

16 h, a large amount of white crystals had formed. The crystals were filtered, and the volume of the filtrate was reduced by half, the filtrate cooled to $-30\text{ }^{\circ}\text{C}$, and a second crop obtained. The combined weight of II obtained was 1.15 g (0.0036 mol), a yield of 94.7%. The crystals obtained in this way were suitable for single-crystal X-ray diffraction studies. ^1H NMR data (250.13 MHz, $20\text{ }^{\circ}\text{C}$, C_6D_6): CH_2 , s, br, 2.57 ppm, 4 H; CH_3 , s, br, 1.69 ppm, 6 H. ^{13}C NMR data (62.9 MHz, $20\text{ }^{\circ}\text{C}$, C_6D_6): CH_3 , 18.9 ppm; CH_2 , 37.1 ppm; CMe , 131.2 ppm, CO , 204.8 and 209.5 ppm. IR data: ($\nu(\text{CO})$, cm^{-1}): 2046, s; 2005, s, br; 1975, s, br. Anal. Calcd for $\text{C}_{20}\text{H}_{20}\text{O}_8\text{Fe}_2\text{Ge}_2$: C, 37.20; H, 3.12. Found: C, 36.93; H, 3.19.

b. X-ray Crystallographic Study of I. Transparent yellow crystals of I were grown from pentane at $-30\text{ }^{\circ}\text{C}$, and the crystal selected for the X-ray study was sealed in a glass capillary under nitrogen. A total of 4820 independent reflections were measured on a Nicolet R3m/v diffractometer. The structure was solved by direct methods using SHELXTL PLUS and was refined by using the full-matrix least-squares method. Positions of hydrogen atoms were varied, but they had fixed isotropic U 's. A final difference Fourier was featureless, with the largest peak being $0.53\text{ e}/\text{\AA}^3$. Details of the crystal data are given in Table I, and atomic coordinates and equivalent isotropic displacement coefficients are given in Table IIa.

c. X-ray Crystallographic Study of II. A suitable crystal was located and transferred to the goniostat of a Picker flow-circle goniostat equipped with a Furnas monochromator and Picker X-ray generator by using standard inert-atmosphere handling techniques employed by the IUMSC.¹⁴ The crystal was cooled to $-155\text{ }^{\circ}\text{C}$ for characterization and

data collection. A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with no symmetry or systematic absences, indicating a triclinic space group. Subsequent solution and refinement of the structure confirmed the centrosymmetric choice $P\bar{1}$. Data were collected in the usual manner by using a rapid ($12^{\circ}/\text{min}$) continuous $\theta-2\theta$ scan with fixed backgrounds. Data were reduced to a unique set of intensities and associated σ 's in the usual manner. The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques. All hydrogen atoms were clearly visible in a difference Fourier synthesis phased on the non-hydrogen parameters. All hydrogen atoms were refined isotropically, and non-hydrogen atoms were refined anisotropically in the final cycles. A final difference Fourier was featureless, with the largest peak being $0.38\text{ e}/\text{\AA}^3$. The crystal data are summarized in Table I, and fractional coordinates and thermal parameters are given in Table IIb.

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Supplementary Material Available: Full listings of bond lengths and angles for I (Tables 3 and 4) and II (Tables 9 and 10), listings of anisotropic displacement coefficients for I (Table 5) and II (Table 8) and H atom coordinates and isotropic displacement coefficients for I (Table 6), and packing diagrams for I (Figures 1S and 2S) and stereoviews for II (Figures 3S and 4S) (13 pages); listings of observed and calculated structure factors for I (Table 7) and II (Table 11) (27 pages). Ordering information is given on any current masthead page.

(14) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1984**, *23*, 1021.

