simple experimental operation. Further studies on the scope of this Cu(II)-mediated reducing system, as well as on the reaction mechanism, are in progress.

Acknowledgment. We thank Shin-Etsu Chemical Co. Ltd. for a gift of hydrosilanes. Support of this work by Grant-in-Aid from the Ministry of Education, Science and Culture, Japan, is gratefully acknowledged.

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Preparation and Structure of $[(C_6H_5)_4P][(C_5H_5)Mo(S_4)_2]$: A Convenient Synthesis of an Organometallic Metal Polysulfide Anion

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Summary: The reaction of $[(C_5H_5)_2Mo_2(CO)_6]$ with 1 equiv of K_2S_3 in 5:1 acetonitrile/DMF generates $[(C_5H_5)Mo(CO)_2(S_2)]^-$ (I), which has been isolated and characterized as its $(C_6H_5)_4P^+$ salt. It contains a $(C_5H_5)Mo(CO)_2^-$ fragment with a side-bonded S_2 ligand. Further reaction of this compound with excess elemental sulfur results in formation of $[(C_5H_5)Mo(S_4)_2]^-$ (II), which has been characterized both spectroscopically and structurally as its $(C_6H_5)_4P^+$ salt. Molecule II contains a Mo(IV) center in a pseudo square-pyramidal geometry, with a $(C_5H_5)^-$ group in the apical position and with two S_4^{2-} chelates occupying the basal sites. This compound is unique because it is an organometallic member of the series $[E{=}Mo(S_4)_2]^{2-}$ (E = O, S), affording an entry into the chemistry of organometallic metal sulfide anions.

The chemistry of transition-metal sulfides has been under intense scrutiny because of their involvement in important catalytic processes, particularly hydrodesulfurization and hydrogenation reactions.[1] Thus binary metal sulfide anions have received a great deal of attention[2] because of their use as model compounds and because of their structural diversity.[3] Also neutral organometallic sulfides have been studied in detail as models for catalytic processes[4,5] and for their novel structural features.[6]

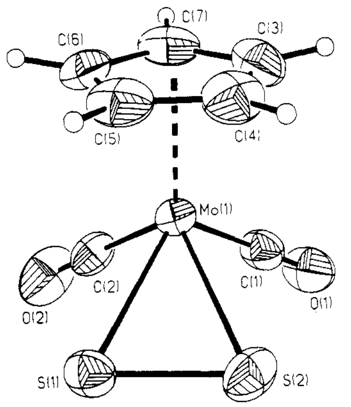

Figure 1. ORTEP view of anionic fragment of I, $[(C_5H_5)Mo(S_2)(CO)_2]^-$, with thermal ellipsoids at 35% probability. Important distances (Å): S(1)-S(2) = 2.020 (2), Mo(1)-S(1) = 2.466 (2), Mo(1)-S(2) = 2.471 (2), Mo(1)-C(1) = 1.923 (6), Mo(1)-C(2) = 1.917 (5), Mo(1)-C(3) = 2.338 (6), Mo(1)-C(4) = 2.387 (6), Mo(1)-C(5) = 2.372 (5), Mo(1)-C(6) = 2.324 (6), Mo(1)-C(7) = 2.305 (5), C(1)-O(1) = 1.170 (7), C(2)-O(2) = 1.181 (7). Important angles: S(1)-Mo(1)-S(2) = 48.3 (1)°, Mo(1)-S(1)-S(2) = 66.0 (1)°, Mo(1)-S(2)-S(1) = 65.7 (1)°, C(1)-Mo(1)-C(2) = 78.2 (2)°.

Recently there has been an upsurge of interest in high-valent organometallic chemistry, particularly species in which an oxo ligand has been replaced by a cyclopentadienyl ligand.[7] We have begun directing our attention to the chemistry of high-valent organometallic chalcogenide complexes. The oxidative decarbonylation of metal carbonyl complexes provides a particularly facile entry to this area of chemistry.[8] In this communication, we report preliminary results on the convenient preparation and structure of the cyclopentadienylbis(tetrasulfido)molybdenum anion $[(C_5H_5)Mo(S_4)_2]^-$ (II) as well as its precursor $[(C_5H_5)Mo(CO)_2(S_2)]^-$ (I).

