

(6) Kung, Y.; Doukov, T. I.; Seravalli, J.; Ragsdale, S. W.; Drennan, C. L. *Biochemistry* **2009**, *48*, 7432–7440.

(7) Hille, R. *Chem. Rev.* **1996**, *96*, 2757–2816.

(8) Romão, M. J. *Dalton Trans.* **2009**, 4053–4068.

(9) Bonin, I.; Martins, B. M.; Purvanov, V.; Fetzner, S.; Huber, R.; Dobbek, H. *Structure* **2004**, *12*, 1425–1435.

(10) Doonan, C. J.; Stockert, A.; Hille, R.; George, G. N. *J. Am. Chem. Soc.* **2005**, *127*, 4518–4522.

(11) Pauff, J. M.; Zhang, J.; Bell, C. E.; Hille, R. *J. Biol. Chem.* **2008**, *283*, 4818–4824.

(12) Pauff, J. M.; Cao, H.; Hille, R. *J. Biol. Chem.* **2009**, *284*, 8760–8767.

(13) Wang, J.-J.; Groysman, S.; Lee, S. C.; Holm, R. H. *J. Am. Chem. Soc.* **2007**, *129*, 7512–7513.

(14) Groysman, S.; Wang, J.-J.; Tagore, R.; Lee, S. C.; Holm, R. H. *J. Am. Chem. Soc.* **2008**, *130*, 12794–12807.

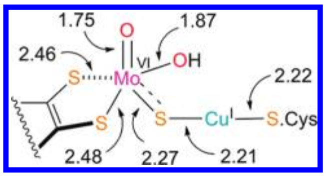


Figure 1. Structure of the oxidized active site of *O. carboxidovorans* carbon monoxide dehydrogenase with bond distances (A); the ene-1,2-dithiolate fragment represents the pyranopterindithiolene ligand found in all mononuclear enzyme sites containing molybdenum and tungsten.

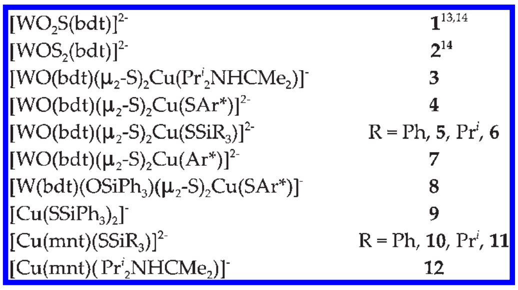
This complex is a member of the series $[WO_{3-n}S_n(bdt)]^{2-}$ (n = 0−2) prepared in this laboratory.[14,15] While $Mo^{VI}(O)-S-Cu^I$ fragments are known, they are often derived from $[MoOS_3]^{2-}$ with consequent tetrahedral Mo^{VI} geometry and nuclearities higher than two (e.g., $[MoOS_3(CuCl_3)_3]^{2-}$[16]). In metallobiomolecules, the $Mo^{VI-IV}-S-Cu^I$ connectivity is unique to Mo−CODH and provides a synthetic challenge in biomimetic chemistry. Two interesting approaches to this problem have been reported. The six-coordinate complex $[(Tp^{iPr})Mo^VO(OAr)(\mu_2\text{-}S)Cu^I(Me_3tacn)]$ contains the elusive unsupported Mo−S−Cu bridge but without dithiolene coordination to molybdenum and thiolate bound to copper.[17] In $[Mo^{VI}O(bdt)(\mu_2\text{-}S)_2Cu^I(SPh)]^{2-}$,[18] the molybdenum atom is square-pyramidal with an apical oxo ligand, bdt simulates pyranopterindithiolene chelation, and copper carries a thiolate ligand; however, there are two sulfido bridges instead of one.

In this work, we have explored the possibility of stabilizing one or more sulfido bridge interactions in complexes that resemble the CODH catalytic site. The complexes $[WO_{3-n}S_n(bdt)]^{2-}$ (n = 1,2) and sterically encumbered species of the type [Cu(SAr*)L],[19] only recently available, provide one potential entry to the problem. To avoid internal reduction, reactants containing W^{VI} rather than Mo^{VI} are employed without structural compromise inasmuch as isoligated molecules in these two oxidation states are always isostructural and nearly isometric.

Experimental Section

Preparation of Compounds. All operations were carried out under a pure dinitrogen atmosphere using standard Schlenk techniques or an inert atmosphere box. Solvents were passed through an MBraun or Innovative Technology solvent purification system prior to use. All volume reduction steps were performed in vacuo. Compounds were identified from combinations of spectroscopic data, analytical results (selected compounds, H. Kolbe, Mülheim, Germany), and X-ray structure determinations.

Chart 1. Designation of Compounds and Abbreviations[a]



$[WO_2S(bdt)]^{2-}$	$1^{13,14}$
$[WOS_2(bdt)]^{2-}$	2^{14}
$[WO(bdt)(\mu_2\text{-}S)_2Cu(Pr^i_2NHCMe_2)]^-$	**3**
$[WO(bdt)(\mu_2\text{-}S)_2Cu(SAr^*)]^{2-}$	**4**
$[WO(bdt)(\mu_2\text{-}S)_2Cu(SSiR_3)]^{2-}$	R = Ph, **5**, Pr^i, **6**
$[WO(bdt)(\mu_2\text{-}S)_2Cu(Ar^*)]^{2-}$	**7**
$[W(bdt)(OSiPh_3)(\mu_2\text{-}S)_2Cu(SAr^*)]^-$	**8**
$[Cu(SSiPh_3)_2]^-$	**9**
$[Cu(mnt)(SSiR_3)]^{2-}$	R = Ph, **10**, Pr^i, **11**
$[Cu(mnt)(Pr^i_2NHCMe_2)]^-$	**12**

[a] Ad = adamantyl, Ar* = 2,6-bis(2,4,6-triisopropylphenyl)phenyl, bdt = benzene-1,2- dithiolate(2-), CODH = carbon monoxide dehydrogenase, lut = 2,6-lutidine, mnt = 3 maleonitriledithiolate(2-), Me tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane, $Pr^i_2NHCMe_2$ = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene, tht = tetrahydrothiophene, Tp^{iPr} = hydrotris(3-isopropylpyrazol-1-yl)borate(1-).

$(Et_4N)_2[WO(bdt)(\mu_2\text{-}S)_2Cu(Pr^i_2NHCMe_2)]$. A solution of the carbene $Pr^i_2NHCMe_2$[20] (8.0 mg, 0.044 mmol) in THF (1 mL) was added dropwise to a solution of $[Cu(MeCN)_4](PF_6)$ (17 mg, 0.045 mmol) in acetonitrile (1 mL). This solution was added to a solution of $(Et_4N)_2[WOS_2(bdt)]$ (29 mg, 0.044 mmol) in acetonitrile (1 mL). The reaction mixture was stirred for 20 min, volatiles were removed, and the residue was dissolved in a mixture of tetrahydrofuran (THF, 1 mL) and acetonitrile (0.3 mL). Vapor diffusion of ether caused separation of the product as red-orange crystals (31 mg, 91%). Absorption spectrum (acetonitrile): λ_{max} (ε_M) 285 (sh, 15200), 315 (9500), 462 (1500) nm. ES-MS$^-$: m/z 404.9 {$[WOS_2(bdt)H]^-$}, 466.8 {$[WO(bdt)S_2Cu]^-$}, 647.0 {$[(WO(bdt)S_2Cu(Pr^i_2NHCMe_2)]^-$}. ^{1}H NMR ($CD_3CN$, anion): δ 1.46 (d, 12), 2.22 (s, 6), 4.52 (sept, 2), 6.82 (m, 2), 7.39 (m, 2). *Anal.* Calcd for $C_{25}H_{45}CuN_3OS_4W$: C, 38.53; H, 5.82; N, 5.39; S, 16.46. Found: C, 38.61; H, 5.92; N, 5.11; S, 15.90.

