backbones of ring-substituted and/or side-chain-substituted vinylbenzene ligands.

2. Although the unsaturated side chains on the arene rings play a crucial role during the formation of the μ_3-arene clusters, they can easily be hydrogenated once the clusters have been formed.

3. From X-ray crystallographic studies considerable expansion but only small Kekulé-type distortions of the μ_3-η^2:η^2:η^2-coordinated arenes are evident. In solution hindered mutual rotation of the $(CpCo)_3$ triangles and C_6 rings takes place, which can be frozen out on the NMR time scale at low temperature.

4. The cluster **5b** exhibits a low chemical reactivity toward a variety of reagents directed to attack the metal cluster, the μ_3-arene ring, or the side chain of the latter. At present it is not yet clear if the deactivation is due to the electronic or steric influence of the $(CpCo)_3$ cluster.

5. The $(CpCo)_3(\mu_3\text{-arene})$ clusters mimic the hollow adsorption sites with $C_{3v}(\sigma_d)$ local symmetry found for benzene on some close-packed metal surfaces. However, distortion from a regular hexagonal geometry of the μ_3-arene rings appears to be much smaller in the molecular clusters.

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Registry No. 3, 69393-67-5; 4, 74811-00-0; **5a**, 132343-54-5; **5b**, 111769-97-2; **6a**, 132373-94-5; **6a**·$0.5C_7H_8$, 132373-95-6; **6b**, 132374-03-9; **7a**, 132373-96-7; **7b**, 132374-04-0; **8**, 132373-97-8; **9**, 132373-98-9; **10**, 132373-99-0; **11**, 132374-00-6; **12**, 132374-01-7; **13**, 105187-37-9; **14**, 33032-03-0; **15**, 132343-55-6; **16**, 132343-56-7; **17**, 132343-57-8; **18**, 132374-02-8; α-methylstyrene, 98-83-9; β-methylstyrene, 637-50-3; allylbenzene, 300-57-2; 1,1-diphenylethylene, 530-48-3; (*E*)-stilbene, 103-30-0; 4-methoxy-(*E*)-stilbene, 1694-19-5; 4-methylstyrene, 622-97-9; 4-methoxystyrene, 637-69-4; 1,1-diphenylpropene, 778-66-5; 4-allylanisole, 140-67-0; 4-phenyl-1-butene, 768-56-9; styrene, 100-42-5.

Supplementary Material Available: Listings of atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and deviations from least-squares planes for **5b** and **6a** and a packing diagram of **6a** (12 pages); listings of observed and calculated structure factors for **5b** and **6a** (21 pages). Ordering information is given on any current masthead page.

Synthesis and Reaction Chemistry of the Readily Available Molybdenum S_2O Complex $[MoO(S_2CNEt_2)_2(S_2O)]$

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The synthesis (by S_2O transfer and S_2 complex oxidation) and characterization by X-ray diffraction of $MoO(S_2CNEt_2)_2(S_2O)$ (1) is reported (monoclinic, $P2_1/n$, $a = 9.4749$ (15) Å, $b = 21.9780$ (32) Å, $c = 9.6714$ (16) Å, $\beta = 107.225$ (13)°, $Z = 4$, $R(F) = 3.46\%$). S_2O is bound to the metal in a side-on manner through both of the sulfurs. The geometry around the metal is a distorted pentagonal bipyramid with both sulfurs of S_2O in the equatorial plane. In a preliminary reactivity study, 1 has been shown to effect sulfur and oxygen transfer to triphenylphosphine. Complex 1 can also be used as a template for thiosulfinate ester (RSS(O)R′) synthesis and as a reagent for oxidative coupling of carbanions.

Introduction

Recently, we have been exploring the reactions of disulfur monoxide (S_2O) with a variety of transition-metal complexes.[1] One goal of this project has been to develop practical syntheses of stable S_2O complexes to enable us to explore their reaction chemistry. If a transition-metal S_2O complex is to be used as a stoichiometric reagent in an organic transformation, it must be readily synthesized on a reasonable scale from inexpensive starting materials. The S_2O complexes that had been reported previously did not appear to fit all these criteria.[2] We have now succeeded in synthesizing $MoO(S_2CNEt_2)_2(S_2O)$ (1) by S_2O transfer and S_2 complex oxidation, and 1 has been char-

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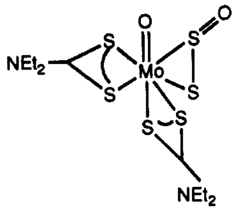
acterized by X-ray diffraction. We also report some results on the reaction chemistry of 1.