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Arsenic-Sulfur Heterocycle Formation via Metal Coordination. Synthesis and Molecular Structure of *cyclo*-(CH_3AsS)_n ($n = 3, 4$), $[(\text{CO})_3\text{Mo}][\eta^3\text{-cyclo}-(\text{CH}_3\text{As})_6\text{S}_3]$, and the Triple-Decker-Sandwich Complex $[\eta^5\text{-}(\text{C}_5\text{H}_5)_2\text{Mo}_2(\eta^2, \mu\text{-As}_3)(\eta^2, \mu\text{-AsS})]$

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Molybdenum hexacarbonyl facilitates the ordered formation of crystalline methylarsathianes (methylarsenic sulfides), *cyclo*-(CH_3AsS)_n, $n = 3$ or 4, from elemental sulfur and pentamethyl-*cyclo*-pentaarsine, *cyclo*-(CH_3As)₅. In the absence of $\text{Mo}(\text{CO})_6$, an array of oligomeric products is formed, many containing S-S or As-As bonds instead of the perfect S-As alternation of the arsathianes. Both heterocycles have been structurally characterized: (CH_3AsS)₃, triclinic, $P\bar{1}$, $a = 8.856$ (3) \AA , $b = 10.189$ (2) \AA , $c = 12.925$ (4) \AA , $\alpha = 75.25$ (2) $^{\circ}$, $\beta = 70.09$ (2) $^{\circ}$, $\gamma = 89.54^{\circ}$, $V = 1056.4$ (5) \AA^3 , $Z = 4$, $R(F) = 4.97\%$; (CH_3AsS)₄, orthorhombic, $Pn2_1a$, $a = 11.495$ (3) \AA , $b = 30.624$ (5) \AA , $c = 8.276$ (2) \AA , $V = 2913.2$ (10) \AA^3 , $Z = 8$, $R(F) = 7.68\%$. Both of the arsathiane cyclooligomers crystallize with two independent, but chemically similar, molecules in the asymmetric unit. The rings adopt the conformations of their cycloalkane isolobal analogues, i.e., cyclohexane and cyclooctane. Possible pathways for the formation of the heterocycles involve, repetitively, initial coordination of the homoarsenic precursor, followed by oxidation by sulfur to form a pentavalent species, and release from the metal and rearrangement by insertion of S into an As-As bond. In support of this pathway is the isolation of a complex containing a partially sulfurated arsenic ring, $[(\text{CO})_3\text{Mo}][\text{cyclo}-(\text{CH}_3\text{As})_6\text{S}_3]$, which contains a nine-membered ring of three (CH_3As)₂S units coordinated exclusively through As to a *fac*- $\text{Mo}(\text{CO})_3$ group. The complex has been structurally characterized: monoclinic, $P2_1/c$, $a = 10.551$ (3) \AA , $b = 10.819$ (3) \AA , $c = 22.407$ (6) \AA , $\beta = 90.33^{\circ}$, $V = 2557.7$ (10) \AA^3 , $Z = 4$, $R(F) = 8.43\%$. Unlike the case for arsaioxanes, (RAsO)_n, which have demonstrated ligand properties, no evidence was found for the formation of coordinated arsathianes in reactions with either $\text{Mo}(\text{CO})_6$ or $[\text{CpMo}(\text{CO})_3]_2$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$). However, reactions of the arsathianes with $[\text{CpMo}(\text{CO})_3]_2$ lead to the formation of several naked arsenic clusters, only one of which contains sulfur: $[\text{CpMo}(\text{CO})_2]_2(\eta^2, \mu\text{-As}_2)$ and $[\text{CpMo}(\text{CO})_2]_2(\eta^2, \mu\text{-As}_2)_2$ are obtained in low yields. The sulfur-containing product, $\text{Cp}_2\text{Mo}_2(\eta^2, \mu\text{-As}_3)(\eta^2, \mu\text{-AsS})$, is a triple-decker sandwich possessing a planar middle deck composed of an allylic As_3 group and an $\text{As}^{\text{III}}\text{S}$ group: monoclinic, $C2/c$, $a = 11.668$ (2) \AA , $b = 11.273$ (3) \AA , $c = 12.881$ (4) \AA , $\beta = 119.63$ (2) $^{\circ}$, $V = 1472.7$ (4) \AA^3 , $Z = 4$, $R(F) = 2.86\%$.