$(Et_4N)_2[WO(bdt)(\mu_2\text{-}S)_2Cu(SAr^*)]$. A solution of $[Cu(SAr^*)(2,6\text{-}lut)]$[19] (34 mg, 0.049 mmol) in THF (2 mL) was added dropwise to a bright red stirred solution of $(Et_4N)_2[WOS_2(bdt)]$[14] (32 mg, 0.048 mmol) in THF (2 mL). The dark red-brown reaction mixture was stirred for 20 min, and volatiles were removed. The solid residue was recrystallized from THF/ether to give the product as a dark red-brown solid (20 mg, 50%). Absorption spectrum (acetonitrile): λ_{max} (ε_M) 303 (18200), 378 (8200), 488 (1100) nm. ES-MS$^-$: m/z 404.2 {$[WOS_2(bdt)]^-$}, 466.8 {{$WOS_2(bdt)Cu]^-$}, 513.8 {$[Ar^*S]^-$}. ^{1}H NMR (CD_3CN, anion): δ 0.99 (d, 12), 1.18 (d, 12), 1.28 (d, 12), 2.90 (sept, 6), 6.75 (m, 2), 6.84 (d, 2), 6.96 (t, 1), 7.08 (s, 4), 7.30 (m, 2).

$(Et_4N)_2[WO(bdt)(\mu_2\text{-}S)_2Cu(SSiPh_3)]$. A solution of $(Et_4N)[Cu(SSiPh_3)_2]$ (39 mg, 0.050 mmol) in acetonitrile (10 mL) was added dropwise to a solution of $(Et_4N)[WO_2(bdt)(OSiMe_3)]$[21] (29 mg, 0.050 mmol) in acetonitrile (2 mL). The solution was stirred for 12 h. Solvent was removed from the reddish-pink solution, and the residue was washed with THF and ether. The pink solid was dissolved in a minimum volume of acetonitrile, the solution was maintained at −30 °C, and ether was diffused in overnight to afford the product as thin needle-shaped pink crystals (16 mg, 31%). Alternatively, 2 equiv of $(Et_4N)[Cu(SSiPh_3)_2]$ resulted in a 60% yield after a reaction time of 2 h. Absorption spectrum (acetonitrile): λ_{max} (ε_M) 244 (16,500), 300 (6760), 318 (sh), 5800), 508 (540) nm. IR (KBr): ν_{WO} 917 cm^{-1}. ESMS: m/z 379.7 ({$WO(bdt)S_2Cu(SSiPh_3)]^{2-}$), 890.0 ({$(Et_4N)[WO(bdt)S_2Cu(SSiPh_3)]$}$^-$). ^{1}H NMR ($CD_3CN$, anion): δ 6.71 (dd, 2), 7.23 (m, 9), 7.27 (dd, 2), 7.72 (m, 6). *Anal.* Calcd for $C_{42}H_{62}CuN_3OS_5SiW$: C, 47.11; H, 5.83; N, 2.75. Found: C, 45.98; H, 5.46; N, 2.69.

$(Et_4N)_2[WO(bdt)(\mu_2\text{-}S)_2Cu(SSiPr^i_3)]$. A solution of $[Cu(MeCN)_4](PF_6)$ (26 mg, 0.070 mmol) in acetonitrile (2 mL) was added dropwise to a solution of $(Et_4N)(SSiPr^i_3)$ (45 mg, 0.14 mmol) in an equal volume of acetonitrile. The colorless solution was stirred for 10 min and added to a solution of $(Et_4N)[WO_2(bdt)(OSiMe_3)]$ (40 mg, 0.070 mmol) in acetonitrile (2 mL). The reaction mixture was stirred for 12 h, solvent was removed, and the residue was thoroughly washed with THF and

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(15) Partyka, D. V.; Holm, R. H. *Inorg. Chem.* **2004**, *43*, 8609–8616.

(16) Clegg, W.; Garner, C. D.; Nicholson, J. R.; Raithby, P. R. *Acta Crystallogr.* **1983**, *C39*, 1007–1009.

(17) Gourlay, C.; Nielsen, D. J.; White, J. M.; Knottenbelt, S. Z.; Kirk, M. L.; Young, C. G. *J. Am. Chem. Soc.* **2006**, *128*, 2164–2165.

(18) Takuma, M.; Ohki, Y.; Tatsumi, K. *Inorg. Chem.* **2005**, *44*, 6034–6043.

(19) Groysman, S.; Holm, R. H. *Inorg. Chem.* **2009**, *48*, 621–627.

(20) Kuhn, N.; Kratz, T. *Synthesis* **1993**, 561562.

(21) Wang, J.-J.; Holm, R. H. *Inorg. Chem.* **2007**, *46*, 11156–11164.

Table 1. Crystallographic Data[a] for W^{VI}-(μ_2S)-Cu^{I} Complexes

complexes	**3**	**4**	**5**	**6**	**8**
formula	$C_{25}H_{44}CuN_3OS_4W$	$C_{58}H_{95}CuN_2O_2S_5W$	$C_{42}H_{62}CuN_3OS_5SiW$	$C_{31}H_{65}CuN_2OS_5SiW$	$C_{70}H_{92}CuNO_{1.50}S_5SiW$
formula weight	778.30	1260.10	1060.73	917.68	1407.23
crystal system	triclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
T, K	193	193	100	100	193
Z	2	4	2	4	4
a, Å	12.061(7)	19.040(2)	9.223(3)	14.551(5)	23.782(6)
b, Å	12.413(7)	15.949(1)	15.324(6)	15.531(5)	18.684(5)
c, Å	12.699(7)	21.698(3)	17.019(6)	17.680(5)	18.789(5)
α, deg	117.797(8)	90.00	97.540(8)	90.00	90.00
β, deg	104.023(9)	107.470(2)	105.259(8)	91.693(5)	104.684(6)
γ, deg	96.789(9)	90.00	101.085(8)	90.00	90.00
V, Å^3	1571.48(1)	6285.0(1)	2234.9(1)	3994(2)	8076(4)
d_{calcd}, g/cm^3	1.645	1.332	1.576	1.526	1.157
μ, mm^{-1}	4.622	2.372	3.344	3.728	1.866
2θ range, deg	3.80−52.0	3.58−50.0	3.36−52.0	2.80−52.44	2.80−50.0
R_1[b] (wR_2[c])	0.0235(0.0575)	0.0616(0.1386)	0.0603(0.1070)	0.0448(0.0914)	0.0653(0.1859)
GOF (F^2)	1.043	1.003	1.041	1.018	1.083

