MS, 97.0% d_0 and 3.0% d_1. (d) Streptothricin F **1f** (92 mg, 0.15 mmol) yielded 8 mg of **26a**: MS, 95.6% d_0 and 6.4% d_1.

Acknowledgment. This work was supported by Publich Health Service Research Grants GM 25996 (S.J.G.) and GM 25919 (D.J.A.) from the National Institute of General Medical Sciences. The potassium [^{15}N]phthalimide was provided by the Stable Isotopes Resource at the Los Alamos Scientific Laboratory, jointly supported by the U.S. Department of Energy and the National Institutes of Health (RR-00962-02, Division of Research Resources). Dr. Chou-Hong Tann and Kazys Martinkus are warmly thanked for expert technical assistance. We are grateful for generous gifts of streptothricin F and *Streptomyces* L-1689-23. Peter Demou of the Chemistry Department, Yale University, is thanked for obtaining the ^{13}C NMR spectra. The Bruker HX-270 NMR instrument facility at Yale used in this work was supported by the National Science Foundation, Grant CHE-7916210, from the Chemistry Division.

Registry No. 1, 3808-42-2; **1**·*x*helianthate, 86118-03-8; **1**·*x*HCl, 18800-56-1; **2**, 74-79-3; **3**, 504-21-2; **10**, 6899-06-5; **10a**·2HCl, 86088-61-1; **13**, 64-19-7; **14**, 922-54-3; **15**, 5460-29-7; **16**, 3184-61-0; **16a**, 79634-10-9; **17**, 35517-18-1; **17a**, 86088-62-2; **18**, 15544-49-7; **18a**, 86101-32-8; **19**, 5680-61-5; **20**, 86088-63-3; **21**, 86088-64-4; **22**, 86088-65-5; **22a**, 86088-66-6; **23**, 86101-33-9; **23a**, 86101-34-0; **24**, 5457-30-7; **24a**, 79634-09-6; **25**, 86088-67-7; **25a**, 86088-68-8; **26**, 86088-69-9; α-lysine 2,3-aminomutase, 9075-20-1.

Communications to the Editor

Novel Alkyne Reactions with Binuclear Molybdenum–Sulfur Complexes: Structure of the Dimethyl Acetylenedicarboxylate Adduct of $[Mo_2O_2(\mu\text{-}S)_2(S_2)_2]^{2-}$

Thomas R. Halbert,* Wie-Hin Pan, and Edward I. Stiefel*

Exxon Research and Engineering Company
Corporate Research-Science Laboratories
Linden, New Jersey 07036

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Recent years have seen dramatic expansion in synthetic and structural molybdenum–sulfur chemistry. Many new inorganic thioanions,[1] organic-ligand-bearing complexes,[2] and polymetallic heteronuclear clusters[3,4] have been prepared and their significance to biochemistry[5] and industry[1a,6,7] has been duly noted. Despite the plethora of new compounds, relatively few studies have been reported on reactivity toward organic reagents. As part of a systematic investigation of such reactivity we have begun to study the reactions of alkynes with Mo–S systems.

Known reactions of alkynes with S-ligand complexes are of two types. In the first or classical type the alkyne adds directly to the metal to form either π-bound[8a–c] or σ-bound[8d] complexes. In the second type the alkyne reacts with sulfide, disulfide, or polysulfide ligands to form a 1,2-dithiolene ligand.[7,8e,f] Here we report preliminary results on reactions of Mo–S complexes with alkynes, including a case in which addition of the alkyne follows neither of the above patterns.

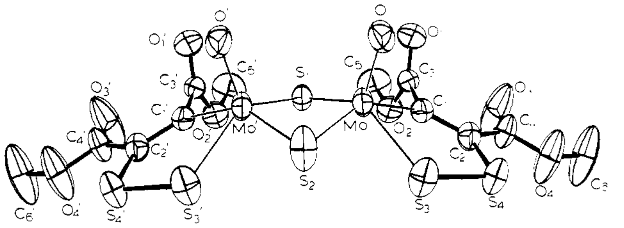

Figure 1. Perspective drawing adapted from ORTEP plot of the $Mo_2O_2S_2(S_2C_2(CO_2CH_3)_2)_2^{2-}$ dianion **4**. Bond lengths: Mo–S_1, 2.318 (2); Mo–S_2, 2.337 (2); Mo–O, 1.676 (6); Mo–S_3, 2.382 (3); Mo–Mo′, 2.882 (1); S_3–S_4, 2.061 (3); S_4–C_2, 1.731 (9); C_1–C_2, 1.36 (1); Mo–C_1, 2.215 (8) Å. Bond angles: Mo–C_1–C_2, 126.0 (6)°; C_1–C_2–S_4, 123.0 (6)°.

