recrystallized from hexane/CH_2Cl_2 (20:1) at −78 °C to give white crystalline $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T\cdot BH_3)$ (**3**) in 89% yield. Complex **3** has also been prepared by the reaction of **2** with $THF\cdot BH_3$ and was fully characterized.[11] The X-ray structure[12] of **3** is very similar to that of **2**, except BH_3 is coordinated to the sulfur. The ability of **2** to displace Me_2S from $Me_2S\cdot BH_3$ demonstrates the strong donor ability of the sulfur in **2**. From other studies in progress, it appears that the sulfur in **2** is also a strong donor toward other electron-pair acceptors.

Acknowledgment. We are grateful to Dr. Lee M. Daniels of the Iowa State University Molecular Structure Lab for determining the structure of **2**. The diffractometer was funded in part by the National Science Foundation (Grant No. CHE-8520787). We thank Johnson Matthey, Inc., for a loan of $IrCl_3$.

Supplementary Material Available: Tables of crystal data, positional and thermal parameters, complete bond distances and angles, and least-squares planes and torsion angles (12 pages); a listing of calculated and observed structure factors (7 pages). Ordering information is given on any current masthead page.

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[11] Anal. Calcd for $C_{16}H_{26}BSIr$: C, 42.38; H, 5.78. Found: C, 42.50; H, 5.91. ^1H NMR ($CDCl_3$): δ 4.46 (s, 2 H), 1.28 (s, 6 H), 1.96 (s, 15 H), 0.91 (m, 3 H, BH_3). EIMS: *m/e* 454 (M^+), 440 ($M^+ - BH_3$). Melting point: 106–108 °C dec.

[12] Chen, J.; Angelici, R. J. *J. Am. Chem. Soc.*, submitted for publication.

Copper(II)-Mediated Stereoselective Reduction of Acetylenic Sulfones by Hydrosilanes

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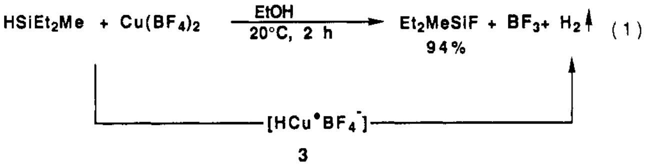
Summary: The stereoselective reduction of acetylenic sulfones to cis vinylic sulfones was effected by using a novel reduction system consisting of copper(II) salts ($Cu(BF_4)_2$, $Cu(OTf)_2$, CuF_2, etc.) and a hydrosilane. The best result was obtained by the use of $Cu(BF_4)_2$. A divalent copper hydride is proposed to be responsible for this reduction.

The usefulness of copper(I) hydride (**1**) as an efficient reagent for conjugate hydride addition to α,β-unsaturated carbonyl compounds has been amply established so far.[1,2] However, little is known concerning the generation and synthetic behavior of copper(II) hydride, such as **2**. We envisaged that an appropriate combination of a metal hydride with a copper(II) salt would give copper(II) hydride **2**,[3] which might exhibit unique reducing behavior different from that of **1**. In this communication, we report that the system consisting of a copper(II) salt and a hydrosilane effects the stereoselective 1,2-reduction of acetylenic sulfones **4** to cis vinylic sulfones **5**, a reaction for which a stereoselective syn addition pathway to the triple bond by the copper(II) hydride, generated in situ from CuX_2 and $HSiR_3$, appears likely.

HCu(I)
1

HCu(II)X
2

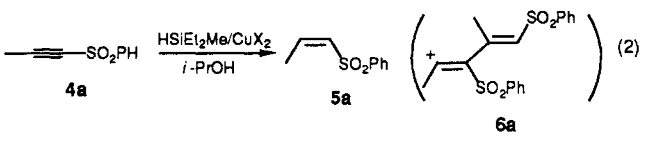
The reaction of $Cu(BF_4)_2$[4] with diethylmethylsilane ($HSiEt_2Me$) in ethanol at 20 °C took place with the evolution of hydrogen gas (identified by GC) and the deposition of copper(0), giving a 94% yield (NMR) of diethylmethylfluorosilane (Et_2MeSiF) after 2 h. This result has suggested that $Cu(BF_4)_2$ reacted with the hydrosilane to give the silyl fluoride and a copper(II) hydride, such as **3**, which then decomposed to yield molecular hydrogen. Similar hydrogen evolution was observed with other copper(II) salts such as $Cu(OTf)_2$, $Cu(NO_3)_2$, and CuF_2.