[a] Mo Kα radiation ($\lambda = 0.71073$). [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 Cu(I) complexes and $[Et_4N][SSiPr^i_3]$

complexes	**9**	**10**	**11**	**12**	$[Et_4N][SSiPr^i_3]$
formula	$C_{44}H_{50}CuNS_2Si_2$	$C_{38}H_{55}CuN_4{-}S_3Si$	$C_{29}H_{61}CuN_4{-}S_3Si$	$C_{23}H_{40}CuN_5S_2$	$C_{17}H_{41}NSSi$
formula weight	776.72	755.71	653.63	514.29	319.67
crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1$	$P2_1/c$	$P2_1/n$	$P2_1$
T, K	193	100	100	100	100
Z	1	2	4	4	4
a, Å	9.448(3)	9.024(5)	18.372(4)	9.346(3)	12.840(1)
b, Å	9.582(3)	24.784(5)	15.257(3)	18.693(6)	11.762(1)
c, Å	12.742(4)	9.108(5)	13.661(3)	15.338(5)	14.337(1)
α, deg	94.349(4)	90.00	90.00	90.00	90.00
β, deg	96.600(5)	106.965(5)	106.746(3)	90.982(6)	106.866(2)
γ, deg	117.022(4)	90.00	90.00	90.00	90.00
V, Å^3	1010.0(5)	1948.4(1)	3666.8(1)	2679.2(1)	2072.2(4)
d_{calcd}, g/cm^3	1.277	1.288	1.184	1.275	1.025
μ, mm^{-1}	0.735	0.784	0.822	0.990	0.209
2θ range, deg	3.26−55.78	3.28−59.70	3.54−57.78	3.44−56.64	2.96−52.0
R_1[b] (wR_2[c])	0.0401(0.1098)	0.0509(0.0808)	0.0578(0.1332)	0.0572(0.1531)	0.0421(0.0895)
GOF (F^2)	1.011	1.060	1.029	1.007	1.046

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

ether . The solid was dissolved in a minimal volume of acetonitrile, ether was diffused in, and the mixture was maintained at −30 °C overnight. The product was obtained as thin needle-shaped, reddish-pink crystals (20 mg, 31%). Alternatively, 2 equiv of $[Cu(MeCN)_4](PF_6)$ and 4 equiv of $(Et_4N)(SSiPr^i_3)$ afforded a 60% yield after a reaction time of 2 h. Absorption spectrum (acetonitrile): λ_{max} (ε_M) 242 (11500), 302 (6880), 336 (sh, 5300), 500 (sh, 580) nm. IR (KBr): v_{WO} 923 cm^{-1}. ES-MS: m/z 466.5 $\{[WOS_2(bdt)Cu]^-\}$. ^{1}H NMR (CD_3CN, anion): δ 1.06 (18), 6.74 (dd, 2), 7.30 (dd, 2).

$(Et_4N)_2[WO(bdt)(\mu_2\text{-}S)_2Cu(Ar^*)]$. A solution of $[Cu(Ar^*)(tht)]$[19] (19 mg, 0.030 mmol) in THF (2 mL) was added dropwise to a stirred solution of $(Et_4N)_2[WOS_2(bdt)]$[14] (19 mg, 0.029 mmol). The dark red solution was stirred for 30 min, and volatiles were removed. The solid residue was washed with hexanes, dissolved in a miminal volume of THF, and the solution was filtered. Addition of ether to the filtrate gave the product as a dark red solid (20 mg, 59%). Absorption spectrum (acetonitrile): λ_{max} (ε_M) 297 (11050), 374 (4700), 499 (900) nm. ES-MS: m/z 466.8 $\{[WOS_2(bdt)Cu]^-\}$, 1063.8 $\{[Et_4N(WO(bdt)S_2Cu)_2]^-\}$, 1660.7 $\{((Et_4N)_2[WO(bdt)S_2Cu]_3)^-\}$. ^{1}H NMR ($CD_3CN$, anion): δ 1.01 (d, 12), 1.22 (d, 12), 1.28 (d, 12), 2.90 (sept, 2), 3.26 (sept, 4), 6.67 (m, 2H), 6.69 (d, 2), 6.87 (s, 4), 6.90 (m, 1), 7.25 (m, 2).

$(Et_4N)[W(bdt)(OSiPh_3)(\mu_2\text{-}S)_2Cu(SAr^*)]$. A solution of $[Cu(SAr^*)(2,6\text{-lut})]$ (20 mg, 0.029 mmol) in THF (1 mL) was added dropwise to a red-brown solution of $(Et_4N)[WS_2(bdt)(OSiPh_3)]$.[21] The reaction mixture was stirred for 10 min, and volatiles were removed. The solid residue was recrystallized from THF/ether to give the product as a red-brown solid (20 mg, 58%). ^{1}H NMR (C_6D_6): δ 1.23 (d, 12), 1.26 (d, 12), 1.43 (d, 12), 2.84 (sept, 4), 3.32 (sept, 4), 6.72 (dd, 2), 6.84 (d, 2), 6.98 (t, 1), 7.15 (m, 15), 7.32 (dd, 2), 7.82 (m, 6).ES-MS: m/z 513 $\{[SAr^*]^-\}$.

$(Et_4N)[Cu(SSiPh_3)_2]$. A solution of Ph_3SiSH (23 mg, 0.079 mmol) in THF (0.5 mL) was added to a solution of $(Et_4N)[Cu(S\text{-}1\text{-}Ad)_2]$[22] (21 mg, 0.040 mmol) in acetonitrile 0.5 mL). The reaction mixture was stirred for 40 min and filtered. Vapor diffusion of ether into the mixture resulted in separation of the product as colorless needle-like crystals (16 mg, 52%).ES-MS: m/z 644.7 $\{[Cu(SSiPh_3)_2]^-\}$. ^{1}H NMR (CD_3CN, anion): δ 7.27 (m, 12), 7.31 (m, 6), 7.66 (m, 12).

$(Et_4N)_2[Cu(mnt)(SSiPh_3)]$. A solution of $(Et_4N)(SSiPh_3)$ (21 mg, 0.050 mmol) in acetonitrile (3 mL) was added dropwise to a light yellow solution of $(Et_4N)[Cu(mnt)(PPh_3)]$[23] (30 mg,

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(22) Fujisawa, K.; Imai, S.; Kitajima, N.; Moro-oka, Y. *Inorg. Chem.* **1998**, *37*, 168–169.

(23) Maiti, B. K.; Pal, K.; Sarkar, S. *Eur. J. Inorg. Chem.* **2008**, 2407–2420.