1

Experimental Section

General Considerations. All infrared spectra were recorded on Perkin-Elmer 1330 or 1620 spectrophotometers. Nuclear magnetic resonance spectra were obtained on a Varian VXR-200 instrument. All absorptions are expressed in parts per million relative to residual protonated solvent. Melting points were determined on a Mel-Temp melting point apparatus and are reported uncorrected. Combustion analyses were performed by Atlantic Microlab, Inc. High-resolution mass spectra were obtained at the Midwest Center for Mass Spectrometry at the University of Nebraska—Lincoln. Tetrahydrofuran and diethyl ether were distilled from sodium/benzophenone under nitrogen immediately prior to use. Dichloromethane was distilled from calcium hydride immediately prior to use. All reactions were carried out under an atmosphere of dry nitrogen unless otherwise noted. $Mo_2O_3(S_2CNEt_2)_4$ (2),[3] $MoO(S_2CNEt_2)_2$ (4),[4] and 4,5-diphenyl-3,6-dihydro-1,2-dithiin 1-oxide (3)[1c] were synthesized according to literature procedures.

Synthesis of $MoO(S_2CNEt_2)_2S_2$ (5). The following is a modification of a literature procedure.[5] Molybdenum dimer 2 (7.56 g, 9.1 mmol) was dissolved in benzene/acetone (1:1, 100 mL), and sulfur (4.66 g, 18.2 mmol) was added to the solution. The solution was stirred for 8 h, during which time it turned green. The solution was then filtered and the solvent removed by rotary evaporation and high vacuum. The crude product was chromatographed on silica gel (230–400 mesh, CH_2CL_2) to give 5 as a green solid (6.56 g, 76%): mp 137–140 °C; IR ($CDCl_3$, cm^{-1}) 1625, 1510, 1290, 1160; ^1H NMR ($CDCl_3$, δ) 4.40–3.78 (m, 6 H), 3.50 (m, 2 H), 1.40 (t, J = 7.0 Hz, 9 H), 1.13 (t, J = 7.0 Hz, 3 H).

Synthesis of $MoO(S_2CNEt_2)_2(S_2O)$ (1) from 5. Disulfur compelx 5 (6.56 g, 13.9 mmol) was dissolved in tetrahydrofuran (175 mL). *m*-Chloroperoxybenzoic acid (85%; 3.57 g, 20.8 mmol; 60% mCPBA can also be used) was also dissolved in tetrahydrofuran (25 mL), and this solution was added dropwise to 5. The solution quickly changed to orange-brown. After 20 min TLC analysis (silica gel, CH_2Cl_2) indicated the reaction had gone to completion. The reaction mixture was placed in an ice bath, and petroleum ether (700 mL) was added. The product 1 precipitated as an orange-brown solid (3.78 g, 56%), which was isolated by vacuum filtration: mp 152–153 °C; IR ($CDCl_3$, cm^{-1}) 2960, 2918, 1518, 1445, 1360, 1281, 1212, 1158, 1078; ^1H NMR ($CDCl_3$, δ) 4.05–3.70 (m, 6 H), 3.52 (m, 2 H), 1.45–1.25 (m, 9 H), 1.08 (t, J = 7.0 Hz, 3 H); FAB HRMS (butylamine matrix, *m/e*) calcd for $M + H^+$ $C_{10}H_{21}N_2O_2S_6{}^{92}Mo$ 484.8987, found 484.8992 $M - S_2O$ 403.9533. Anal. Calcd for $C_{10}H_{20}N_2O_2S_6Mo$: C, 24.59; H, 4.10; S, 39.34. Found: C, 24.46; H, 4.18; S, 39.18.

Synthesis of 1 from 2. Molybdenum oxo dimer 2 (0.073 g, 0.087 mmol) was dissolved in CH_2Cl_2 (5 mL). Dithiin 1-oxide 3 (0.090 g, 0.31 mmol) was added to this solution, and the reaction was monitored by TLC (silica gel, 20:1 CH_2Cl_2/Et_2O). After the mixture was stirred for 4 h, the solvent was removed by rotary evaporation and high vacuum. The crude product was chromatographed on silica gel (230–400 mesh). Elution with petroleum ether/CH_2Cl_2 (1:1) yielded 2,3-diphenylbutadiene (0.056 g, 87%; identical by spectroscopic comparison with an authentic sample).[6] Elution with CH_2Cl_2/Et_2O (20:1) yielded 1 (0.026 g, 30%), identical by spectroscopic comparison with the material isolated above.