We chose the dianion $[Mo_2S_2(\mu\text{-}S)_2(SCH_2CH_2S)_2]^{2-}$ (**1**), whose structure contains a *syn*-$Mo_2S_4^{2+}$ core,[9] as a starting point for our studies. When a red-orange solution of the tetraethylammonium salt of **1** in CH_3CN at 0 °C is treated with two or more equivalents of dimethyl acetylenedicarboxylate (DMAC), the solution rapidly darkens and 2 equiv of ethylene are liberated (as quantitated by GC). Apparently, in the major reaction the activated acetylene attacks the 1,2-ethanedithiolate ligands to displace ethylene[10] rather than adding to the *syn*-$Mo_2S_4^{2+}$ core by a process analogous to that observed for the *anti*-$Mo_2S_4^{2+}$ core in $(Me_nCp)_2Mo_2S_2(\mu\text{-}S)_2$ (n = 1, 5) complexes.[7] Identification of pure Mo/S products from the reaction of **1** with DMAC has proved troublesome, perhaps due to some reactivity at the $Mo_2S_4^{2+}$ core in

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(10) The reaction of acetylene with $CpMo(SCH_2CH_2S)_2MoCp$ has been reported to liberate $H_2C{=}CH_2$.[7a] This reaction involves a bridging ethanedithiolate, whereas the currently reported reaction starts with terminal ethanedithiolate ligands. In a related organic reaction DMAC displaces ethylene from ethylene trithiocarbonate (O'Conner, B. R.; Jones, F. N. *J. Org. Chem.* **1970**, *35*, 2002).

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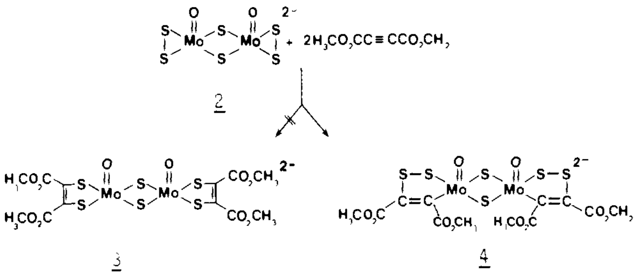
addition to that at the 1,2-ethanedithiolate ligand. We thus turned to the well-known anion $[Mo_2O_2(\mu\text{-}S)_2(S_2)_2]^{2-}$ (**2**),[1b] where we expected that addition of DMAC would occur only at the terminal S_2^{2-} ligands to yield the bis-1,2-dithiolene complex (**2** → **3**).



Addition of 2 equiv of DMAC to a concentrated CH_3CN solution of $[N(C_2H_5)_4]_2[Mo_2O_2(\mu\text{-}S)_2(S_2)_2]$ at room temperature leads quickly to precipitation of an air-stable canary-yellow microcrystalline product.[11] Elemental analysis[12] indicates the formulation $[N(C_2H_5)_4]_2[Mo_2O_2(\mu\text{-}S)_2(S_2)_2\cdot 2DMAC]$. However, while spectroscopic information[13] suggests retention of the $Mo_2O_2S_2^{2+}$ core and involvement of the S–S group, it requires an asymmetric environment for the acetylene-derived fragment. A single-crystal X-ray diffraction study was carried out to unambiguously determine the structure.

Single crystals were grown by slow vapor diffusion of 2-propanol into an acetonitrile solution of $[N(C_2H_5)_4]_2[Mo_2O_2(\mu\text{-}S)_2(S_2)_2\cdot 2DMAC]$, and a full three-dimensional X-ray diffraction study was carried out.[14] The crystal contains ordered $Mo_2O_2(\mu\text{-}S)_2[S_2C_2(CO_2CH_3)_2]_2^{2-}$ dianions **4** as illustrated in Figure 1, along with disordered tetraethylammonium cations.[15] The source of the ligand asymmetry indicated by the spectroscopy is immediately clear and quite surprising: the acetylenes have inserted into Mo–S bonds of the terminal disulfides (rather than into S–S bonds) to form novel five-membered metalla-2,3-dithiacyclopent-4-ene rings. The dimensions of the five-membered rings are consistent with the presence of Mo—C_1, Mo—S_3, S_3–S_4, and C_2—S_4 single bonds and a $C_1{=}C_2$ double bond in an "vinyl disulfide" ligand. The "vinyl disulfide" ligand is very nearly planar (maximum deviation of 0.05 Å for a plane containing C_1, C_2, S_3, and S_4). The Mo atom lies out of this plane by 0.47 Å. The coordination geometry about each Mo is roughly square pyramidal with terminal oxo at the apex. The dimensions of the $Mo_2O_2S_2^{2+}$ core are little changed from those in the starting $[Mo_2O_2(\mu\text{-}S)_2(S_2)_2]^{2-}$.[16] The MoS_1S_2–$Mo'S_1S_2$ dihedral angle of 146.7° is slightly more acute than the average of 150–160° for known $Mo_2O_2S_2^{2+}$ core complexes.[1b]