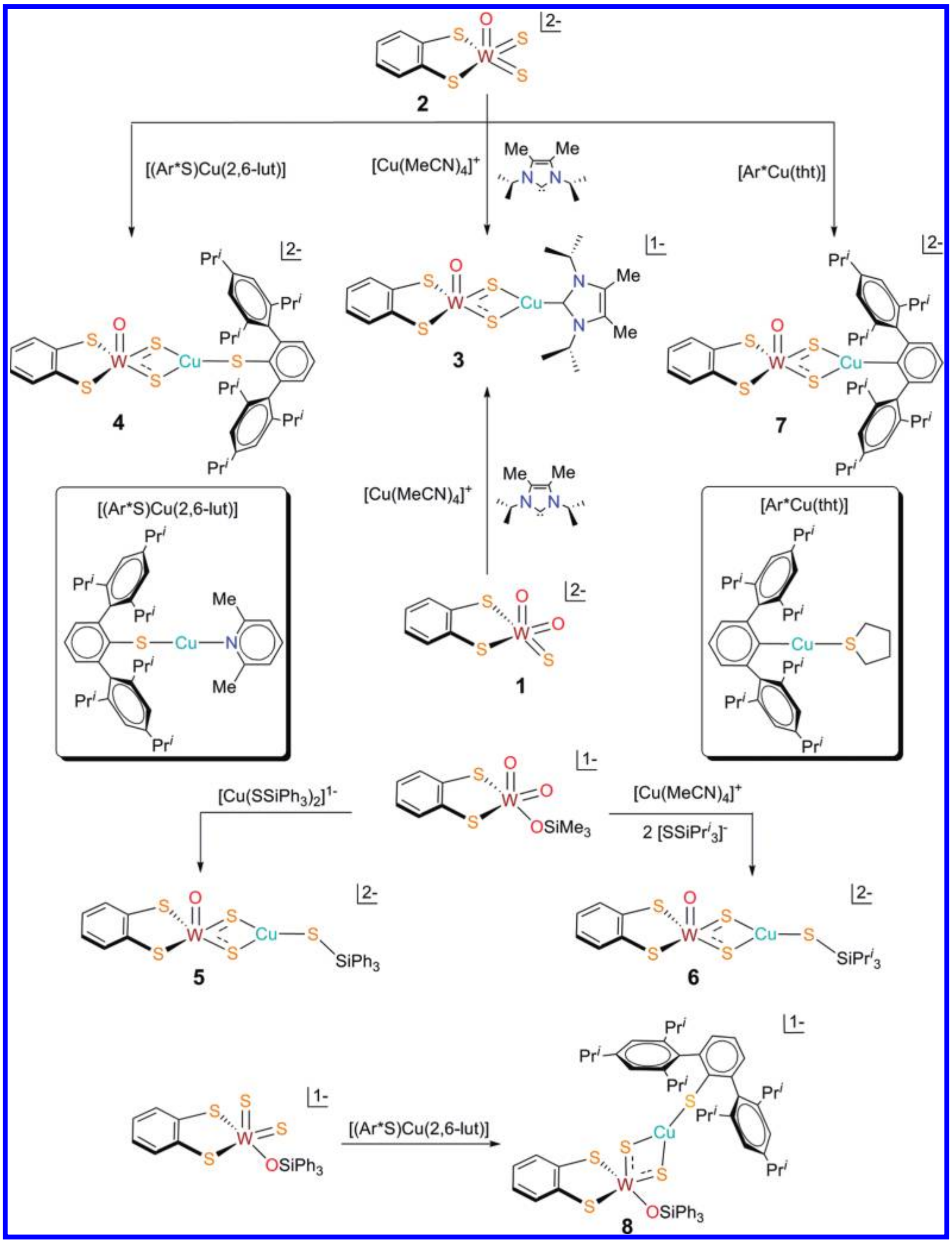

Figure 2. Synthetic scheme affording complexes **2**−**8** containing the core bridge unit $W^{VI}(\mu_2\text{-S})_2Cu^{I}$. Structures of two Cu^{I} reactants are shown in the boxes.

0.050 mmol) in acetonitrile (2 mL). The solution was stirred for 1 h to give a light orange solution. Solvent was removed and the light orange residue was washed with benzene and dried. The solid was dissolved in acetonitrile (1 mL), ether was added by vapor diffusion, and the mixture maintained at −30 °C overnight. The product was isolated as a yellow-orange crystalline solid (29 mg, 77%). Absorption spectrum (acetonitrile): λ_{max} (ε_M) 245 (sh, 3830), 293 (1790), 381 (970), 408 (1170) nm. IR (KBr): ν_{CN} 2178 cm^{-1}. ^1H NMR (CD_3CN, anion): δ 7.21 (m, 3), 7.71 (m, 2). *Anal.* Calcd for $C_{38}H_{55}CuN_4S_3Si$: C, 60.40; H, 7.34; N, 7.41. Found: C, 60.16; H, 7.11; N, 7.39.

$(Et_4N)_2[Cu(mnt)(SSiPr^i_3)]$. The preceding preparation but with use of $(Et_4N)(SSiPr^i_3)$ was followed on the same scale. The product was isolated as a yellow-orange crystalline solid (24 mg, 73%). Absorption spectrum (acetonitrile): λ_{max} (ε_M) 236 (6260), 321 (2560), 386 (sh, 950), 414 (1550) nm. IR (KBr): ν_{CN} 2178 cm^{-1}. ^1H NMR (CD_3CN, anion): δ 1.06 (d).

$(Et_4N)[Cu(mnt)(Pr^i_2NHCMe_2)]$. A solution of $Pr^i_2NHCMe_2$ (18 mg, 0.010 mmol) in THF (2 mL) was added dropwise to a solution of $(Et_4N)[Cu(mnt)(PPh_3)]$ (30 mg, 0.050 mmol) in acetonitrile (2 mL). The reaction mixture was stirred for 1 h to give a yellow-orange solution, solvent was removed, and the light orange residue was washed with benzene and dried. The residue was dissolved in acetonitrile (1 mL), and ether was diffused in at −30 °C overnight. The product was obtained as yellow-orange needles (20 mg, 77%). Absorption spectrum (acetonitrile): λ_{max} (ε_M) 240 (sh, 2360), 296 (2240), 392 (1550) nm. IR (KBr): ν_{CN} 2178 cm^{-1}. ^1H NMR (CD_3CN, anion): δ 1.52 (d, 6), 2.10 (s, 3), 4.52 (sept, 1). *Anal.* Calcd for $C_{23}H_{41}CuN_5$: C, 53.61; H, 8.02; N, 13.59; S, 12.45. Found: C, 53.84; H, 8.01; N, 13.41; S, 12.25.

