equilibrium process. The extreme sensitivity of the reaction to oxygen suggests that an electron-transfer process may be involved.[14]

These results establish the identity of the "Kharasch reagent" as a mixture of activated zero-valent iron and Grignard reagent.[15] Using this reagent, it is now possible for the first time to regioselectively prepare endocyclic "thermodynamic" dienol ethers from the corresponding enones. In some cases, it is also possible to prepare the exocyclic "thermodynamic" dienol ethers regioselectively using Fe(0) alone.

Now that both endocyclic and exocyclic "thermodynamic" dienol ethers are readily available, we have begun to explore their utility in a variety of new synthetic endeavors. The results of these studies will be reported in due course.

Acknowledgment. We thank the National Cancer Institute for generous financial support of our program.

(14) Such processes have been implicated in other reactions involving ferric chloride and Grignard reagents. See, for example: (a) Tamura, M.; Kochi, J. K. *Synthesis* **1971**, 303. (b) Ashby, E. C. *Pure Appl. Chem.* **1980**, *52*, 545.

(15) Mixtures of products (with 1,2-addition predominant) were obtained when enone was added to a mixture of Grignard reagent plus iron(0). It is on this basis that we formulate the "reagent" as a mixture of the two species operating in tandem rather than a reaction product of Grignard reagent and iron(0).

Synthesis and Structures of Molecular Sulfo Salts $(CH_3C_5H_4)_3Ti_2OAsS_3$, $[Mo_2O_2As_4S_{14}]^{2-}$, and $[Mo_4O_4As_4S_{14}]^{4-}$

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Sulfo salts are a large class of minerals which are comprised of anionic trigonal pyramidal XE_3 subunits where X = As, Sb, Bi and E = S, Se, Te.[2] These pyramidal fragments occur in the lattice as both isolated anions or as interconnected rings, chains, and nets of XE_3 subunits. In this report we describe the synthesis and structural characterization of the first molecular sulfo salts starting from the minerals orpiment, As_2S_3(**1**), and realgar, As_4S_4 (**2**).

It has long been known that pale yellow solutions result when **1** is treated with aqueous sodium sulfide (1.5 equiv/As_2S_3),[3,4] and our results support the view that this procedure affords the AsS_3^{3-} anion.[5] Addition of these aqueous solutions to acetone slurries of $(MeCp)_2TiCl_2$ (MeCp = η^5–$CH_3C_5H_4$) leads to rapid formation of a dark green precipitate.[6] Filtration of CH_2Cl_2 extracts of these precipitates through silica gel and dilution of the effluent with hexanes afforded a dark brown crystalline product, which by fast atom bombardment mass spectroscopy and microanalysis had the formula $(MeCp)_3Ti_2AsS_3O$ (**3**) (42% yield).[7] The oxygen is presumed to arise from the silica gel workup. The cleavage of a MeCp ring was indicated and is known to occur in other reactions of Cp_2TiCl_2 with anionic chelates.[8] The ^{1}H NMR spectrum of **3** was particularly informative as it established the presence of an equivalent pair of MeCp groups while the unique MeCp is bisected by the only symmetry plane present in the molecule.[9] This was confirmed by a single-crystal X-ray diffraction study on crystals of **3** grown by the slow evaporation of a saturated CH_2Cl_2 solution.[10]