Introduction

In recent years we have reported in some detail the synthesis and structural characterization of a large number of metal carbonyl and cyclopentadienylmetal carbonyl complexes containing homoatomic rings and chains of arsenic atoms both with and without organic substitution.¹ In one of these communications,

we also reported that the exposure of a reactant, *cyclo*-(CH_3As)₅, to dioxygen led first to the formation of a heterocyclic arsaioxane ring system, *cyclo*-(CH_3AsO)₄, which subsequently combined with $\text{Mo}(\text{CO})_6$ to form the ring-expansion complex $[\text{Mo}(\text{CO})_3]_2[\text{cyclo}-(\text{CH}_3\text{AsO})_6]$ (1).² Complex 1 contains a highly puckered 12-membered ring of alternating As and O atoms facially coordinated to two $\text{Mo}(\text{CO})_3$ groups to form, overall, a flattened

(1) References are available in our recent review article. DiMaio, A.-J.; Rheingold, A. L. *Chem. Rev.*, in press.

(2) Rheingold, A. L.; DiMaio, A.-J. *Organometallics* **1986**, *5*, 393.

Table I. Crystallographic Parameters for 2-5

	2	3	4	5
formula	C ₉ H ₁₈ As ₆ MoO ₃ S ₃	C ₃ H ₉ As ₃ S ₃	C ₄ H ₁₂ As ₄ S ₄	C ₁₀ H ₁₀ As ₄ Mo ₂ S
fw	815.87	366.04	488.06	653.80
cryst system	monoclinic	triclinic	orthorhombic	monoclinic
space group	P2 ₁ /c	P $\bar{1}$	Pn2 ₁ a	C2/c
a, Å	10.551 (3)	8.856 (3)	11.495 (3)	11.668 (2)
b, Å	10.819 (3)	10.189 (2)	30.624 (5)	11.273 (3)
c, Å	22.407 (6)	12.925 (4)	8.276 (2)	12.881 (4)
α , deg	90	75.25 (2)	90	90
β , deg	90.33 (2)	70.09 (2)	90	119.63 (2)
γ , deg	90	89.54 (2)	90	90
V, Å ³	2557.7 (10)	1056.4 (5)	2913.2 (10)	1472.7 (4)
Z	4	4	8	4
ρ (calcd), g cm ⁻³	2.119	2.302	2.226	2.949
μ (Mo K α), cm ⁻¹	88.73	99.19	95.91	111.93
temp, °C	22	23	22	23
T(max)/T(min)	2.13	2.38	2.46	1.57
R(F), %	8.43	4.97	7.68	2.86
R(wF), %	9.16	5.81	8.86	3.10

cuboctahedral structure. This result and those arising from our continuing study of arsaioxane reactivity stimulated our interest in a study of the metal-mediated formation and reactivity of other arsachalcanses, RAsE, E = S and Se. We now report a study of the metal-mediated formation and structural characterization of the arsathianes *cyclo*-(CH₃AsS)_n, n = 3 (3) and 4 (4), a metal-bound precursor to the arsathianes, {(CO)₃Mo[*cyclo*-(CH₃AsS₂)₃]} (2), and a product of the reaction of methylarsathiane with [CpMo(CO)₃]₂ (Cp = η^5 -C₅H₅) that forms a new addition to the growing group of triple-decker-sandwich complexes containing As atom middle decks, specifically, (Cp₂Mo₂(η^2 , μ -As₃)(η^2 , μ -AsS) (5).

Experimental Section

Equipment and Materials. Unless otherwise specified, all manipulations were carried out under an atmosphere of N₂ or in evacuated (Carius) tubes. Melting points were measured on a Mel-Temp apparatus. Infrared spectra were recorded on a Nicolet 50XB FTIR spectrophotometer as KBr pellets or as solutions in CH₂Cl₂ or CHCl₃. ¹H NMR spectra were obtained on a Bruker 250-MHz spectrometer in deuterated chloroform with TMS as an internal reference. Mass spectra were obtained on a VG 7070 mass spectrometer. All new compounds provided satisfactory elemental analyses or isotope patterns and are air-stable as solids unless otherwise noted.

Toluene, methylene chloride, octane, and ethyl acetate were all purified and distilled under N₂ according to established procedures.³ Mo(CO)₆ (Strem) and S₈ (Fisher) were sublimed before use. *cyclo*-(AsCH₃)₃⁴ and [C₃H₅Mo(CO)₃]₂⁵ were prepared by standard procedures.