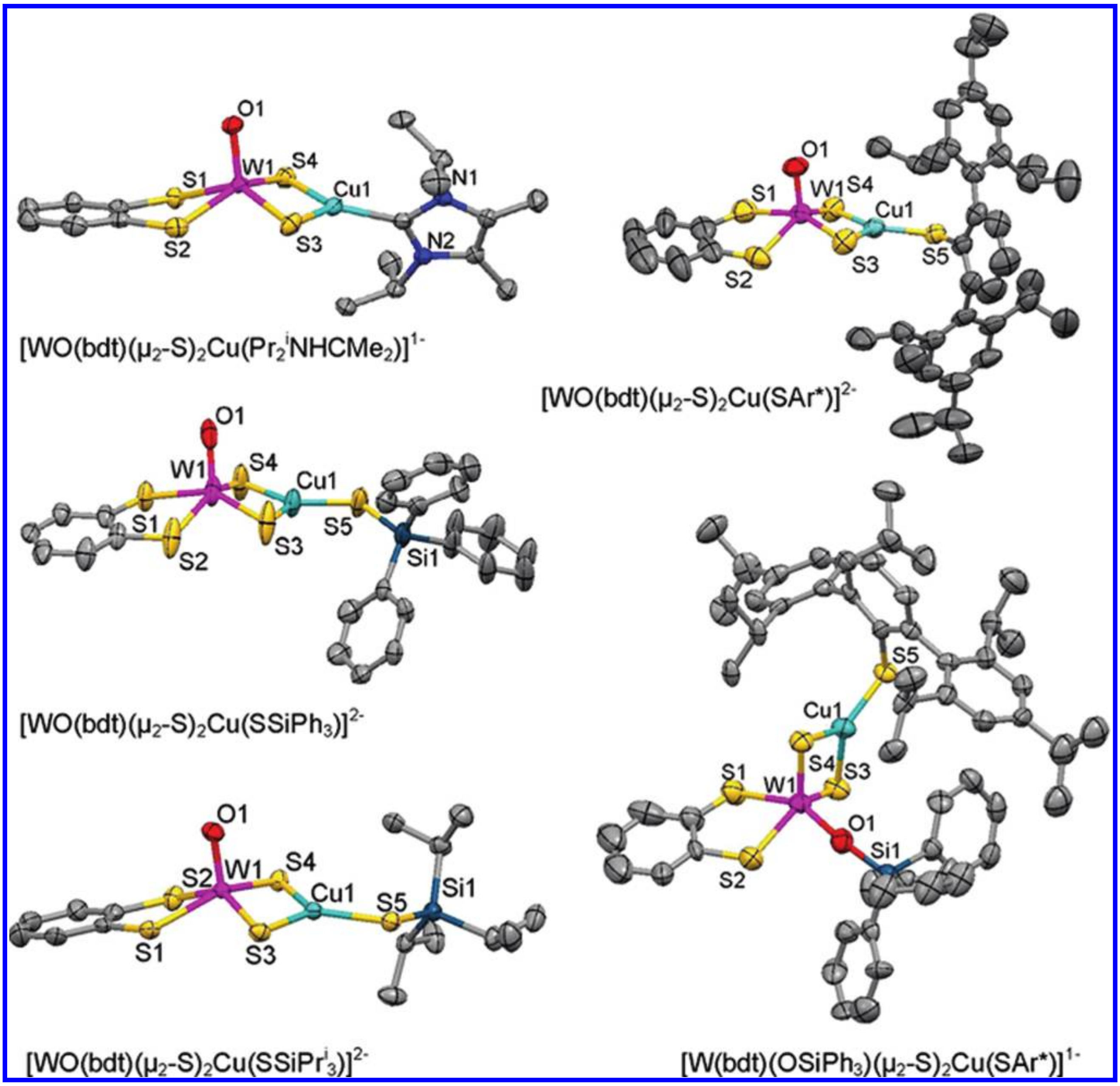

Figure 3. Structures of complexes **3**, **5**, and **6** (left) and **4** and **8** (right) showing 50% probability ellipsoids and partial atom labeling schemes.

$(Et_4N)(SSiPh_3)$. NaOMe (108 mg, 2.00 mmol) was added to a mixture of Ph_3SiSH (585 mg, 2.00 mmol) and Et_4NCl (331 mg, 2.00 mmol) in acetonitrile (30 mL). The mixture was stirred for 12 h and filtered. The filtrate was reduced to obtain a pale yellow solid, which was dissolved in acetonitrile (80 mL) and diluted with ether (100 mL) producing a white solid. This material was dissolved in a minimum volume (~60 mL) of acetonitrile, ether was added by diffusion, and the mixture was maintained at −30 °C for 1 d. The product was obtained as colorless block-shaped crystals (674 mg, 80%). ^{1}H NMR (CD_3CN, anion): δ 7.18 (m, 3), 7.64 (m, 2).

$(Et_4N)(SSiPr^i_3)$. The preceding preparation but with use of Pr^i_3SiSH was followed on the same scale. The product was isolated as colorless crystals (575 mg, 90%). ^{1}H NMR (CD_3CN, anion): δ 0.97 (d).

In the following sections, complexes and reactants are designated according to Chart 1.

X-ray Structure Determinations. The structures of the 10 compounds in Tables 1 and 2 were determined. Diffraction-quality crystals were obtained by ether diffusion into acetonitrile ($(Et_4N)_2$[**5**,**6**], $(Et_4N)_2$[**9**, **10**, **11**], $(Et_4N)(SSiPr^i_3)$), acetonitrile/THF ($((Et_4N)$[**3**, **8**], $(Et_4N)_2$[**4**]) and THF ((Et_4N)[**7**]) solutions. Crystal mounting and data collections were performed as described[24] on a Siemens (Bruker) SMART CCD diffractometer using Mo Kα radiation. Data reductions were performed with SAINT, which corrects for Lorentz polarization and decay. Space groups were assigned by analysis of symmetry, and systematic absences determined by XPREP. Structures were solved by direct methods and refined against all data in the 2θ ranges by full-matrix least-squares on F^2 using SHELXS-97 and SHELXL-97. Hydrogen atoms at idealized positions were included in final refinements. Refinement details and explanations (wherever necessary) are included in the individual CIF files. Oak Ridge Thermal Ellipsoid Plot Program (ORTEP) plots were produced using the Mercury 2.2 program. Crystallographic data and final agreement factors are given in Table 1.[25]

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(24) Groysman, S.; Holm, R. H. *Inorg. Chem.* **2007**, *46*, 4090–4102.

(25) See paragraph at the end of this article for Supporting Information available.

Table 3. Selected Bond Distances (Å) and Angles (degree) for W^{VI}-(μ_2-S)$_2$-Cu^I Complexes

	complexes				
parameters	**3**	**4**	**5**	**6**	**8**
W−S_{bdt}	2.430(8)	2.409(3)	2.395(3)	2.400(1)	2.381(5)
	2.450(8)	2.461(3)	2.437(2)	2.438(2)	2.428(5)
W−S	2.298(8)	2.282(2)	2.248(3)	2.260(1)	2.185(4)
	2.299(8)	2.286(3)	2.282(3)	2.283(1)	2.193(4)
W−O	1.709(2)	1.748(6)	1.765(1)	1.733(4)	1.867(1)
W−Cu	2.618(4)	2.630(1)	2.585(1)	2.594(1)	2.642(2)
δ^a	0.607	0.587	0.579	0.586	
Cu−S	2.196(9)	2.189(3)	2.155(3)	2.170(1)	2.212(4)
	2.200(9)	2.198(3)	2.187(3)	2.191(2)	2.217(5)
Cu−C/S	1.926(3)	2.188(2)	2.169(3)	2.180(2)	2.156(5)
W−S−Cu	71.12(3)	71.87(8)	71.24(1)	71.22(5)	73.72(1)
	71.21(3)	71.95(8)	71.30(1)	71.29(6)	73.76(1)
S−W−S	104.80(3)	104.23(9)	104.58(1)	104.82(6)	106.98(1)
S−Cu−S	111.89(3)	110.55(1)	111.24(1)	111.33(7)	105.20(1)
θ^b	135.13	133.84	135.81	135.52	101.97
fold angle	23.6	20.5	16.74	15.8	14.6
τ^c	0.11	0.29	0.08	0.13	0.14

[a] W perpendicular displacement from [S1S2S3S4] basal plane. [b] Dihedral angle between WS1S2 and WS3S4 planes, τ^c: The shape parameter τ[14] is defined as $(\alpha-\beta)/60$, where α and β are the largest and next largest interligand bond angles, respectively. For idealized SP geometry $\tau = 0$, for idealized TBP geometry $\tau = 1$.