Synthesis of 1 from 4. Molybdenum oxo monomer 4 (0.050 g, 0.12 mmol) was dissolved in CH_2Cl_2 (10 mL) and 3 (0.137 g, 0.48 mmol) was added. After it was stirred for 5.5 h, the solution had turned orange-brown. The solvent was removed by rotary evaportion and high vacuum. The crude product was chromatographed on silica gel. Elution with CH_2Cl_2/Et_2O (20:1) yielded 1 (0.045 g, 75%), identical by spectroscopic comparison with the material isolated above.

Reaction of 1 with PPh_3 at 25 °C. S_2O complex 1 (0.105 g, 0.215 mmol) and PPh_3 (0.057 g, 0.215 mmol) were dissolved in THF (5 mL), and the solution was stirred under nitrogen for 0.5 h. The solution changed from orange-brown to reddish-purple. The solvent was removed by rotary evaporation and high vacuum. The crude product was triturated with diethyl ether (6 × 5 mL) to remove PPh_3S (0.038 g, 60%), identical with an authentic sample (Aldrich) by ^1H NMR and chromatographic comparison. The ether-insoluble material (0.086 g, 96%) was identical with an authentic sample of dimer 2[3] by ^1H NMR and chromatographic comparison.

Reaction of 1 with PPh_3 (THF Reflux). Molybdenum S_2O complex 1 0.105 g, 0.22 mmol) was dissolved in THF (5 mL) along with PPh_3 (0.059 g, 0.22 mmol). The solution was refluxed overnight and the solvent then removed by rotary evaporation and high vacuum. The crude product was chromatographed on a 1.0-mm silica gel preparative TLC plate (CH_2Cl_2). PPh_3S (0.043 g, 65%; R_f 0.8; identical by TLC and spectroscopic comparison with an authentic sample (Aldrich)) was isolated. Disulfur complex 5 (0.033 g, 32%; R_f 0.4; identical with an authentic sample[5] by spectroscopic comparison) and PPh_3O (0.011 g, 18%; R_f 0; identical with an authentic sample (Aldrich) by spectroscopic comparison) were also recovered. We know PPh_3O is not a contaminant in our PPh_3, and we also ran the control experiment of heating PPh_3 in THF in the absence of 1 and noted no PPh_3O formation.

Reaction of 1 with Phenyllithium/Iodomethane. Disulfur monoxide complex 1 (0.300 g, 0.60 mmol) was dissolved in THF (30 mL), and the solution was cooled to −78 °C. Phenyllithium (0.33 mL of a 2.0 M solution in cycloihexane/diethyl ether, 0.66 mmol) was added to the solution containing 1 dropwise via syringe. After it was stirred 1.25 h, the solution had turned green. Iodomethane (0.045 mL, 0.66 mmol) was added, and the solution was warmed to 25 °C over 0.5 h. The solvent was removed by rotary evaporation (40 °C) and high vacuum. The crude product was then chromatographed on silica gel (230–400 mesh). Elution with petroleum ether yielded biphenyl (0.031 g, 32%), identified by spectroscopic comparison with an authentic sample (Aldrich), followed by a foul-smelling light yellow oil (0.047 g, 46%), which by ^1H NMR comparison with literature data[7] was a 1:1.2:1 (integration of SMe resonances) mixture of 6, 7, and 8. Analysis of this mixture by GC/MS showed only the following (*m/e*): 6, M^+ 156 (100), $M - CH_3$ 141 (60), $M - SCH_3$ 109 (50), $M - SSCH_3$ 77 (40); 8, M^+ 188 (100), $M - SCH_3$ 141 (50). Elution with petroleum ether/CH_2Cl_2 (1:1) yielded 5 (0.141 g, 49%), identical with an authentic sample[5] by spectroscopic comparison.