The following reactions involve the use of sealed medium-walled Pyrex Carius tubes 15 mm in diameter and approximately 35 mL in volume. **Caution!** These tubes, when heated, may reach pressures of 30 atm and may explode. All heating of these tubes should be done after placing the sealed glass tube in end-capped, perforated steel tubes. Also, the reactions generate carbon monoxide gas as a side product. Reaction tubes should be opened only after freezing the contents in N₂(l).

Formation of *cyclo*-(CH₃AsS)_n [n = 3 (3); n = 4 (4)]. Mo(CO)₆ (0.60 g, 2.27 mmol) and S₈ (0.60 g, 2.34 mmol) were combined in a Carius tube with 1.3 g (2.89 mmol) of *cyclo*-(AsCH₃)₃ dissolved in 10 mL of prepurified toluene. The tube was evacuated with three freeze-pump-thaw cycles, flame sealed, and heated at 125 °C for 48 h in an oven. After slow cooling to room temperature, the tube was opened and the contents of the tube filtered. The filtrate was stripped of solvent, and the solid redissolved in a minimum of methylene chloride, and the solution loaded onto a 30-cm partially deactivated alumina column. After an initial flush of hexanes, 3 and 4 were eluted together as a clear, colorless band with 10/90 mixture of ethyl acetate and methylene chloride. Pure samples of 3 and 4 were initially obtained by microscopic separation according to their different morphologies (3 as rectangular bricks, 4 as plates). Chromatography on a longer (100 cm) column also afforded separation. Very pale yellow diffraction-grade crystals of 3 and 4 were obtained from the slow diffusion of pentane into a methylene

chloride solution. Yield: 0.37 g of 3 and 0.12 g of 4 (53% based on S₈). Found for 3: ¹H NMR (CDCl₃) δ = 1.99 ppm (singlet); mp 109–111 °C; m/e 366 (M⁺). Found for 4: ¹H NMR (CDCl₃) δ = 1.89 ppm (singlet); mp 120–124 °C; m/e 488 (M⁺).

Formation of [Mo(CO)₃(CH₃As)₆S₃] (2). Although trace quantities of 2 are found in the above reaction, 2 can be isolated in better yield (20%) from the reaction of an excess of *cyclo*-(AsCH₃)₃ (1.17 g, 2.6 mmol) with Mo(CO)₆ (0.5 g, 1.9 mmol) and S₈ (0.27 g, 1.1 mmol) in a Carius tube at 100 °C for 48 h. After the tube was opened and the reaction mixture was filtered, 2 was eluted as a slightly air-sensitive yellow band from 10% methylene chloride in hexanes. Yellow crystals were grown from methylene chloride/hexanes. Found for 2: ¹H NMR (CDCl₃) δ = 2.42, 2.38, and 2.19 (coordinated AsCH₃), 1.20, 1.19, and 1.08 (uncoordinated AsCH₃) (all are singlets); IR (KBr pellet) ν_{CO} = 1957 (s), 1878 cm⁻¹ (s); dec pt 205–210 °C. The mass spectrum of 2 shows M⁺ at m/e 816 with the appropriate Mo isotope pattern.

Reaction of *cyclo*-(CH₃As)₃ with S₈. Equimolar amounts of *cyclo*-(AsCH₃)₃ and S₈ were combined with 15 mL of toluene in a Carius tube, with the tube evacuated and sealed as described above, and then heated for 48 h at 125 °C. After slow cooling of the reaction tube, the seal was broken and the toluene solution chromatographed on an aluminum column with 10% methylene chloride in hexanes. Chromatography yielded oligomeric methylarsine sulfides of various sizes, identifiable by fragmentation of their parent ions in mass spectral analysis.