Other Physical Measurements. All measurements were performed under anaerobic conditions. ^{1}H NMR spectra were recorded with Varian Mercury 300/400/500 spectrometers. Absorption spectra were obtained with a Cary 50 Bio spectrophotometer and infrared spectra on a Nicolet 5PC FT-IR instrument. Electrospray mass spectra were measured on acetonitrile solutions directed infused into a LCT mass spectrometer.

Results and Discussion

In this work, we seek monosulfido or disulfido W^{VI}−Cu^I species related to the active site of Mo−CODH (Figure 1) by containing a W−S−Cu bridge, dithiolene coordination simulating that of the native pyranopterindithiolene ligand, and square pyramidal stereochemistry with apical oxo and basal dithiolene and sulfido ligation. The reaction scheme developed is presented in Figure 2. Structures of binuclear product complexes **3**−**6** and **8** are set out in Figure 3 and selected metric parameters are collected in Table 3.

Two synthetic approaches have been explored. In the first, the reactions 1 (n = 1,2) of complexes **1** and **2** with dicoordinate Cu^I have been examined. This approach utilizes

$$[WO_{3-n}S_n(bdt)]^{2-} + [Cu(R)L] \rightarrow [WO_{3-n}(\mu_2\text{-}S)_n(bdt)Cu(R)]^{-/2-} + L \qquad (1)$$

copper complexes with neutral ligands L such as thiourea Ph_3P, 2,6-lut, tht, and the *N*-heterocyclic carbene $Pr^i{}_2NHCMe_2$ as well as the sterically encumbering R ligands ArS* and Ar*[19] intended to minimize coordination at Cu^I. Of the three sulfur-containing potential precursors, only [Cu(SAr*)(2,6-lut)] reacted cleanly with **2**, yielding red-brown binuclear complex **4** (50%) This species, like all other binuclear complexes isolated in this work, approximates square pyramidal stereochemistry and contains two W-(μ_2-S)-Cu bridges in the form of a WS_2Cu rhombic core.

Unlike the successful reaction of disulfido **2** and [Cu(SAr*)(2,6-lut)], multiple attempts to obtain a product from the reaction of this reagent and monosulfido **1** led to complex product mixtures. The only pure product isolated from such mixtures was crystalline $(Et_4N)_2$[**4**] in low yield. The desired product $[WO_2(bdt)(\mu_2\text{-}S)Cu(SAr^*)]^{2-}$ was never detected. Copper(I) binding was investigated further in the reaction between [Cu(SAr*)(2,6-lut)] and $[W(bdt)(OSiPh_3)S_2]^-$,[14] which presents apical and basal sulfido ligands with a somewhat larger S−W−S bond angle of 107.8° than in **2** (102.1°) and with W−S bond lengths 0.07 Å shorter. This reaction afforded **8** (58%), which retains the stereochemistry of the starting complex with a mean W−S bond distance (2.189(6) Å) and S−W−S bond angle 106.98(1)° intermediate between **2** and the starting complex. The small dimensional differences and different orientation of sulfido ligands compared to **2** did not retard formation of the WS_2Cu bridge rhomb. In contrast, the reaction between monosulfido $[W(bdt)(OSiPh_3)OS]^-$ and [Cu(SAr*)(2,6-lut)] did not lead to a tractable product.

Further reactions involved Cu^I complexes with large aryl or carbene ligands instead of thiolate. The premise was that these ligands, upon binding to Cu^I without an intervening sulfur atom, might lead to a different bridging mode and/or stereochemical outcome. [Cu(Ar*)(tht)] reacts cleanly with **2** to yield sterically crowded aryl-ligated complex **7** (59%). Diffraction-quality crystals were not obtained; however, mass spectroscopic data and the ^{1}H NMR spectrum (very similar to **4**) are consistent with the double-bridged formulation. The reaction of **1** with [Cu(Ar*)(tht)] failed to yield an identifiable product.

We initially sought as a reactant the complex $[Cu(Pr^i{}_2NHCMe_2)(MeCN)_x]^+$ having *N*-isopropyl groups proximal to the bound carbon atom (Figure 2). However, the reaction of 1 equiv each of $[Cu(MeCN)_4]^+$ and the carbene proceeded by reaction 2. Formation of the bis(carbene) complex was demonstrated by isolation of its PF_6^- salt and an X-ray structure determination.[26] Increasing the bulk of the carbene with *N*-2,6-$Pr^i{}_2C_6H_3$ substituents did not prevent formation of a bis(carbene) as shown by the cell parameters of the reaction product.[27] However, reaction 3 readily affords in high yield (Et_4N)[**3**] (91%). The reactivity

$$[Cu(MeCN)_4]^+ + 2Pr^i{}_2NHCMe_2 \rightarrow [Cu(Pr^i{}_2NHCMe_2)_2]^+ + 4MeCN \qquad (2)$$

$$[WOS_2(bdt)]^{2-} + [Cu(MeCN)_4]^+ + Pr^i{}_2NHCMe_2 \rightarrow [WO(bdt)(\mu_2\text{-}S)_2Cu(Pr^i{}_2NHCMe_2)]^- + 4MeCN \qquad (3)$$

of monosulfido **1** was then investigated in a system analogous to reaction 3. The outcome was examined by electrospray mass spectrometry, as seen in Figure 4. The spectrum in the higher mass region corresponds exactly to **3** whereas in the lower mass region the spectrum is indicative of the

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(26) $[Cu(Pr^i{}_2NHCMe_2)_2](PF_6)$ crystallizes in orthorhombic space group *Fddd* with a = 14.262(8) Å, b = 18.295 Å, c = 20.59(1) Å, and Z = 8 (R_1 = 0.0679, T = 193 K).

(27) Díez-González, S.; Stevens, E. D.; Scott, N. M.; Petersen, J. L.; Nolan, S. P. *Eur. J. Inorg. Chem.* **2008**, *14*, 158–168.