Unlike most copper(I) hydride species, which effect conjugate reduction of α,β-unsaturated ketones,[1,2] the present system consisting of a hydrosilane and a copper(II) salt reduced them only reluctantly under similar reaction conditions.[5] However, it was found that when acetylenic sulfone **4a** was treated with $HSiEt_2Me$ in the presence of copper(II) salts in *i*-PrOH, syn reduction of **4a** took place to give the cis vinylic sulfone **5a** in good yields (Table I). Among the copper(II) salts examined, $Cu(BF_4)_2$ gave the best result. The use of CuF_2 resulted in the formation of significant amounts of dimeric product **6a** together with vinylic sulfone **5a**.

Table II presents the results of the reductions of several acetylenic sulfones **4**[6] by $HSiEt_2Me/Cu(BF_4)_2$. Reduction proceeded smoothly to give the corresponding cis vinylic sulfones **5** in good yield after purification by flash chro-

Table I. Effect of Copper Salt in the Reduction of Acetylenic Sulfone 4a[a]



run[a]	copper salt	condn (°C, h)	yield,[b] % 5a	yield,[b] % 6a	recovered 4a
1	$Cu(BF_4)_2$	15, 3	94		
2[c]	CuF_2	25, 6	48[d]	31[d]	
3	$Cu(OTf)_2$	15, 6	55		45
4	$Cu(NO_3)_2$	15, 6	55		25
5	$CuCl_2$	15, 3			97
6	*e*	15, 3			99

[a] Unless otherwise specified, reduction was carried out by adding $HSiEt_2Me$ (2 equiv) to a mixture of **4a** (1 equiv) and copper salt (2 mol equiv) in *i*-PrOH. [b] Determined by GLC analysis. [c] Reaction was conducted in MeOH. [d] Isolated yield after purification by PTLC. [e] $BF_3\cdot OEt_2$ (2 equiv) was used in place of copper salts.

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[1] For ate complexes of **1**, see: (a) Tsuda, T.; Yoshida, T.; Kawamoto, T.; Saegusa, T. *J. Org. Chem.* **1987**, *52*, 1624. (b) Tsuda, T.; Fujii, T.; Kawasaki, K.; Saegusa, T. *J. Chem. Soc., Chem. Commun.* **1980**, 1013. (c) Semmelhack, M. F.; Stauffer, R. D.; Yamashita, A. *J. Org. Chem.* **1977**, *42*, 3180. (d) Ashby, E. C.; Lin, J.-J.; Goel, A. B. *Ibid.* **1978**, *43*, 183. (e) House, H. O.; DuBose, J. C. *Ibid.* **1975**, *40*, 788. (f) Semmelhack, M. F.; Stauffer, R. D. *Ibid.* **1975**, *40*, 3619. (g) Boeckman, R. K., Jr.; Michalak, R. *J. Am. Chem. Soc.* **1974**, *96*, 1623. (h) Masamune, S.; Bates, G. S.; Georghiou, P. E. *Ibid.* **1974**, *96*, 3686.

[2] For phosphine complexes of **1**, see: (a) Mahoney, W. S.; Brestensky, D. M.; Stryker, J. M. *J. Am. Chem. Soc.* **1988**, *110*, 291. (b) Brestensky, D. M.; Huseland, D. E.; McGettigan, C.; Stryker, J. M. *Tetrahedron Lett.* **1988**, *29*, 3749. (c) Sorrell, T. N.; Pearlman, P. S. *J. Org. Chem.* **1980**, *45*, 3449. (d) Whitesides, G. M.; Filippo, J. S., Jr.; Stedronsky, E. R.; Casey, C. P. *J. Am. Chem. Soc.* **1969**, *91*, 6542. (e) Dilts, J. A.; Shriver, D. F. *Ibid.* **1969**, *91*, 4088.