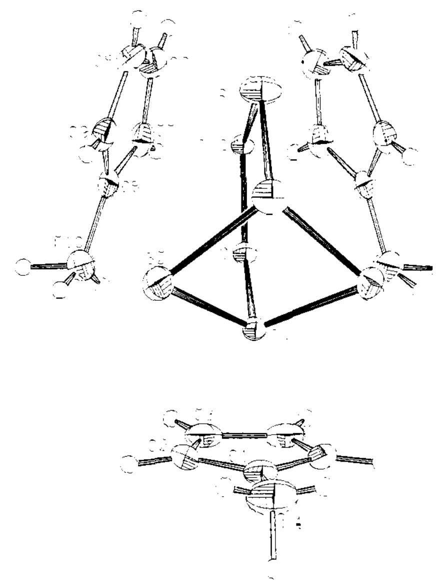

Figure 1. ORTEP drawing of $(MeCp)_3Ti_2OAsS_3$ showing the labeling scheme for all non-hydrogen atoms (35% probability boundaries, hydrogen atoms are assigned arbitrary thermal coefficients). Some selected bond angles for **3** are as follows: Ti(1)–O–Ti(2) 145.2 (1)°, S(2)–Ti(1)–S(2)′ 93.71 (3)°, S(1)–As–S(2) 106.78 (2)°, S(2)–As–S(2)′ 96.54 (3)°.

The molecular structure of **3** is shown in Figure 1. The molecule possesses approximate C_s symmetry with the mirror plane defined by both titanium atoms, the oxygen, arsenic, and sulfur(1). This is the first example of a molecular metal complex of an XS_3 ligand (X = pnictnide) and the structural parameters for the arsenic trisulfide group (As–S(1) 2.1922 (10) Å, As–S(2) 2.2621 (7) Å) are similar to those in orpiment itself.[11] The oxygen atom links the two titanium centers and the differing Ti–O distances (Ti(1)–O 1.794 (2) Å, Ti(2)–O 1.872 (2) Å) reflect the relative π-acidities expected for these electron-deficient titanium atoms.[12] This same compound can be prepared in lower yields from $(MeCp)_2Ti(CO)_2$ and As_4S_4 employing a workup as described above.[13]

(1) Alfred P. Sloan Fellow 1983–1985, Camille and Henry Dreyfus Teacher-Scholar 1983–1988.

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(5) Behrens, H.; Glasser, L. *Z. Anorg. Allg. Chem.* **1955**, *278*, 174–83. The $(NH_4)_3AsS_3$ as reported here was found to be unstable above −78 °C.

(6) In a typical reaction 125 mg (0.5 mmol) of **1** was added to a stirred solution of 360 mg (1.5 mmol) of $Na_2S{\cdot}9H_2O$ in 10 mL of H_2O. The resulting pale yellow solution was added to an acetone (25 mL) slurry of $(MeCp)_2TiCl_2$ (550 mg, 2.0 mmol) and stirred for 30 min. Yield: 250 mg.

(7) Anal. Calcd for $C_{18}H_{21}TiOS_3As$: C, 41.55; H, 4.07; Ti, 18.41. Found: C, 41.85; H, 4.40; Ti 18.05.

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(9) ^{1}H NMR of **3** (360 MHz, CD_2Cl_2) δ 6.29(m, 2 H), 6.22(m, 2 H), 6.21(m, 2 H), 6.05(m, 2 H), 5.92(m, 2 H), 5.76(m, 2 H), 2.18(s, 3 H), 2.06 (s, 6 H).

(10) Compound **3** crystallizes in the monoclinic space group $P2_1/m$ with dimensions a = 10.404 (6) Å, b = 12.932 (9) Å;, and c = 7.491 (6) Å; β = 98.82 (6)°; V = 996 (1) Å^3; Z = 2. The data was collected on a Syntex $P2_1$ automated four-circle diffractometer at ambient temperatures with monochromatized Mo Kα (λ = 0.71069 Å) radiation. Of the 2681 reflections collected 2092 independent reflections with $I > 2.58\sigma(I)$ were used in the structure solution and refinement, which converged to R = 2.7% and R_W = 4.0% with all non-hydrogen atoms refined anisotropically and all hydrogen atoms refined isotropically.