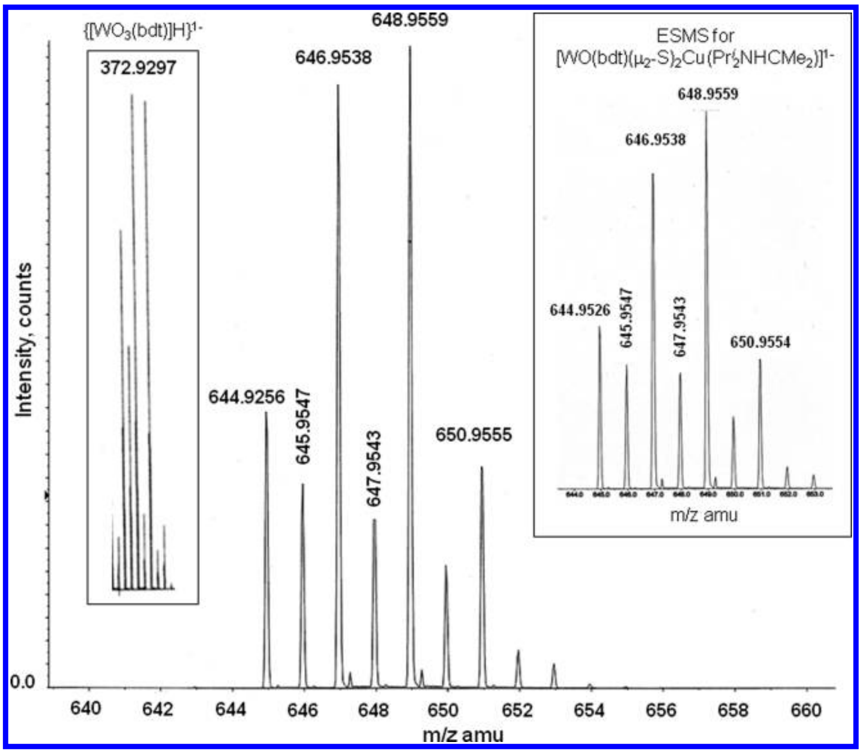

Figure 4. Electrospray mass spectroscopic data for the reaction products of **2** and $[Cu(MeCN)_4]^+/Pr^i_2NHCMe_2$ in acetonitrile/THF. The experimental spectrum in the region m/z 640−660 is shown together with features at lower m/z values centered at 373 corresponding to $[WO_3(bdt)H]^-$ (left box). The spectrum of an authentic sample of **3** (right box) is also presented.

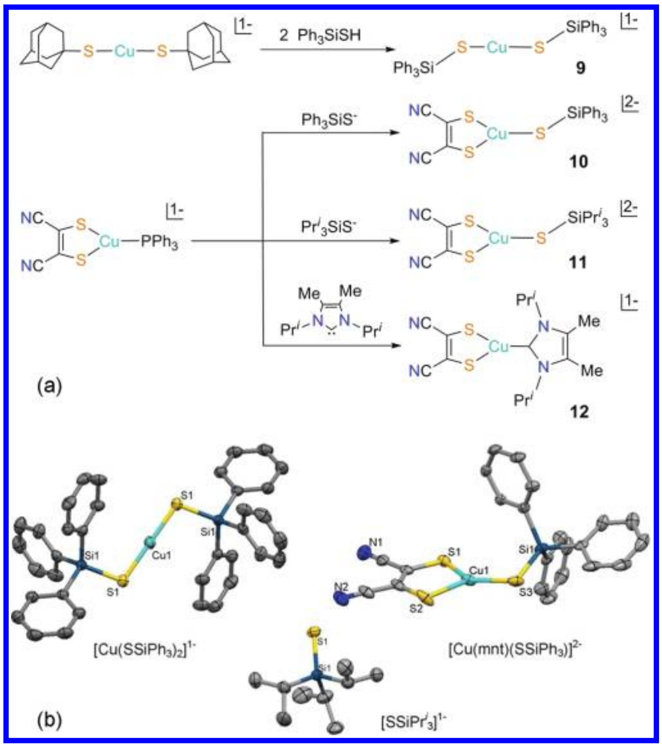

Figure 5. (a) Synthetic scheme leading to Cu^I silylthiolate complexes **9**−**12**, three of which contain dithiolene chelate rings. Note the use of **9** in the formation of **5** (Figure 2). (b) Structures of Cu^I complexes **9** (imposed centrosymmetry) and **12** and $Pr^i_3SiS^-$ (two independent anions) as the Et_4N^+ salt. Selected bond distances (A) and angles (deg): **9**, Cu−S 2.1477(8), Si−S 2.094(1); **12**, Cu−S1 2.259(1), Cu−S2 2.266(1), Cu−C 1.932(23), S1−Cu−S2 94.71(4), S1−Cu−C 132.4(1), S2−Cu−C 132.7(1); $Pr^i_3SiS^-$, Si−S 2.071(8), 2.072(8).

formation of $[WO_3(bdt)H]^-$. Evidently any monosulfido bridged species formed undergoes disproportionation with the tentative stoichiometry of reaction 4, doubtless driven by the stability of the WS_2Cu core unit.

$$\begin{aligned} &2[WO_2(bdt)(\mu_2\text{-}S)Cu(Pr^i{}_2NHCMe_2)]^- \rightarrow \\ &[WO(bdt)(\mu_2\text{-}S)_2Cu(Pr^i{}_2NHCMe_2)]^- \\ &+[WO_3(bdt)]^{2-}+[Cu(Pr^i{}_2NHCMe_2)(solv)_x]^+ \qquad (4) \end{aligned}$$

A second approach utilizes Cu^I silylthiolate reactants and is based on the difference of 25−40 kcal/mol between Si−O and Si−S bond dissociation energies.[28−30] Preparations and structures of possible reactants are contained in Figure 5. That of immediate interest is **9**, isolated from the reaction of Ph_3SiSH and $[Cu(S\text{-}1\text{-}Ad)_2]^-$ (52%). Like the other three examples of mononuclear homoleptic two-coordinate Cu^I thiolates,[22,31,32] complex **9** has linear coordination (Cu−S 2.148(1) Å).

Reaction 5 is readily conceived with the desired monosulfido-bridged complex and a siloxane as products. However, the reaction takes a different course, and the only isolable tungsten−copper product is the disulfido-bridged complex **5** (31%, Figure 3). When the reactant mol ratio is 2:1, the yield of **5** is increased to 60%. Apparently, any monosulfido-bridged product formed is subjected to a further reaction to form doubly bridged **5**. This reaction is described as 6, under which stoichiometry a Cu^I-sulfide species is required. Any such species is likely

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[28] Luo, Y.-R. *Handbook of Bond Dissociation Energies in Organic Compounds*; CRC Press: New York, 2003.

[29] Basch, H. *Inorg. Chim. Acta* **1996**, *252*, 265–279.

[30] Leroy, G.; Temsamani, D. R.; Wilante, C. *J. Mol. Struct.* (*Theochem*) **1994**, *306*, 21–39.

[31] Koch, S. A.; Fikar, R.; Millar, M.; O'Sullivan, T. *Inorg. Chem.* **1984**, *23*, 121–124.

[32] Zeevi, S.; Tshuva, E. Y. *Eur. J. Inorg. Chem.* **2007**, 5369–5376.

to be insoluble in acetonitrile and would be removed in the

$$[\mathrm{WO_2(bdt)(OSiMe_3)}]^- + [\mathrm{Cu(SSiPh_3)_2}]^- \rightarrow [\mathrm{WO_2(bdt)(\mu_2\text{-}S)Cu(SSiPh_3)}]^{2-} + \mathrm{Ph_3SiOSiMe_3} \quad (5)$$

$$[\mathrm{WO_2(bdt)(OSiMe_3)}]^- + 2[\mathrm{Cu(SSiPh_3)_2}]^- \rightarrow [\mathrm{WO(bdt)(\mu_2\text{-}S)_2Cu(SSiPh_3)}]^{2-} + \mathrm{Ph_3SiOSiMe_3} + (\mathrm{Ph_3Si})_2\mathrm{O} + [\mathrm{CuS}]^- \quad (6)$$

workup procedure. A second reaction system with different silyl substituents was also investigated. Because the compound (Et$_4$N)[Cu(SSiPr$^i{}_3$)$_2$] could not be isolated, the reaction was performed with a 1:1 mol ratio of [Cu(MeCN)$_4$](PF$_6$) and (Et$_4$N)(SSiPr$^i{}_3$), which was separately prepared and structurally characterized (Figure 5). The use of 1 and 2 equiv of the silylthiolate afforded doubly bridged **6** in 31% and 60% yields, respectively. Again, no monosulfido bridged species could be identified.