Reaction of 1 with Lithium Diphenylcuprate/Iodomethane. Cuprous bromide (0.032 g, 0.22 mmol) was added to diethyl ether (5 mL), and the solution was cooled to 0 °C. Phenyllithium (0.22 mL of a 2.0 M solution in cyclohexane/diethyl ether, 0.44 mmol) was added by syringe, and the solution quickly turned brown. The solution was stirred for 0.5 h, and then 1 (0.100 g, 0.205 mmol in THF (10 mL)) was added to the cuprate and the solution was stirred for 4 h, after which time the solution was green. Iodomethane (0.014 mL, 0.22 mmol) was added, and the solution was warmed to 25 °C over 0.5 h. The solvent was removed by rotary evaporation and high vacuum. The crude product was chromatographed on a 1.0-mm silica gel preparative TLC plate (1:1 petroleum ether/CH_2Cl_2). Biphenyl (0.024 g, 71%; R_f 0.8) was isolated as a white solid identical by spectroscopic comparison

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Table I. Crystallographic Data for $Mo(O)(S_2CNEt_2)_2(S_2O)$

(a) Crystal Parameters

formula	$C_{10}H_{20}Mo-N_2O_2S_6$	V, Å^3	1923.6 (5)
		Z	4
space group	$P2_1/n$	cryst dimens, mm	0.26 × 0.32 × 0.34
cryst syst	monoclinic	D(calc), g/cm^3	1.687
a, Å	9.4749 (15)	μ(Mo Kα), cm^{-1}	12.95
b, Å	21.9780 (32)	temp, °C	23
c, Å	9.6714 (16)		
β, deg	107.225 (13)		

(b) Data Collection

diffractometer	Nicolet R3m
monochromator	graphite
scan technique	Wyckoff
radiation	Mo Kα (λ = 0.71073 Å)
2Θ scan range, deg	4–55
data collected (hkl)	±13,+29,+13
no. of rflns collected	5898
no. of indpt rflns	5479
R(merg), %	2.00
no. of indpt rflns obsd, $F_o > 5\sigma(F_o)$	4075
std rflns	3 std/197 rflns
var in stds, %	<1

(c) Refinement

$R(F)$, %	3.46	$\Delta(\rho)$, e Å^{-3}	0.369
R(wF), %	4.00	N_o/N_v	21.4
Δ/σ (max)	0.009	GOF	1.126

with an authentic sample (Aldrich) and identified as biphenyl by GC/MS (m/e): M$^+$ 154 (100), 77 (10). Disulfur complex **5** (R_f 0.4) was also isolated (0.042 g 45%) and found to be identical with an authentic sample[5] by spectroscopic comparison.

In a control experiment, where all conditions were kept identical with those above except the addition of **1** was ommitted, biphenyl was isolated in only 16% yield.

X-ray Data Collection for $Mo(O)(S_2CNEt_2)_2(S_2O)$. Crystal data, details of the data collection, and refinement parameters for **1** are collected in Table I. A crystal was mounted on a glass fiber with epoxy cement. The unit-cell parameters were obtained from the least-squares fit of 25 reflections (20° ≤ 2θ ≤ 25°). Preliminary photographic characterization showed $2/m$ Laue symmetry, and systematic absences in the diffraction data uniquely established the space group as $P2_1/n$. No absorption correction was applied (well-shaped crystal, low μ).

Structure Solution and Refinement. The structure was solved by direct methods. The remaining non-hydrogen atoms were located from subsequent difference Fourier syntheses. All hydrogen atoms are included as idealized isotropic contributions. All non-hydrogen atoms were refined with anisotropic thermal parameters. All computer programs and the sources of the scattering factors are contained in the SHELXTL program library (version 5.1 by G. Sheldrick, Nicolet Corp., Madison, WI).