The precursor I can be prepared and isolated in straightforward fashion by reaction of the dimer $(C_5H_5)_2Mo_2(CO)_6$ with 2 equiv of K_2S_3 dissolved in a 5:1 acetonitrile/DMF mixture. The choice of solvent is important because use of pure DMF leads to facile formation of MoS_4^{2-} as a contaminant. Compound I could be isolated as an orange-red tetraphenylphosphonium salt by the addition of $(C_6H_5)_4PBr$.[9] The compound was characterized by analytical, spectroscopic,[10] and crystallographic methods.[11] It contains a side-bonded S_2^{2-} ligand, along with a cyclopentadienyl ring and two CO ligands (see Figure 1). The S–S distance is 2.020 (2) Å, which is typical

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(9) In a typical procedure, 0.10 g (0.57 mmol) of K_2S_3, 0.14 g (0.29 mmol) of $[(C_5H_5)_2Mo_2(CO)_6]$, and 0.24 g (0.57 mmol) of $(C_6H_5)_4PBr$ was dissolved in 5 mL of acetonitrile and 1 mL of DMF and stirred for 3 h at 25 °C. The resulting red-brown solution was filtered and layered with 3 mL of diethyl ether. The flask was stored at 4 °C overnight, and red-orange needle crystals of the product were isolated in 35% yield (60 mg) based on molybdenum

(10) Anal. Calcd for $[(C_6H_5)_4P][(C_5H_5)Mo(CO)_2(S_2)]$ ($C_{31}H_{25}O_2PMoS_2$, I): C, 60.00; H, 4.03. Found: C, 60.28; H, 4.06. IR (cm^{-1}, Nujol mull): 1885 (s), 1786 (s). ^1H NMR (200 MHz, CD_3CN): 5.24 ppm (s). Anal. Calcd for $[(C_6H_5)_4P][(C_5H_5)Mo(S_4)_2]$ ($C_{29}H_{25}PMoS_8$, II): C, 46.03; H, 3.31. Found: C, 46.11; H, 3.27. ^1H NMR (200 MHz, CD_3CN): 5.05 ppm (s).

(11) A red orange needle was sealed in epoxy and mounted and a Nicolet R3 diffractometer. Data were collected in the range $3.5° < 2\theta < 45°$ at room temperature, and the structure was solved by using the SHELXTL program and refined by using the standard Nicolet package of programs: space group monoclinic, $P2_1/c$, $Z = 4$, $a = 11.319$ (5) Å, $b = 18.186$ (9) Å, $c = 13.580$ (4) Å, $\beta = 96.98$ (4)°, $V = 2774$ (2) Å^3, $R = 0.0352$, $R_w = 0.0485$.

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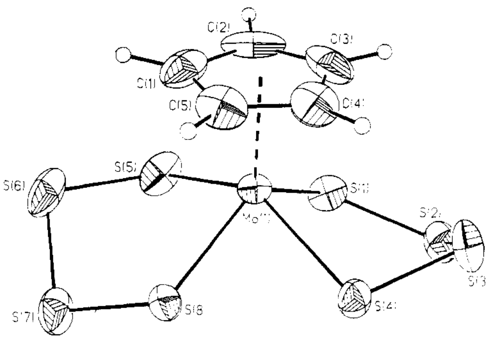


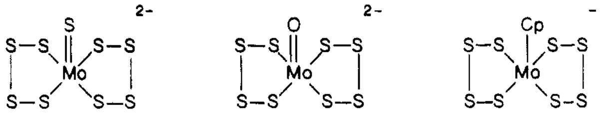
Figure 2. ORTEP view of anionic fragment of II, $[(C_5H_5)Mo(S_4)_2]^-$, with thermal ellipsoids at 35% probability. Important distances (Å): Mo(1)-S(1) = 2.305 (2), Mo(1)-S(4) = 2.446 (2), Mo(1)-S(5) = 2.430 (1), Mo(1)-S(8) = 2.336 (2), S(1)-S(2) = 2.141 (2), S(2)-S(3) = 2.031 (2), S(3)-S(4) = 2.061 (2), S(5)-S(6) = 2.073 (3), S(6)-S(7) = 2.022 (3), S(7)-S(8) = 2.124 (2), Mo(1)-C(1) = 2.310 (7), Mo(1)-C(2) = 2.286 (8), Mo(1)-C(3) = 2.334 (6), Mo(1)-C(4) = 2.368 (5), Mo(1)-C(5) = 2.349 (6). Some important angles: S(1)-Mo(1)-S(4) = 86.2 (1)°, S(1)-Mo(1)-S(5) = 76.4 (1)°, S(4)-Mo(1)-S(8) = 74.5 (1)°, S(5)-Mo(1)-S(8) = 87.1 (1)°, Mo(1)-S(1)-S(2) = 114.7 (1)°, Mo(1)-S(4)-S(3) = 101.8 (1)°, Mo(1)-S(5)-S(6) = 104.0 (1)°, Mo(1)-S(8)-S(7) = 113.7 (1)°, S(1)-S(2)-S(3) = 100.4 (1)°, S(2)-S(3)-S(4) = 101.0 (1)°, S(5)-S(6)-S(7) = 100.3 (1)°, S(6)-S(7)-S(8) = 99.3 (1)°.

for side-bonded disulfide ligands. The compound is isostructural with the previously reported $[(C_5H_5)Mo(CO)_2(Se_2)]^-$ anion,[12] and the neutral $(C_5H_5)Re(CO)_2(S_2)$,[13] and is otherwise unremarkable.