Dithiolate complexes **10**–**12** are prepared by reaction of silylthiolates R$_3$SiS$^-$ or the carbene with [Cu(mnt)(PPh$_3$)]$^-$ (Figure 5). The CuS$_3$ and CuS$_2$C coordination units are planar; Si–S bond distances are increased by about 0.02 Å upon binding. Metric features are unexceptional. The intention was to utilize **10** and **11** in place of **9** in reaction 5, leading to complexes with one W–S–Cu bridge and a CuS$_3$ unit. Unfortunately, the Cu$^{\mathrm{I}}$ silylthiolates are somewhat unstable in solution and did not yield pure products in multiple attempts. Complexes **10**–**12** are initial examples of a three-coordinate Cu$^{\mathrm{I}}$ dithiolate with silylthiolate or carbene ligands, prompting their report here. Of the set, **12** and the parent phosphine complex are stable in anaerobic solution.

Structural Features. Complexes **3**–**6** exhibit the common features of distorted square pyramidal stereochemistry, planar W$^{\mathrm{VI}}$(μ_2-S)$_2$Cu$^{\mathrm{I}}$ bridge rhombs, displacements δ = 0.58–0.61 Å of the tungsten atom above the S$_4$ basal plane, angles θ = 134–136° between coordination planes, τ = 0.08–0.29, and WS$_2$/bdt dihedral or fold angles of 15–24° (Table 3). The latter has been implicated in stabilization of multiple redox states in molybdo- and tungstoenzymes.[33] Reduced metal centers form nearly planar chelate rings (fold angle ~0°) whereas oxidized centers as in the present set of complexes cause folded rings. The effect enables overlap of filled sulfur p-orbitals with the metal in-plane vacant d-orbital. Copper(I) coordination to sulfido bridge ligands removes some electron density such that the fold angles of **3** (23.6°) and **4** (20.5°) are larger than in precursor **2** (13.6°), and in **8** (14.6°) compared to [WS$_2$(bdt)(OSiPh$_3$)]$^-$. Complex **8** differs from the others because the bridge rhomb contains apical and basal sulfur atoms with consequent differences in structure parameters, most notably θ = 102°. The M$^{\mathrm{VI}}$(μ_2-S)$_2$Cu$^{\mathrm{I}}$ bridge rhomb is a ubiquitous structural element in the cluster chemistry of molybdenum and tungsten,[34–36] and is also present in recent dinuclear Mo–Cu complexes relevant to the CODH site.[18] In tungsten chemistry, individual W$^{\mathrm{VI}}$(μ_2-S)$_2$Cu$^{\mathrm{I}}$ rhombs are most uncommon. These rhombs tend to be bridged to other such units either through metal atom or through sulfido atoms leading to μ_3-S structures.[37–40] As a result, the rhombs are dimensionally somewhat variable; metric features of **3**–**6** and **8**, occurring within known limits, are not exceptional.

Summary

Reactions of the disulfido complex **2** with a set of Cu$^{\mathrm{I}}$ reactants affords previously unknown square pyramidal complexes of the type [WO(bdt)S$_2$Cu(R)]$^{2-/-}$ with R = Ar*S, Ar*, carbene, and R'$_3$SiS, a W$^{\mathrm{VI}}$(μ_2-S)$_2$Cu$^{\mathrm{I}}$ bridge rhomb core, and trigonal planar Cu$^{\mathrm{I}}$. The thiolate-ligated complexes, with apical oxo and basal dithiolato and sulfido coordination (excluding **8**), terminal ligation at Cu$^{\mathrm{I}}$, and W–S–Cu bridging, bear a structural relation to the CODH site (Figure 1). The presence of two such bridges and the absence of a basal oxo or hydroxo ligand are significant departures from the desired structure. All attempts thus far to obtain molecules with the latter two features have not been successful. Our conjecture, underscored by the formulation of reaction 4, is that disproportion of an initially formed monobridged species, minimally represented as 2O$_2$W–S–Cu → OWS$_2$Cu + WO$_3$ + Cu, is a reasonable rationalization of the double-bridged structure. The driving force would be the stability of the WS$_2$Cu bridge rhomb abetted by the formation of Si–O bonds in reaction 6. Suppression of this reaction by steric means would require considerable frontside hindrance, possibly attainable in the precursor [WOS(bdt)(OSiR$_3$)]$^-$ with exceptionally capacious R substituents. The stability of the only known molecule with an unsupported Mo–S–Cu bridge[17] may derive from coordinative saturation and steric congestion at the Mo$^{\mathrm{V}}$ center. While the desired structure was not realized, the present results should be of use in the design of future experiments based on monodithiolene complexes intended to eliminate double-bridged products.

Acknowledgment. This research was supported by NSF Grants CHE 0547734 and 0846397. We thank Drs. L. Deng and W. Lo for experimental assistance.

Supporting Information Available: ESMS for complex **5**, ^{1}H NMR for the complexes **3**–**12**, (Et$_4$N){SSiPh$_3$] and (Et$_4$N)-{SSiPr$^i{}_3$]. X-ray crystallographic files in CIF format for the 10 compounds in Tables 1 and 2. This material is available free of charge via the Internet at http://pubs.acs.org.

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(33) Joshi, H. K.; Cooney, J. J. A.; Inscore, F. E.; Gruhn, N. E.; Lichtenberger, D. L.; Enemark, J. H. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 3719–3724.

(34) Sarkar, S.; Mishra, S. B. S. *Coord. Chem. Rev.* **1984**, *59*, 239–264.

(35) Hou, H.-W.; Xin, X.-Q.; Shi, S. *Coord. Chem. Rev.* **1996**, *153*, 25–56.

(36) Lang, J.-P.; Ji, S.-J.; Xu, Q.-F.; Shen, Q.; Tatsumi, K. *Coord. Chem. Rev.* **2003**, *241*, 47–60.

(37) Li, Z.-H.; Du, S.-W.; Wu, X.-T. *Polyhedron* **2005**, *24*, 2988–2993.

(38) Huang, Y.-J.; Song, Y.-L.; Chen, Y.; Li, H.-X.; Zhang, Y.; Lang, J.-P. *Dalton Trans.* **2009**, 1411–1421.

(39) Beheshti, A.; Clegg, W.; Dale, S. H.; Hyvadi, R.; Hussaini, F. *Dalton Trans.* **2007**, 2949–2956.

(40) Wei, Z.-H.; Li, H.-X.; Cheng, M.-L.; Tang, X.-Y.; Chen, Y.; Zhang, Y.; Lang, J.-P. *Inorg. Chem.* **2009**, *48*, 2808–2817.