recrystallized from hexane/CH₂Cl₂ (20:1) at -78 °C to give white crystalline Cp*Ir(η^{4} -2,5-Me₂T·BH₃) (3) in 89% yield. Complex 3 has also been prepared by the reaction of 2 with THF·BH₃ and was fully characterized.¹¹ The X-ray structure¹² of 3 is very similar to that of 2, except BH₃ is coordinated to the sulfur. The ability of 2 to displace Me₂S from Me₂S·BH₃ 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.

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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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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 $\alpha_{,\beta}$ -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

HCu(l)	HCu(II)X
1	2

bond by the copper(II) hydride, generated in situ from

 CuX_2 and $HSiR_3$, appears likely.

The reaction of $Cu(BF_4)_2^4$ with diethylmethylsilane (HSiEt₂Me) 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 (Et₂MeSiF) 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 HSiEt₂Me 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(BF₄)₂ gave the best result. The use of CuF₂ 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

	-SO ₂ PH HSiE12M /-Pr	Me/CuX ₂	58	h (+		_/ ^{SO2Ph}	(2)
					(6a	
				yield	l,º %		
runª	copper salt	condn (°C	.h)	5a	6a	recovere	d 4a

runª	copper salt	condn (°C, h)	5a	6 a	recovered 4a
1	$Cu(BF_4)_2$	15, 3	94		
2°	CuF_2	25, 6	48 ^d	31ª	
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. ^cReaction was conducted in MeOH. ^d Isolated yield after purification by PTLC. ^eBF₃·OEt₂ (2 equiv) was used in place of copper salts.

⁽¹¹⁾ Anal. Calcd for $C_{16}H_{26}BSIr$: C, 42.38; H, 5.78. Found: C, 42.50; H, 5.91. ¹H NMR (CDCl₃): δ 4.46 (s, 2 H), 1.28 (s, 6 H), 1.96 (s, 15 H), 0.91 (m, 3 H, BH₃). EIMS: m/e 454 (M⁺), 440 (M⁺ – BH₃). Melting point: 106–108 °C dec.

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Table II. Stereoselective Reduction of Acetylenic Sulfones 4 to Vinylic Sulfones 5 by HSiEt₂Me/Cu(BF₄)₂^a

run	acetylenic sulfones 4	vinylic sulfones 5	IR $(\nu_{c=c})$; MS (m/e) ; ¹ H NMR (=CH, ppm)	yield, ^{b,c} %
1	SO ₂ Ph	SO ₂ Ph	1628 cm ⁻¹ ; 182 (M ⁺); 6.31 (d, $J = 11.3$ Hz), 6.39 (dq, $J = 11.3$, 6.7 Hz)	72
2	so ₂ Ph	5a	1628 cm ⁻¹ ; 274 (M ⁺); 6.30 (d, $J = 10.6$ Hz) 6.41 (dd, $J = 10.6$, 8.6 Hz)	82
3	Hơ 4b SO ₂ CF ₃	6н \$0 ₂ Ph 5b SO ₂ CF ₃	1618 cm ⁻¹ ; 230 (M ⁺); 6.22 (d, $J = 11$ Hz), 6.90 (dt, $J = 11$, 7.9 Hz)	74
4	SO ₂ CF ₃	5c SO ₂ CF ₃	1600 cm ⁻¹ ; 236 (M ⁺); 6.38 (d, $J = 12.2$ Hz), 7.62 (d, $J = 12.2$ Hz)	73
5		5d SO ₂ CF ₃	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. ^bIsolated yield after purification by flash chromatography on silica gel using AcOEt/*n*-hexane. ^cIn every case stereochemical purity of product was ~100%, which was determined by ¹H and ¹³C NMR.



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

(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.; Oggawa, 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 (HSiEt₂Me/Cu(BF₄)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.

(8) Attempted reduction of 4a with HSiEt₂Me/Cu(BF₄)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.

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 Cu²⁺ and HSiR₃, 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-(BF₄)₂/HSiEt₂Me occurred readily. In contrast to the case of 4a, 8 gave a dimeric product, 10,¹⁰ as the major product.¹¹

$$MeO_{2}C \longrightarrow CO_{2}Me \xrightarrow{\text{HSIE1}_{2}Me/Cu(BF_{4})_{2}}{(1.2 \text{ equiv}) \over 1.\text{PrOH, } 20^{\circ}C, 3 \text{ h}}$$
8
$$MeO_{2}C \longrightarrow CO_{2}Me \xrightarrow{\text{MeO}_{2}C} \xrightarrow{\text{CO}_{2}Me}{(3)}$$
9
10
23%
56%

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

⁽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. HSiEt₂Me (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 NH₄Cl solution and the organic part was extracted into three portions of ether. The combined ethereal layer was washed with 5% aqueous NaHCO₃ and dried over MgSO₄. Purification by flash chromatography (SiO₂) using AcOEt/*n*-hexane (1/1) gave cis vinylic sulfone 5a (0.131 g, 72%).

⁽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 (CDCl₃) 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 C₁₂H₁₄O₈: 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.

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.

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Preparation and Structure of $[(C_8H_5)_4P][(C_5H_5)Mo(S_4)_2]$: 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 attention² 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 highvalent 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 $(C_5-H_5)_2Mo_2(CO)_6$ 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 $[(C_5H_6)_2Mo_2(CO)_6]$, and 0.24 g (0.57 mmol) of $(C_6H_6)_2PBr$ 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

mg) based on molyodenum (10) Anal. Calcd for $[(C_8H_5)_4P][(C_5H_5)Mo(CO)_2(S_2)](C_{31}H_{25}O_2PMoS_2,$ 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, CD₃CN): 5.24 ppm (s). Anal. Calcd for $[(C_8H_5)_4P][(C_5H_5)Mo(S_4)_2](C_{28}H_{25}PMoS_8, II): C, 46.03; H, 3.31.$ Found: C, 46.11; H, 3.27. ¹H NMR (200 MHz, CD₃CN): 5.05 ppm (s). (11) A definite proceeded into account of monty and mounted and a

⁽¹¹⁾ A red orange needle was sealed in epoxy and mounted and a Nicolet R3 diffractometer. Data were collected in the range $3.5^{\circ} < 2\theta < 45^{\circ}$ 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, $P_{2_1/c}$, Z = 4, a = 11.319 (5) Å, b = 18.186 (9) Å, c = 13.580 (4) Å, $\beta = 96.98$ (4)°, V = 2774 (2) Å³, R = 0.0352, $R_w = 0.0485$.