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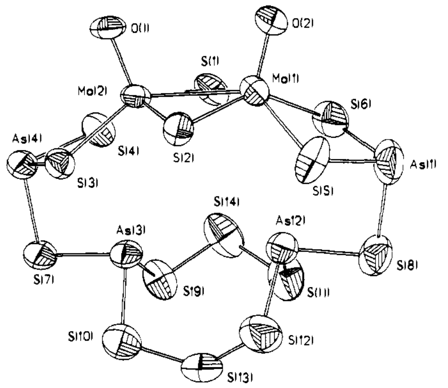


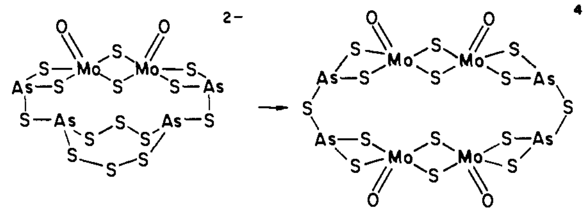
Figure 2. ORTEP drawing of $Mo_2O_2As_4S_{14}^{2-}$ showing the labeling scheme for the dianion (35% probability boundaries). Bond distances subtended at the molybdenums (Å): Mo(1)–Mo(2) 2.828 (3), Mo(1)–S(1) 2.320 (5), Mo(1)–S(2) 2.294 (6), Mo(1)–S(5) 2.441 (5), Mo(1)–S(6) 2.447 (8), Mo(1)–O(2) 1.688 (14), Mo(2)–S(1) 2.301(7), Mo(2)–S(2) 2.308 (4), Mo(2)–S(3) 2.455 (6), Mo(2)–S(4) 2.448 (6), Mo(2)–O(1) 1.718 (11).

We have also succeeded in isolating a stable salt of AsS_3^{3-} in crystalline form.[14] Solutions prepared from **1** and aqueous Na_2S when treated with ethanolic PPNCl (PPN = bis(triphenylphosphine)iminium), followed by removal of the ethanol, afforded colorless needles of $(PPN)_3AsS_3$ in 91% yield.[15] This salt is bronze colored when dry and its solutions are fairly stable even upon prolonged exposure to air. The conductivity of acetonitrile solutions of $(PPN)_3AsS_3$ is consistent with a 3:1 electrolyte.[16,17]

The fact that **1** is so readily attacked by sulfide ion prompted us to examine the reactions of **1** and **2** with the transition metal nucleophile MoS_4^{2-}.[18] While reactions occur in both cases, so far we have only succeeded in obtaining a pure crystalline product from the reaction of **2** with MoS_4^{2-}. Treatment of acetonitrile solutions of $(Ph_4P)_2MoS_4$ with an excess of **2** gave orange precipitates which were extracted into DMF and reprecipitated with Et_2O. Blocklike crystals of $(Ph_4P)_2Mo_2O_2As_4S_{14}$,[19,20] obtained in 40% yield upon careful recrystallization from Me_2SO–EtOH, were subjected to a single-crystal X-ray diffraction study.[21]

The $[Mo_2O_2As_4S_{14}]^{2-}$ anion consists of the familiar $Mo_2O_2S_2^{2+}$ fragment strapped by an $As_4S_{12}^{4-}$ chelate (Figure 2). On the basis of its unexceptional bond distances and angles, the $Mo_2O_2S_2^{2+}$ core appears to be contained in a relatively strain-free environment provided by the $As_4S_{12}^{4-}$ chelate.[22] The S–Mo–S bite angles of the outer chelates (79.5 (2)° and 78.5 (2)°) are closer to those found in five-membered rings reflecting the effect of the large arsenic atom. The conformation of the As_2S_6 ring resembles that observed in $S_8(AsF_6)_2$.[23] The As(4)–S(7) and As(1)–S(8) distances of 2.335 (6) and 2.301 (7) Å are elongated relative to the others observed here.

The $[Mo_2O_2As_4S_{14}]^{2-}$ ion reacts readily with $(Ph_4P)_2MoO_2S_2$ (2 equiv, DMF solution, 25 °C, 10 min.) to give a 78% yield of $(PPh_4)_4Mo_4O_4As_4S_{14}$.[24] The symmetrical 16-membered macrocyclic structure shown in eq 1 is consistent with its spectral



(1)

properties which resemble those for $(PPh_4)_2Mo_2O_2As_4S_{14}$.[25] This ring expansion reaction further extends the generality of the reactions of anionic molybdenum sulfides with sulfur-rich substrates.[18]

The results presented in this paper demonstrate two fairly simple but quite useful principles. First, the coordination chemistry of bidentate polychalcogen dianions can be extended into three dimensions simply by incorporation of thiophilic trivalent atoms like arsenic. Second, certain sulfide minerals, which are common in nature,[26] are reactive precursors to novel molecular compounds.