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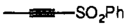
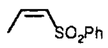
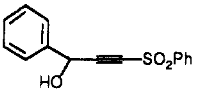
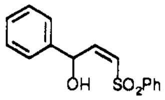
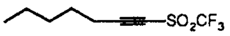
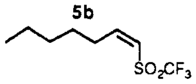
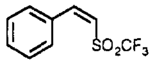
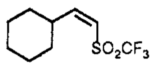
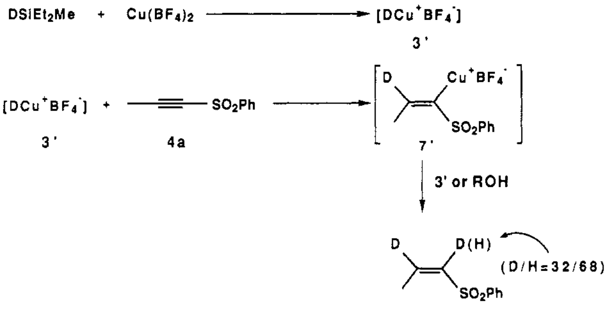
Table II. Stereoselective Reduction of Acetylenic Sulfones 4 to Vinylic Sulfones 5 by $HSiEt_2Me/Cu(BF_4)_2$[a]

run	acetylenic sulfones 4	vinylic sulfones 5	IR ($\nu_{c=c}$); MS (m/e); ^1H NMR (=CH, ppm)	yield,[b,c] %
1	 **4a**	 **5a**	1628 cm^{-1}; 182 (M$^+$); 6.31 (d, J = 11.3 Hz), 6.39 (dq, J = 11.3, 6.7 Hz)	72
2	 **4b**	 **5b**	1628 cm^{-1}; 274 (M$^+$); 6.30 (d, J = 10.6 Hz) 6.41 (dd, J = 10.6, 8.6 Hz)	82
3	 **4c**	 **5c**	1618 cm^{-1}; 230 (M$^+$); 6.22 (d, J = 11 Hz), 6.90 (dt, J = 11, 7.9 Hz)	74
4	 **4d**	 **5d**	1600 cm^{-1}; 236 (M$^+$); 6.38 (d, J = 12.2 Hz), 7.62 (d, J = 12.2 Hz)	73
5	 **4e**	 **5e**	1619 cm^{-1}; 242 (M$^+$); 6.11 (d, J = 11.1 Hz), 6.69 (t, J = 11.1 Hz)	70

[a] All reactions were performed at 20 °C for 3 h by using 2–2.3 equiv of $Cu(BF_4)_2/HSiEt_2Me$ and *i*-PrOH as a solvent. [b] Isolated yield after purification by flash chromatography on silica gel using AcOEt/*n*-hexane. [c] In every case stereochemical purity of product was ~100%, which was determined by ^1H and ^{13}C NMR.

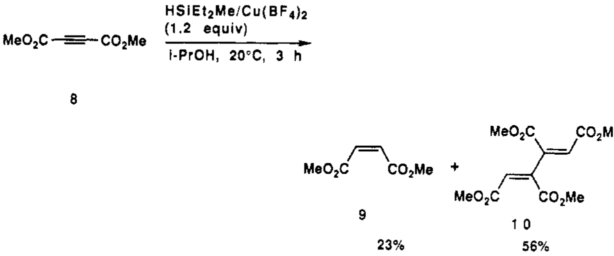
Scheme I



matography.[7] Noteworthy is the high chemoselectivity of the present system which does not affect carbonyl and haloalkyl functions due to the *modest* reactivity of the present copper hydride species.[8] No further reduction of **5a** was observed in any reactions performed.