Insertions of alkynes into transition-metal hydride[17] and carbon[18,19] bonds to form vinyl complexes are well-known and one example has been reported of a reaction that may involve alkyne insertion into a Ni–P bond.[20] Although analogous insertions into transition-metal–sulfur bonds have also been claimed,[21] to our knowledge **4** is the first structurally characterized product of such an insertion. The factors that lead to such insertion rather than 1,2-dithiolene formation or direct π-coordination to molybdenum are not yet understood.[22] It seems likely that frontier molecular orbitals of molybdenum–sulfur complexes exhibit significant metal and sulfur character. The reactions of such complexes may involve coordinatively unsaturated sites on the metal,[8a-d] direct reactions with S ligands,[7,8e,f] or, as we have demonstrated here for the first time, reaction at a multicenter metal–sulfur site leading to insertion of a molecule into a metal–sulfur bond. Further systematic reactivity studies combined with theoretical treatments are required to fully understand these systems. Such work is in progress.

Acknowledgment. We thank Kathleen McGauley for technical assistance and Dr. Cynthia S. Day of Crystalytics Co. for carrying out the single-crystal X-ray diffraction study.

Registry No. 1(TEA)$_2$, 65137-01-4; **2**(TEA)$_2$, 76123-92-7; **4**(TEA)$_2$, 86197-46-8; DMAC, 762-42-5.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond lengths and bond angles, structure factors, and perspective drawings of TEA$^+$ cations (21 pages). Ordering information is given on any current masthead page.

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[11] Yield on the basis of the formula $[N(C_2H_5)_4]_2Mo_2O_2(\mu\text{-}S)_2(S_2C_2(CO_2CH_3)_2)_2$ is typically 60–65%.

[12] Anal. Calcd for $C_{28}H_{52}O_{10}S_6N_2Mo_2$: C, 35.00; H, 5.45; N, 2.92; S, 20.02. Found: C, 34.62; H, 5.31; N, 2.89; S, 19.84.

[13] Infrared (KBr) $\nu_{Mo{=}O}$ 947, $\nu_{Mo-S-Mo}$ 473; ν_{S-S} 520 cm^{-1} in starting material is gone; ^{1}H NMR (Me$_2$SO-d_6) δ 3.77 (s, 6, ester CH$_3$), 3.72 (s, 6, ester CH$_3$), 3.13 (q, 16, cation CH$_2$), 1.11 (t, 24, cation CH$_3$); ^{13}C (Me$_2$SO-d_6) δ 177.4, 176.6, 161.7, 149.3, 52.18, 51.85, 51.42, 51.31, 51.15, 50.55, 6.89.

[14] Crystal data: space group P_{nma}-D_{2h}^{16} (No. 62) with $a = 18.314$ (5) Å, $b = 25.358$ (6) Å, $c = 8.916$ (2) Å, $V = 4141$ Å,^{3} $Z = 4$. The structure was solved by conventional heavy-atom methods, difference Fourier synthesis and full-matrix least-squares refinement. $R_F = 0.048$, $R_{wF} = 0.057$ for 2276 independent diffracted intensities ($I > 3.0\sigma(I)$) with $3° < 2\theta < 55°$ (Mo K$\bar{\alpha}$ radiation). Anisotropic thermal parameters were employed for all 31 independent non-hydrogen atoms.

[15] Perspective drawings of the two independent tetraethylammonium cations are included in the supplementary material. Both cations, though disordered, were fully characterized.

[16] For the $Mo_2O_2S_2^{2+}$ core[1b] in $[N(C_2H_5)_4]_2Mo_2O_2(\mu\text{-}S)_2(S_2)_2$, Mo═O is 1.67 Å, Mo—$S_{bridge}$ average 2.324 Å, Mo—Mo is 2.825 Å.

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[22] For example, the reaction of MoS_9^{2-} with DMAC produces a Kelly-green product, which has recently been characterized in an X-ray study by Coucouvanis and co-workers[23] as the tris(1,2-dithiolene) complex. Thus, even in simple molybdenum thioanions, different modes of alkyne addition occur.

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Novel Approach to Vicinal Stereocontrol during Carbon–Carbon Bond Formation. Stereocontrolled Synthesis of (±)-*threo*-Juvabione

David J. Morgans, Jr.,* and Gregg B. Feigelson

Department of Chemistry, University of California
Santa Cruz, California 95064

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The establishment of defined, vicinal stereorelationships in the construction of organic molecules is a central requirement for efficient synthesis of many structurally complex substances. An approach involving formation of the carbon–carbon bond linking two asymmetric centers can often provide a useful solution to the problem, particularly in acyclic systems. Schemes of this type (Scheme I) frequently involve bond formation between trigonal carbons (route a). The striking developments in stereocontrolled aldol reactions[1] provide testimony to the utility of this approach. An alternative to this strategy involves bond formation between a trigonal and *nontrigonal* carbon atom[2] (shown for a tetrahedral

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[*] Address correspondence to this author at Syntex Research, 3401 Hillview Avenue, Palo Alto, CA 94304.

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