Acknowledgment. This research was supported by the National Science Foundation (CHE-81-06781). We would like to thank Dr. Robert Haushalter at Exxon for directing us to much of the sulfo-salt literature and Dr. Mark Draganjac for help with the molybdenum chemistry.

(13) In a typical reaction 525 mg (2.0 mmol) of $(MeCp)_2Ti(CO)_2$ as a THF (25 mL) solution was added to a THF (50 mL) slurry of **2** (428 mg, 1.0 mmol) and stirred 24 h. Subsequent workup yielded 150 mg **3** (29% yield).

(14) Na_3AsS_3 has been prepared from the high-temperature reaction of As_2S_3 and molten sodium sulfide (Palazzi, P.M. *Bull. Soc. Chim. Fr.* **1972**, 528–531) and later structurally characterized: Palazzi, P.M. *Acta Crystallgr. Sect. B* **1976**, *B32*, 3175–3177.

(15) In a typical reaction 246 mg (1.0 mmol) of **1** was added to a solution of 720 mg (3.0 mmol) of $Na_2S{\cdot}9H_2O$ in 30 mL of H_2O. After 15 min PPNCl (3.5g) is added as a EtOH (30 mL) solution and stirred for 1 h. Yield: 3.25 g. Anal. Calcd for $C_{108}H_{90}N_3P_6AsS_3$: C, 72.60; H, 5.04; N, 2.35; P, 10.42; As, 4.20; S, 5.38. Found: C, 69.34; H, 5.16; N, 2.23; P, 10.12; As, 4.14; S, 5.23.

(16) Conductivity measurements were made employing a Barnstead E-3411 glass dip cell with a Barnstead PM-70CB conductivity bridge at 20 °C, over a concentration range of 10^{-1} to 10^{-4} M.

(17) (a) Using the Onsager limiting law ($\Lambda_0 - \Lambda_e = Ac^{1/2}$) a plot of the equivalent conductance vs. the square root of the concentration afforded a straight line with equivalent conductivity at infinite dilution $\Lambda_0 = 266\ \Omega^{-1}\ cm^2\ equiv^{-1}$ and a slope of $A = -1405$ which are in accord with 3:1 electrolytes. (b) Callahan, K. P.; Cichon, E. J. *Inorg. Chem.* **1981**, *20*, 1941–1944. (c) Davison, A.; Howe, D. V.; Shawl, E. T. *Inorg. Chem.* **1967**, *6*, 458–463.

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(19) In a typical reaction 904 mg of $(Ph_4P)_2MoS_4$ (1.0 mmol) and 428 mg of **2** are stirred in CH_3CN (50mL) for 48 h. Subsequent removal of the CH_3CN followed by extraction with DMF (100 mL) yielded solutions from which $(Ph_4P)_2Mo_2O_2As_4S_{14}$ may be precipitated with Et_2O. Recrystallization from Me_2SO–EtOH gave 321 mg of red-orange crystals. Anal. Calcd for $C_{48}H_{40}P_2Mo_2O_2As_4S_{14}$: C, 34.91; H, 2.44; P, 3.75; S, 27.19; Mo, 11.62. Found: C, 34.74; H, 2.47; P, 4.05; S, 26.79; Mo, 11.33.

(20) UV–vis of $(Ph_4P)_2Mo_2O_2As_4S_{14}$ in DMF: shoulder at 430 nm (ϵ 2250). Infrared spectrum (mineral oil mull, cm^{-1}): 940 (ν Mo–O), 740, 715, 680, 520 (ν Ph_4P^+), 455 (ν Mo–S), 405, 360, 305 (ν As–S and S–S). Conductance in DMF solutions gives an equivalent conductance at infinite dilution $\Lambda_0 = 164\ \Omega^{-1}\ cm^2\ equiv^{-1}$ and $A = -682$.