To probe the path of hydrogen transfer, reaction of **4a** with $DSiEt_2Me$ (3 equiv)/$Cu(BF_4)_2$ (2 equiv) was carried out. The usual calculation from the intensity of observed ^1H NMR spectra indicated that the deuterium was transferred regioselectively from DSi to the β-carbon of acetylenic sulfones and that both the deuteron and proton were incorporated into the α-carbon in the ratio of 32/68. Accordingly, the formation of **5** appears to involve regioselective syn addition of the copper hydride, such as **3**, derived from Cu^{2+} and $HSiR_3$, to give a vinylcopper(II) species, **7**, as the key intermediate (Scheme I). Judging from the scrambled result at the α-position, both terminating pathways, i.e., coupling of the vinylcopper intermediate with DCu(II)X and protonolysis by ROH, would take place.[9]

While the present Cu(II) system does not work well for acetylenes without electron-attracting substituents (e.g. PhC≡CPh, EtC≡CEt, MeC≡CSPh, etc.), the reaction of DMAD (dimethyl acetylenedicarboxylate, **8**) with $Cu(BF_4)_2/HSiEt_2Me$ occurred readily. In contrast to the case of **4a**, **8** gave a dimeric product, **10**,[10] as the major product.[11]



(3)

Copper(II) hydride, generated in situ by the reaction of divalent copper salts and a hydrosilane, thus is a novel reducing agent, which nicely converts acetylenic sulfones to vinylic sulfones[12,13] in a stereoselective manner, in a

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[3] Desilylative ring opening of siloxycyclopropane by $Cu(BF_4)_2$ leading to the generation of β-(acyl)alkylcopper(II) species, see: Ryu, I.; Ando, M.; Ogawa, A.; Murai, S.; Sonoda, N. *J. Am. Chem. Soc.* **1983**, *105*, 7192.

[4] Purchased from Alfa. Prior to use, it was dried under reduced pressure (50 °C, 1 mmHg, overnight).

[5] Attempted conjugate reduction of typical enones by the present reducing system ($HSiEt_2Me/Cu(BF_4)_2$/*i*-PrOH, 20 °C, 2 h) gave only low to moderate yields of saturated ketones (for cyclohexanone: trace, for MVK: 40%).

[6] Acetylenic sulfones 4 were prepared according to literature procedures. For **4a**, see: Truce, W. E.; Markley, L. D. *J. Org. Chem.* **1970**, *35*, 3275. For **4c–e**, see: Hanack, M.; Wilhelm, B.; Subramanian, L. R. *Synthesis* **1988**, 592. **4b** was prepared by *m*-chloroperbenzoic acid oxidation of the condensation product from LiC≡CSPh and benzaldehyde.

[7] A typical experiment: **4a** (0.180 g, 1 mmol), $Cu(BF_4)_2$ (0.474 g, 2 mmol), and *i*-PrOH (5 mL) were placed in a 10-mL flask. $HSiEt_2Me$ (0.204 g, 2 mmol) was added to the reaction mixture in one portion by syringe. The blue color of $Cu(BF_4)_2$ gradually turned green and finally dark brown with deposition of copper(0). After being stirred for 2 h at 20 °C, the reaction mixture was poured into aqueous saturated NH_4Cl solution and the organic part was extracted into three portions of ether. The combined ethereal layer was washed with 5% aqueous $NaHCO_3$ and dried over $MgSO_4$. Purification by flash chromatography (SiO_2) using AcOEt/*n*-hexane (1/1) gave cis vinylic sulfone **5a** (0.131 g, 72%).

[8] Attempted reduction of **4a** with $HSiEt_2Me/Cu(BF_4)_2$ (*i*-PrOH, 15 °C, 2 h) in the presence of cyclohexenone and 2-phenylethyl bromide gave **5a** as the sole product with complete recovery of the latter two.

[9] The possibility of the intervention of other copper hydride species involving HCu^I, as well as the precise structure of the proposed copper(II) hydride, has not been elucidated yet.

[10] **10**: white crystalline solid; mp 90.5–91.0 °C; IR(KBr) 1710 cm^{-1} (br); ^1H NMR ($CDCl_3$) δ 3.78 (s, 6 H), 3.92 (s, 6 H), 6.09 (s, 2 H); MS m/e 286, 255, 227, 199, 59. Anal. Calcd for $C_{12}H_{14}O_8$: C, 50.35; H, 4.93. Found: C, 50.28, H, 4.98. It is tempting to speculate that the addition of vinylcopper to another DMAD would lead to the dimer **10**, as suggested for the formation of **6a**, but an alternative pathway involving two molecular coupling of vinylcopper(II) has not been rigorously excluded at this stage.