Formation of (η^2 -C₅H₅)₂Mo₂As₄S (5). In a Carius tube, 0.26 g of (CH₃AsS)_n (n = 3, 4) (2.13 mmol of CH₃AsS) and 0.74 g of [η^5 -C₅H₅Mo(CO)₃]₂ were combined and 15 mL of dry, degassed toluene was added. The tube was evacuated with three freeze-pump-thaw cycles, sealed, and then heated for 48 h at 125 °C. On slow cooling of the tube, a black precipitate formed. Once cool, the tube was opened and the precipitate removed by filtration. The dark red filtrate was evaporated to dryness, the solid then redissolved in a minimum of CH₂Cl₂, and the solution eluted on a partially deactivated alumina column. (η^5 -C₅H₅)₂Mo₂As₄S (5) was separated as a blackish red band with 5% CH₂Cl₂ in hexanes in 10% yield. Crystals were grown by the slow evaporation of a concentrated methylene chloride solution. Found for 5: ¹H NMR (CDCl₃) δ = 5.00 ppm; dec pt 310–312 °C. Anal. Calcd: C, 18.63; H, 1.55; As, 46.58. Found: C, 18.96; H, 1.71; As, 46.92. The mass spectrum of 5 contains M⁺ at m/e 654 with an appropriate Mo isotope pattern.

Crystallographic Structural Determinations. Crystal data and data collection and refinement parameters are summarized in Table I. All samples were mounted with epoxy cement on glass fibers. A Nicolet R3m/ μ diffractometer with Mo K α radiation (λ = 0.71073 Å) and a graphite monochromator was used throughout. All data sets were corrected for absorption by empirical procedures. All structures were solved by direct methods and completed by subsequent difference Fourier syntheses. Hydrogen atoms were treated as idealized contributions (d -(CH) = 0.96 Å). All computations used SHELXTL software (G. M. Sheldrick, Nicolet XRD, Madison, WI). Tables II–V contain atomic coordinates and isotropic thermal parameters.

Mo(CO)₃[(CH₃As)₆S₃] (2). The space group P2₁/c was uniquely determined from systematic absences. The nine-membered As₆S₃ ring is disordered in the following way: As(1), As(2), and As(3) have a site occupancy factor (sof) of 1 and the six remaining positions are sulfur/arsenic composites. Two of the composites were resolved, S(y)/As*(2) and S(x)/As*(4), which are 78.5 (7) and 83.5 (8)% arsenic, respectively. S(4) and S(6) were refined at unit occupancy, but likely contain some

(3) *The Chemist's Companion*; Gordon, A. J., Ford, R. A., Eds.; Wiley: New York, 1972.

(4) Rheingold, A. L. *Organomet. Synth.* 1986, 3, 618.

(5) King, R. B.; Eisch, J. J. *Organomet. Synth.* 1965, 1, 109.

Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($\text{\AA}^2 \times 10^3$) for 2

	x	y	z	U^a
Mo(1)	1850 (2)	7660 (2)	615 (1)	66 (1)*
As(1)	1213 (3)	9161 (3)	1447 (1)	70 (1)*
As(2)	4056 (3)	7629 (3)	1081 (1)	75 (1)*
As(3)	1269 (3)	5891 (3)	1299 (1)	71 (1)*
As*(1)	-254 (4)	8312 (3)	2206 (1)	84 (2)*
As*(2)	2818 (5)	10050 (5)	2143 (4)	92 (3)*
As*(3)	4767 (4)	9380 (4)	1705 (2)	102 (2)*
S(4)	4545 (7)	6075 (8)	1790 (3)	81 (3)*
As*(4)	3014 (5)	4637 (4)	1707 (2)	109 (2)*
S(x)	2720 (32)	5254 (31)	2073 (14)	41 (9)
S(y)	2953 (48)	10448 (69)	1749 (33)	124 (26)*
S(6)	203 (13)	6400 (8)	2171 (3)	132 (5)*
O(1)	2490 (22)	9812 (23)	-232 (11)	134 (12)*
O(2)	2763 (27)	5944 (27)	-410 (9)	159 (15)*
O(3)	-906 (19)	7536 (19)	68 (10)	105 (9)*
C(1)	282 (36)	10706 (28)	1249 (15)	142 (20)*
C(2)	5529 (29)	7404 (29)	560 (15)	118 (17)*
C(3)	160 (30)	4605 (29)	1039 (13)	112 (16)*
C(4)	2220 (38)	9118 (31)	103 (13)	115 (17)*
C(5)	2430 (28)	6519 (30)	-14 (12)	112 (18)*
C(6)	46 (28)	7626 (28)	292 (12)	90 (13)*
C(7)	-1741 (42)	8177 (50)	1659 (18)	178 (26)*
C(8)	4877 (61)	10674 (41)	1021 (21)	211 (32)*
C(9)	2595 (48)	8882 (50)	2863 (15)	190 (31)*
C(10)	3668 (45)	4137 (43)	882 (19)	131 (16)