(21) $(Ph_4P)_2Mo_2O_2As_4S_{14}$ crystallizes in the triclinic space group $P\bar{1}$ with dimensions a = 13.140 (6) Å, β = 14.634 (7) Å, and c = 18.589 (8) Å; α = 112.52 (3)°, β = 95.99 (3)°, γ = 108.65 (3)°; V = 3021.6 (31) Å^3; Z = 2. Data was collected with an ω scan technique at ambient temperatures with monochromatized Mo Kα (λ = 0.71069 Å) radiation. Of the 7549 reflections collected 4737 independent reflections with $I > 2.5\sigma$ (I) to which an empirical ψ scan absorption correction was applied (maximum transmittance = 0.956, minimum transmittance = 0.723) were used in the structure solution and refinement, which converged to R = 9.4% and R_w = 9.2%.

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(24) In a typical reaction 165 mg (0.1 mmol) of $(Ph_4P)_2Mo_2O_2As_4S_{14}$ and 175 mg (0.2 mmol) of $(Ph_4P)_2MoO_2S_2$ are stirred in DMF (10 mL) for 30 min under N_2. Subsequent dilution to 25 mL with DMF followed by addition of EtOH (25 mL) and slow addition of Et_2O (30 mL) afforded 200 mg of red analytically pure $(Ph_4P)_4Mo_4O_4As_4S_{14}$ (78% yield). Anal. Calcd for $C_{96}H_{80}Mo_4O_4As_4S_{14}$: C, 45.14; H, 3.15; P, 4.85; S, 17.58; Mo, 15.02. Found: C, 44.93; H, 3.22; P, 4.92; S, 17.21; Mo, 14.90.

(25) UV–vis of $(Ph_4P)_4Mo_4O_4As_4S_{14}$ in DMF: 505 nm (ϵ 3600) and shoulders at 443 nm (ϵ 5400) and 428 nm (ϵ 6300). Infrared spectrum (mineral oil mull, cm^{-1}): 940(ν Mo–O), 740, 720, 680, 520 (Ph_4P^+), 465 (ν Mo–S), 310 (ν As–S). Conductance in DMF: $\Lambda_0 = 299\ \Omega^{-1}\ cm^2\ equiv^{-1}$ and $A = -2845$.

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Supplementary Material Available: Description of X-ray data collection parameters, positional and thermal parameters for all atoms, a complete listing of bond distances and angles, and observed and calculated structure factors for **3** and $(Ph_4P)_2Mo_2O_2As_4S_{14}$ (55 pages). Ordering information is given on any current masthead page.

Study of Carbonyl Oxide Formation in the Reaction of Singlet Oxygen with Diphenyldiazomethane[1]

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Carbonyl oxides are believed to be important reaction intermediates in the ozonolysis reaction. Criegee was the first to make this suggestion,[2,3] and carbonyl oxides are frequently referred to as Criegee intermediates. More recently it has been proposed[4] that they may be involved in the metabolic activation of carcinogenic polycyclic aromatic hydrocarbons to yield arene oxides.[5] In spite of their importance, carbonyl oxides have only recently been detected in a handful of examples. Cyclopentadienone oxide has been detected by IR spectroscopy in matrices at low temperatures,[6] while in solution only the intermediates produced by reaction of oxygen with 10,10-dimethyl-10-silaanthracen-9-(10*H*)-ylidene,[7] diphenylcarbene,[8] and fluorenylidene[9] have been detected by using laser flash photolysis.

Murray et al., in a detailed series of studies,[10-14] showed that carbonyl oxides can be conveniently produced by reaction of singlet oxygen with diazo compounds. However, we do not know of any examples where the carbonyl oxide produced in this manner has been detected directly. In this communication (a) we report the spectrum of the carbonyl oxide produced by reaction of singlet oxygen with diphenyldiazomethane, (b) we show that this intermediate is identical with that produced by reaction of triplet carbenes with oxygen,[15] thus providing conclusive proof of the mechanism proposed by Murray,[10-14] and (c) we have examined the kinetics of the reaction of singlet oxygen with the diazo precursor.