Reaction of I with S_8, either in situ or after isolation and redissolving in acetonitrile, results in formation of $[(C_5H_5)Mo(S_4)_2]^-$ (II) as a dark red-purple compound. It can be isolated as well-formed dark purple crystals in the presence of $(C_6H_5)_4PBr$.[14] Compound II has been characterized both analytically[10] and crystallographically.[15] It contains a well-separated $(C_6H_5)_4P^+$ cation and II in the unit cell. Compound II has a Mo(IV) central atom in a pseudo square-based pyramid, with the two S_4^{2-} chelates occupying the basal positions and the cyclopentadienyl ligand occupying the axial site (see Figure 2). Alternatively, the geometry could be defined as a piano-stool configuration[16] with the sulfide ligands as four legs of the stool.

The Mo-S distances in compound II show considerable variation, ranging from 2.305 (2) to 2.446 (2) Å. The S-S distances show a real but not very pronounced bond alternation around the rings, varying from 2.022 (3) to 2.141 (2) Å. This variation has been fully discussed previously.[17] The five-membered rings are in an envelope configuration and do not appear to be perturbed by the presence of the cyclopentadienyl ring. Similarly, the molybdenum-ring carbon distances average 2.33 Å, which is typical for these types of complexes. Thus the cyclopentadienyl group does not appear to exert any steric strain upon the complex.

The bis(tetrasulfido) complex II is of considerable interest as it extends the homologous series $[S{=}Mo(S_4)_2]^{2-}$ and $[O{=}Mo(S_4)_2]^{2-}$[17] to $[(Cp)Mo(S_4)_2]^-$.



In addition to providing a comparison between the reactivity of oxo, sulfido, and cyclopentadienyl groups, it is one of the very few organic derivatives of a molybdenum sulfide anion. It should be noted that two very interesting high-valent complexes of rhenium and vanadium have been reported, which contain cyclopentadienyl, oxo, and tetrasulfido ligands.[18] The chemistry of the molybdenum sulfide anions is extensive, as is that of the neutral organometallic sulfides. However, to our knowledge no cyclopentadienyl anion has been previously isolated and characterized. Compound II can be conveniently prepared and may provide an entry into some unusual and useful metal sulfide chemistry.

Acknowledgment. Support by the National Science Foundation (CHE-8802217) is gratefully acknowledged.

Registry No. $I{\cdot}(C_6H_5)_4P^+$, 122116-26-1; $II{\cdot}(C_1H_5)_4P^+$, 122116-28-3; $[(C_5H_5)_2Mo_2(CO)_6]$, 12091-64-4; K_2S_3, 37488-75-8.

Supplementary Material Available: Complete crystal data, tables of positional parameters, complete tables of distances and angles, and tables of anisotropic thermal parameters for both compounds (14 pages); listings of observed and calculated structure factors (30 pages). Ordering information is given on any current masthead page.

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[15] The crystallographic determination of II was performed similarly to that described above: space group monoclinic, $P2_1/n$, $Z = 4$, $a = 12.462$ (2) Å, $b = 16.879$ (3) Å, $c = 15.823$ (2) Å, $\beta = 106.88$ (1)°, $V = 3185$ Å^3, $R = 0.0434$, $R_w = 0.0561$.

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Proton Transfer from (Methoxymethylcarbene)pentacarbonylchromium(0) in Aqueous Solution

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Summary: Evidence is presented that the reaction of (methoxymethylcarbene)pentacarbonylchromium(0) with OH^- and piperidine leads to reversible deprotonation of the methyl group and has a $pK_a = 12.3$. The rate constants are found to be remarkably low, even for a proton transfer from carbon that leads to the formation of a resonance-stabilized carbanion.

We wish to report a kinetic study of the proton transfer from (methoxymethylcarbene)pentacarbonylchromium(0) (1).[2] 1 is a prototype Fischer transition-metal carbene complex.[3,4] It has been known for ca. 20 years that the

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[1] Permanent address: Department of Chemistry, California State University, Fresno, CA 93740.

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