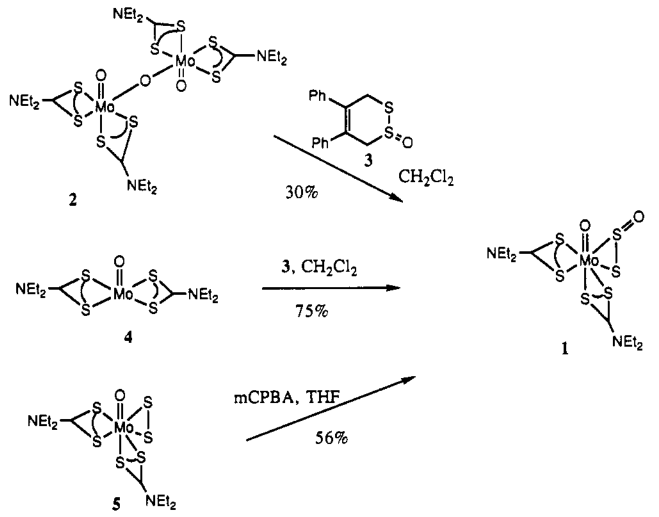
Results and Discussion

Syntheses of S_2O Complex 1. Two of our synthetic routes (Scheme I) to **1** begin with the molybdenum dimer $Mo_2O_3(S_2CNEt_2)_4$ (**2**), which is readily available on a large scale.[3] In previous work, we had shown that 4,5-diphenyl-3,6-dihydro-1,2-dithiin 1-oxide (**3**) could serve as a disulfur monoxide source via a transition-metal-assisted retro Diels-Alder reaction.[1a,c] When **2** was treated with 2 equiv of **3**, the molybdenum S_2O complex **1** was isolated, albeit in only 30% yield.

From our earlier studies,[1c] we also knew that **3** was susceptible to additional oxidation, and we suspected that **2** was oxidizing **3** to some extent before it could function as a S_2O source. To avoid this potential problem, we prepared **1** from the reaction of molybdenum oxo monomer **4**[4] with **3**. This did indeed produce **1** in a reasonable yield (75%); however, **3** reacted very sluggish with **4** and 4 equiv of **3** was required to produce this yield of **1** after 6 h.

Where disulfur (S_2) complexes are available, the simplest route to $\eta^2(S,S)$-S_2O complexes is via oxidation (assuming the complexed sulfur can be oxidized without competing oxidative decomposition of the S_2 complex). Molybdenum S_2 complex **5** has been synthesized by different routes in several groups previously.[2g,5] We have chosen to use the method of Rakowski-DuBois[5a] to produce **5**, and we find that it can be synthesized on a large scale (15 mmol) in good isolated yield (76%). When **5** was treated with m-chloroperoxybenzoic acid (mCPBA) in tetrahydrofuran, we found that **1** could be isolated as an orange-brown solid (56%) by a simple precipitation upon addition of petroleum ether. S_2O complex **1** appears to be quite stable in air at 25 °C.

Scheme I



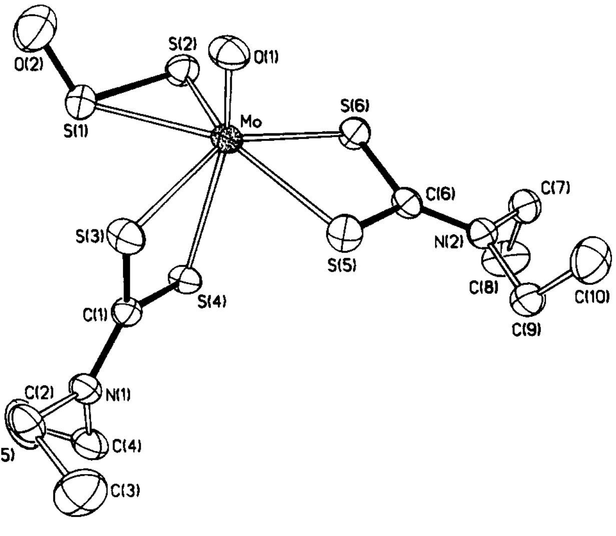


Figure 1. Molecular structure of **1**.

Structural Aspects of 1. Only three of the known S_2O complexes have been characterized crystallographically;[2a,d,g] thus, we were interested in obtaining structural data on complex **1** (Figure 1). The S–S bond length in **1** is 2.029 (1) Å, which is slightly longer than the S–S bond in the S_2 complex[2g] **5** (2.010 (5) Å) and significantly longer than the S–S bond in S_2O (1.884 Å).[8] The S–S bond length in **1** is intermediate when compared to those in other known manganese[2d] (2.013 (8) Å) and molybdenum[2g] (2.094 (5) Å) S_2O complexes and slightly shorter than the S–S bond in the other known molybdenum oxo S_2O complex (2.050 (3) Å).[2a] The Mo–S bonds show the same asymmetry (Mo–S(1) = 2.500 (1) Å and Mo–S(2) = 2.401 (1) Å) that