^a U values marked with an asterisk are the equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($\lambda^2 \times 10^3$) for 3

	x	y	z	U^a
As(1)	454	4921	3188	43
As(2)	557	8161	3087	42
As(3)	1812	7252	669	45
As(4)	-3833	10129	6701	42
As(5)	-3724	6902	6730	41
As(6)	-2894	7878	8715	47
S(1)	-1244	6317	4022	46
S(2)	207	8787	1397	48
S(3)	105	5335	1491	51
S(4)	-5387	8555	6466	41
S(5)	-4482	6205	8650	47
S(6)	-4512	9599	8615	47
C(1)	-1019	3263	3911	62
C(2)	-750	9468	3744	60
C(3)	1377	7669	-755	57
C(4)	-5251	11588	6631	58
C(5)	-5019	5413	6606	59
C(6)	-3420	7369	10360	56

^aEquivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

unresolved As character. Both As*(1) and As*(3) contain some unresolved S character; these atoms were refined with reduced occupancy (sof As*(1) = 94.1 (10)%, and sof As*(3) = 83.5 (8)%). Methyl group occupancies were adjusted to correspond to the As content at all sites. All non-hydrogen atoms were refined anisotropically except for C(10), which was repeatedly found to produce nonpositive-definite thermal parameters.

cyclo-(CH₃AsS)₃ (3). The centrosymmetric triclinic space group, $P\bar{1}$, was initially suggested by the distribution of E values and later confirmed by the well-behaved solution and refinement of the structure. The asymmetric unit consists of two independent molecules. All non-hydrogen atoms were refined anisotropically.

cyclo-(CH₃AsS)₄ (4). Systematic absences in the diffraction data determined either of the orthorhombic space groups $Pnma$ or $Pn2_1a$ (nonstandard $Pna2_1$). The absence of mirror plane symmetry relating the two independent molecules of the asymmetric unit restricted processing to the acentric alternative, $Pn2_1a$. The chemically reasonable results of refinement confirm the validity of this choice. To conserve data, only the As and S atoms were refined anisotropically.

(η^3 -C₂H₅Mo)₂As₄S (5). Of the two monoclinic space groups determined from systematic absences, $C2/c$ and Cc , the former was suggested by the distribution of E values and the presence of 2-fold rotational

Table IV. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($\lambda^2 \times 10^3$) for 4

	x	y	z	U^a
As(1)	-779 (4)	2513 (2)	3588 (6)	46 (2)*
As(2)	536 (4)	2379	7301 (7)	40 (2)*
As(3)	2211 (4)	3256 (2)	6493 (5)	44 (2)*
As(4)	935 (6)	3372 (3)	2759 (7)	48 (2)*
As(5)	1778 (4)	510 (2)	3727 (6)	48 (2)*
As(6)	3468 (5)	-371 (3)	2821 (7)	44 (2)*
As(7)	4779 (4)	-270 (2)	6499 (5)	43 (2)*
As(8)	3161 (4)	593 (2)	7401 (6)	42 (2)*
S(1)	252 (10)	2023 (4)	4953 (16)	57 (5)*
S(2)	2501 (12)	2575 (7)	7183 (21)	65 (6)*
S(3)	2699 (9)	3289 (4)	3894 (14)	53 (4)*
S(4)	549 (10)	2720 (5)	1734 (17)	49 (5)*
S(5)	3139 (11)	315 (5)	1917 (19)	54 (5)*
S(6)	5281 (10)	-307 (4)	3878 (14)	56 (4)*
S(7)	5036 (11)	446 (6)	7067 (22)	59 (6)*
S(8)	2752 (11)	1013 (5)	5199 (17)	58 (5)*
C(1)	-1449 (46)	2073 (20)	2310 (59)	65 (18)
C(2)	801 (33)	1837 (13)	8602 (51)	39 (11)
C(3)	3676 (38)	3490 (14)	7234 (59)	67 (14)
C(4)	1653 (43)	3596 (19)	683 (67)	86 (19)
C(5)	912 (48)	957 (21)	2316 (62)	59 (19)
C(6)	4024 (38)	-592 (17)	686 (60)	68 (16)
C(7)	6323 (32)	-455 (11)	7269 (49)	39 (11)
C(8)	3382 (37)	1087 (16)	8862 (62)	66 (15)