[11] Reduction of methyl 3-phenylpropiolate with the present copper(II) hydride system was also attempted ($HSiEt_2Me/Cu(BF_4)_2$/*i*-PrOH, 20 °C, 2 h). GC analysis showed only a 6% conversion to methyl cinnamate, suggesting that the reduction proceeded quite sluggishly. Cf. ref 1a, 1c, and 1f.

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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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(12) For reduction of silylacetylenic sulfones, see: (a) Paquette, L. A.; Williams, R. V. *Tetrahedron Lett.* **1981**, *22*, 4643. (b) Carr, R. V. C.; Williams, R. V.; Paquette, L. A. *J. Org. Chem.* **1983**, *48*, 4976. (c) Eisch J. J.; Behrooz, M.; Dua, S. K. *J. Organomet. Chem.* **1985**, *285*, 121.

(13) Vinylic sulfones are versatile intermediates in organic synthesis. For reviews, see: (a) Lucchi, O. D.; Pasquato, L. *Tetrahedron* **1988**, *44*, 6755. (b) Magnus, P. D. *Ibid.* **1977**, *33*, 2019. (c) Field, L. *Synthesis* **1978**, 713.

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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Received June 1, 1989

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]

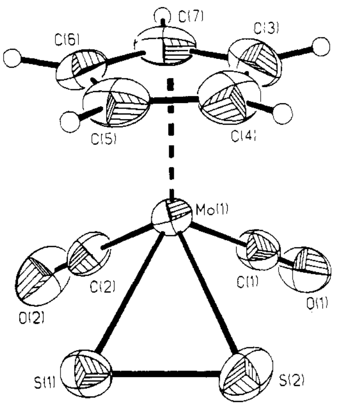

Figure 1. ORTEP view of anionic fragment of I, $[(C_5H_5)Mo(S_2)(CO)_2]^-$, with thermal ellipsoids at 35% probability. Important distances (Å): S(1)–S(2) = 2.020 (2), Mo(1)–S(1) = 2.466 (2), Mo(1)–S(2) = 2.471 (2), Mo(1)–C(1) = 1.923 (6), Mo(1)–C(2) = 1.917 (5), Mo(1)–C(3) = 2.338 (6), Mo(1)–C(4) = 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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(1) (a) Massoth, F. E. *Adv. Catal.* **1978**, *27*, 265. (b) Topsoe, H.; Claussen, B. S. *Catal. Rev.—Sci. Eng.* **1984**, *26*, 295. (c) Chianelli, R. R. *Catal. Rev.—Sci. Eng.* **1984**, *26*, 361.

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(3) For an example of the structural diversity of these compounds see: Sola, J.; Do, Y.; Berg, J. M.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 1706.

(4) Rakowski Dubois, M. *Chem. Rev.* **1989**, *89*, 1.

(5) Casewit, C. J.; Coons, D. E.; Wright, L. L.; Miller, W. K.; Rakowski Dubois, M. *Organometallics* **1986**, *5*, 951.

(6) Tremel, W.; Hoffmann, R.; Jemmis, E. D. *Inorg. Chem.* **1989**, *28*, 1213.

(7) (a) Herrmann, W. A.; Herdtweck, E.; Flöel, M.; Kulpe, J.; Küsthardt, U.; Okuda, J. *Polyhedron* **1987**, *6*, 1165. (b) Herrmann, W. A. *Angew Chem., Int. Ed. Engl.* **1988**, *27*, 1297.

(8) (a) O'Neal, S. C.; Kolis, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 1971. (b) O'Neal, S. C.; Kolis, J. W. *Inorg. Chem.*, in press.

(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). ^{1}H 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. ^{1}H 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, $R = 0.0352$, $R_w = 0.0485$.