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Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for $Mo(O)(S_2CNEt_2)_2(S_2O)$

	x	*y*	*z*	U^a
Mo	7264.1 (3)	8833.2 (1)	2754.3 (3)	32.3 (1)
S(1)	7040 (1)	7786 (1)	3676 (1)	46 (1)
S(2)	5683 (1)	7998 (1)	1684 (1)	45 (1)
S(3)	9586 (1)	8765 (1)	4899 (1)	41 (1)
S(4)	9415 (1)	8285 (1)	2072 (1)	36 (1)
S(5)	8568 (1)	9774 (1)	2380 (1)	41 (1)
S(6)	6199 (1)	9189 (1)	268 (1)	39 (1)
O(1)	6336 (3)	9165 (1)	3787 (3)	47 (1)
O(2)	6314 (4)	7769 (2)	4806 (4)	82 (2)
N(1)	11883 (3)	8238 (1)	4290 (3)	38 (1)
N(2)	7594 (3)	10164 (1)	−364 (3)	37 (1)
C(1)	10483 (3)	8402 (2)	3823 (3)	33 (1)
C(2)	12782 (4)	8337 (2)	5799 (4)	46 (1)
C(3)	13675 (6)	8911 (2)	5961 (5)	72 (2)
C(4)	12608 (4)	7928 (2)	3338 (4)	51 (1)
C(5)	12465 (6)	7254 (2)	3327 (5)	70 (2)
C(6)	7465 (4)	9776 (2)	612 (4)	34 (1)
C(7)	6617 (4)	10151 (2)	−1859 (4)	48 (1)
C(8)	7248 (5)	9789 (3)	−2839 (4)	69 (2)
C(9)	8739 (4)	10640 (2)	−12 (4)	44 (1)
C(10)	8213 (6)	11214 (2)	548 (5)	62 (2)

[a] Equivalent isotropic *U*, defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

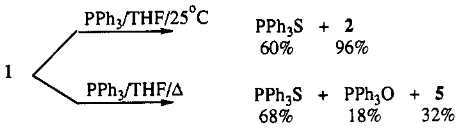
Table III. Selected Bond Distances and Angles for $Mo(O)(S_2CNEt_2)_2(S_2O)$

(a) Bond Distances (Å)			
Mo–S(1)	2.500 (1)	Mo–S(2)	2.401 (1)
Mo–S(3)	2.542 (1)	Mo–S(4)	2.615 (1)
Mo–S(5)	2.490 (1)	Mo–S(6)	2.444 (1)
Mo–O(1)	1.681 (3)	S(1)–S(2)	2.029 (1)
S(1)–O(2)	1.454 (4)	C(6)–S(5)	1.720 (3)
C(1)–S(3)	1.721 (4)	C(6)–S(6)	1.726 (3)
C(1)–S(4)	1.716 (3)	C(6)–N(2)	1.305 (5)
C(1)–N(1)	1.319 (4)	S(1)–O(2)	1.454 (4)
(b) Bond Angles (deg)			
S(1)–Mo–S(2)	48.9 (1)	S(2)–Mo–S(3)	125.8 (1)
S(1)–Mo–S(3)	78.4 (1)	S(2)–Mo–S(4)	88.4 (1)
S(1)–Mo–S(4)	79.7 (1)	S(2)–Mo–S(5)	147.7 (1)
S(1)–Mo–S(5)	156.2 (1)	S(2)–Mo–S(6)	78.3 (1)
S(1)–Mo–S(6)	126.2 (1)	S(2)–Mo–O(1)	102.6 (1)
S(1)–Mo–O(1)	94.2 (1)	S(3)–Mo–S(4)	68.2 (1)
S(4)–Mo–S(5)	83.6 (1)	S(3)–Mo–S(5)	79.7 (1)
S(4)–Mo–S(6)	91.4 (1)	S(3)–Mo–S(6)	145.8 (1)
S(4)–Mo–O(1)	159.1 (1)	S(3)–Mo–O(1)	91.1 (1)
S(5)–Mo–S(6)	70.7 (1)	S(6)–Mo–O(1)	108.0 (1)
S(5)–Mo–O(1)	95.4 (1)	Mo–S(1)–S(2)	63.0 (1)
Mo–S(2)–S(1)	68.1 (1)	Mo–S(1)–O(2)	113.6 (2)
S(2)–S(1)–O(2)	114.3 (1)	S(3)–C(1)–S(4)	114.5 (2)
S(5)–C(6)–S(6)	111.9 (2)	Mo–S(3)–C(1)	89.8 (1)
Mo–S(5)–C(6)	88.0 (1)	Mo–S(4)–C(1)	87.5 (1)
Mo–S(6)–C(6)	89.3 (1)		

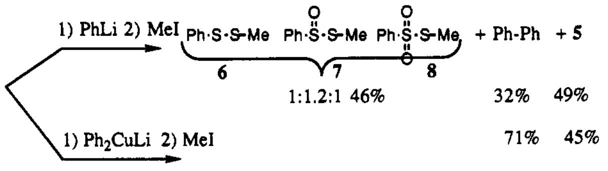
has been seen in other S_2O complexes.