Singlet oxygen was generated by using methylene blue (MB) as a sensitizer in oxygen-saturated acetonitrile. MB, typically 4 μM, was excited with 587-nm pulses from a flash pumped dye laser.[16] The MB triplet ($\lambda_{max} \sim 430$ nm) was very long lived ($\geqslant 10$ μs) in deaerated solutions, but decayed essentially during

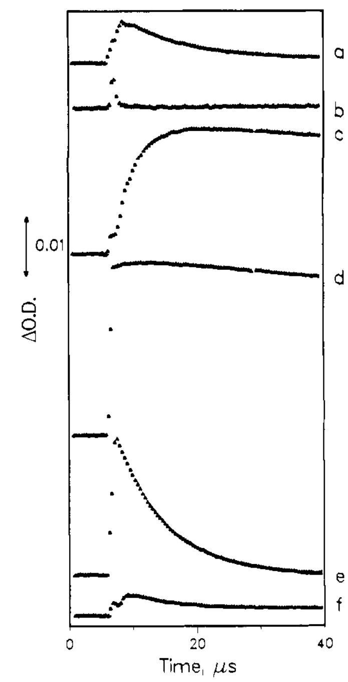

Figure 1. Time profiles obtained at 410 nm in acetonitrile at 300 K from a sample with 4 μM MB: (a) under N_2, λ_{ex} = 587 nm; (b) containing 7.7 mM O_2, λ_{ex} = 587 nm; (c) same as b with 1 mM Ph_2CN_2, λ_{ex} = 587 nm; (d) same as c, excited at 337.1 nm; (e) same as d containing 0.21 M 2,5-dimethyl-2,4-hexadiene, λ_{ex} = 337.1 nm; (f) same as e, λ_{ex} = 587 nm, note the initial "blip" due to MB^{*}.

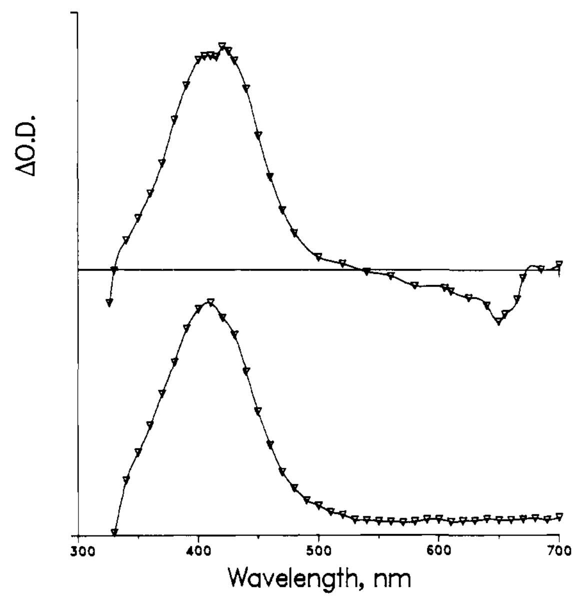

Figure 2. Transient spectrum (top) obtained by 587-nm excitation of an acetonitrile solution containing 4 μM MB, 1 mM Ph_2CN_2, and 7.7 mM O_2, at 300 K. Signal monitored between 8 and 12 μs after excitation. The bottom spectrum corresponds to benzophenone oxide produced by reaction of diphenylcarbene and oxygen,[8] under comparable conditions (λ_{ex} = 308 nm).

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(16) A flash-pumped dye laser (Candela UV-500M) operated with rhodamine 6G delivering 587-nm pulses (up to 1 J, ~250 ns) was used as excitation source. The concentration of MB used, 4 μM, ensures that the amount of energy absorbed by the sample is much less than that available during the laser pulse. Diphenyldiazomethane in acetonitrile does not yield any signals when irradiated under the same conditions in the absence or presence of oxygen. Details of our laser facility have been reported elsewhere.[17] All experiments were carried out using a flow system employing solutions saturated with O_2, N_2, or O_2/N_2 mixtures of known composition.

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