The S–O bond in the complexed S_2O here (1.454 (4) Å) is considerably shorter than in any other S_2O complex (1.482 (6),[2a] 1.482 (9),[2g] 1.521 (13) Å[2d]). The metal in complex 1 has the highest formal oxidation state of any known S_2O complex. Therefore, one would predict that the S_2O in this complex is binding primarily as a donor rather than as a strong π-acceptor ligand. More $d\pi$ donation from the metal into a π antibonding orbital with respect to S–S would be expected to lengthen the S–S as well as S–O bonds. The π^* LUMO for S_2O is bonding with respect to the unoxidized sulfur and the oxygen. As this orbital is populated, one would also expect S–S–O bond angles to decrease. While noting that many times it is difficult to separate steric from electronic influences on structure, when one compares our molybdenum oxo S_2O complex with the other known molybdenum oxo S_2O complex, the trends predicted from these bonding arguements hold. $Me_5CpMo(O)CH_3(S_2O)$[2a] (S–S = 2.050 (3) Å, S–O = 1.482 (6) Å, S–S–O = 113.3 (3)°) has longer S–S and S–O bond lengths and a smaller S–S–O bond angle than 1 (S–S = 2.029 (1) Å, S–O = 1.454 (4) Å, S–S–O = 114.3 (1)°). Similar arguments have been made for η^2-SO_2 complexes.[9]

Reaction Chemistry of 1. In a preliminary investigation of the reaction chemistry of 1 we have found that it will effect sulfur transfer[10] to triphenylphosphine at 25°C, yielding PPh_3S (60%) and 2[3] (96%). By thin-layer chromatography analysis, 4 appears to be the first molybdenum complex present in solution after sulfur transfer but before workup. We made no attempt to exclude oxygen from this reaction on workup, which probably accounts for the isolation of 2 as the molybdenum-containing product. When 1 was refluxed in tetrahydrofuran with PPh_3, some PPh_3O (18%)[11] and 5 (32%) were recovered in addition to PPh_3S (65%). No production of 5 was noted in the 25 °C reaction between 1 and PPh_3. The isolation of 5 from the thermal reaction could conceivably result from transfer of oxygen from either molybdenum or sulfur to PPh_3.



We have also been investigating transition-metal-mediated thiosulfinate ester synthesis,[1b,e] and we have some preliminary results from our attempts to use 1 as a template for acyclic thiosulfinate ester synthesis.[12] Thiosulfinate esters are a class of organosulfur compounds that have been shown to exhibit a wide range of biological activities.[13] We envisioned subjecting S_2O complexes to sequential treatment with nucleophiles and electrophiles as a route to thiosulfinate ester synthesis. When 1 was treated with phenyllithium followed by iodomethane, we did indeed isolate products (6–8) of nucleophile/electrophile reactions with S_2O (46% combined yield).[7] Compounds 6 and 8 are disproportionation products from 7, and their isolation is not surprising given the known ease of disproportionation of acyclic thiosulfinate esters.[14] When care was taken to avoid heat in the solvent removal from the phenyllithium/iodomethane reaction, 7 was isolated (28%) with only a trace of 6 and 8 noted by ^1H NMR spectroscopy.[7] We see no evidence by ^1H NMR measurements for the production of the other possible regioisomer, PhSS(O)Me, which would result from initial nucleophilic attack at the nonoxidized sulfur.[7]



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What was most surprising about this reaction was that we isolated some biphenyl (32%) (the product of an S_2O-complex-induced oxidative carbon–carbon coupling?) as well as complex **5** (49%). When **1** was treated with Ph_2CuLi followed by iodomethane, we saw no **6**, **7**, or **8**, and instead, we isolated only biphenyl (71%) along with **5** (45%). Oxidative coupling of carbanions by Cu(II)[15] and Fe(III)[16] has been reported previously. The formal oxidation state of the molybdenum in **1** is +4; thus, this oxidative-coupling reactivity may not be surprising here. The recovery of **5** from these reactions poses interesting questions about the mechanism of this oxidative coupling. We do not know the fate of the oxygen lost from **1**. Oxygen labeling studies will be required to determine whether the sulfur-bound oxygen or the molybdenum-bound oxygen is lost. Future work will involve investigation of **1**'s ability to effect S or O transfer to alkenes and the possible use of **1** to effect oxidative coupling of enolates as well as the synthesis of other S_2O complexes in lower formal oxidation states.

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Supplementary Material Available: Tables of all bond lengths and angles, thermal parameters, and calculated hydrogen positions (4 pages); a table of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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[16] Ferric chloride oxidative coupling of phenols has been extensively studied. For a review see: Kametani, T.; Fukumoto, K. *Synthesis* **1972**, 657. For an example of ferric chloride mediated coupling of carbanions see: Frazier, R. H.; Harlow, R. L. *J. Org. Chem.* **1980**, *45*, 5408.

Synthesis and Thermolysis of Di- and Triarsenic Complexes of Chromium. Crystal Structure of $[CpCr(CO)_2]_2As_2$

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The cothermolysis of $[CpCr(CO)_3]_2$ (Cp = η^5-C_5H_5) with excess gray arsenic in refluxing toluene for 1–1.5 h resulted in the isolation of $Cp_2Cr_2(CO)_4(\mu$-η^2-$As_2)$ (**2**), $CpCr(CO)_2(\eta^3$-$As_3)$ (**3**), $Cp_2Cr_2(CO)_4(Cr{\equiv}Cr)$ (**4**), and $Cp_2Cr_2AsO_5$ (**6**) in 20.4, 14.2, 5.3, and 13.6% yields, respectively. The reaction when extended to 16 h gave **3**, $Cp_2Cr_2As_5$ (**5**), **6**, and $Cp_5Cr_5As_4O_8$ (**7**) in 5, 22, 39, and 8% yields, respectively. In refluxing xylene for 6 h, the reaction produced **3** (3%) and **7** (15%). **4** likewise reacted with excess elemental arsenic in refluxing toluene, yield **2** (18.5%), **3** (31.9%), and **6** (38.3%) after 1 h but only **2** (18.6%) and **6** (44.2%) after 5 h. Thermal degradation of **2** at 110 °C for 16 h yielded **6** (46.5%) and **7** (28%). **3** also degrades to **5**, but at a much slower rate. **2** crystallizes as dark purple needles. Crystal data: space group $C2/c$ (No. 15), $Z = 4$, $a = 15.551$ (3) Å, $b = 7.453$ (1) Å, $c = 13.446$ (2) Å.

Introduction

Since the first synthesis of the arsenic complexes $Co_2(CO)_6As_2$ and $Co(CO)_3As_3$ from the reaction of $Co_2(CO)_8$ with $AsCl_3$ and *cyclo*-$(MeAs)_5$, respectively,[1] and again later from the reaction of $Na[Co(CO)_4]$ with AsX_3 (X = Cl, Br, I),[2] there has been a gradual development in the role of these As_2 and As_3 units as ligands in complexes of other transition metals. Thus, diarsenic complexes have been derived from the reactions of the M—M-bonded $[CpM(CO)_3]_2$ dimers with *cyclo*-$(PhAs)_6$ (for M = Mo, Cp = C_5H_5),[3] with *cyclo*-$(MeAs)_5$ (for M = Mo, Cp = MeC_5H_4),[4] and with metallic As (for M = Mo, W, Cp = C_5H_5),[5] M≡M-bonded $[(C_5Me_5)Mo(CO)_2]_2$ with As_4S_4[6] and yellow As_4,[7] $CpW(CO)_3H$ with *cyclo*-$(PhAs)_6$,[3] $Na_2W_2(CO)_{10}$ or $W(CO)_5(THF)$ with $AsCl_3$,[8] $[(C_5Me_5)Mn(CO)_2(THF)]$ with AsH_3,[9] metal carbonyl fragment abstraction of $Cp(CO)_2MAs[Cr(CO)_5]_2$ (M = Mo, W), and reductive coupling of $Cp(CO)_2Mn_2AsCl$.[10] *cyclo*-As_3 complexes are less common. Only two other examples are known, viz. $(C_5Me_5)Mo(CO)_2As_3$[6] and the triple-decker $[(triphos)(Co)(As_3)Co(triphos)](PPh_4)_2$ complexes formed from the reaction

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