^a U values marked with an asterisk are the equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table V. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($\lambda^2 \times 10^3$) for 5

	x	y	z	U^a
As(1)	-445 (1)	913 (1)	3743 (1)	43 (1)
Sas	-261 (1)	-1617 (1)	3227 (1)	45 (1)
As(3)	0	2161 (1)	2500	42 (1)
Mo(1)	1284 (1)	38 (1)	3324 (1)	29 (1)
C(1)	3331 (9)	-916 (10)	4196 (11)	68 (6)
C(2)	2992 (10)	-781 (8)	5064 (9)	58 (5)
C(3)	2947 (9)	428 (8)	5270 (8)	54 (4)
C(4)	3247 (8)	1060 (8)	4520 (8)	54 (4)
C(5)	3472 (9)	229 (10)	3806 (10)	64 (5)

^aEquivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

symmetry. All processing was confined to the centrosymmetric alternative. The S-As group in the central plane is disordered about the 2-fold axis and was refined as a 50/50 S/As composite atom labeled Sas. All non-hydrogen atoms were anisotropically refined.

Results and Discussion

Research activity in arsenic-chalcogen heterocycles, particularly those containing sulfur and selenium, has increased recently due to interest in their optical and electronic properties.⁶ Although the inorganic chemistry of these heterocycles is reasonably well developed, the related chemistry of organic derivatives, primarily that of the RAsE cyclooligomers (E = S, Se), is comparatively less developed; additionally, of the existing body of knowledge, most reports concern aromatic derivatives.⁷ The few reports that exist of the preparation of aliphatic derivatives such as RAsS (R = alkyl), which are more desirable in materials applications, have involved the metathesis of a primary alkylarsenic dihalide with hydrogen sulfide (or alkali-metal sulfides).⁷ Modern characterization of these products reveal the formation of oils containing a complex mixture of RAsS oligomers usually contaminated with species with excess sulfur, e.g., R₂As₂S₃.⁸

(6) Sowerby, D. B. In *The Chemistry of Inorganic Homo- and Heterocycles*; Haiduc, I., Sowerby, D. B., Eds.; Academic: London, 1987; Vol. 2, p 713.

(7) Reference 6, p 721.

(8) Cordes, A. W.; Gwinup, P. D.; Malmstrom, M. C. *Inorg. Chem.* **1972**, *11*, 836. Volka, K.; Adamek, P.; Schulze, H.; Barber, H. J. *J. Mol. Struct.* **1974**, *21*, 457.

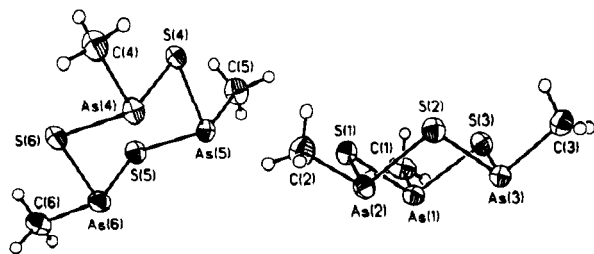


Figure 1. Molecular structure and labeling scheme for *cyclo*-(CH₃AsS)₃ (3). The two crystallographically independent molecules of 3 are shown in their correct, relative lattice positions.

Table VI. Selected Bond Distances (Å) and Angles (deg) for [Mo(CO)₃][(CH₃As)₆S₃] (2)^a

Bond Distances			
Mo(1)-As(1)	2.564 (4)	As(3)-As*(4)	2.458 (6)
Mo(1)-As(2)	2.546 (4)	As*(4)-S(4)	2.249 (9)
Mo(1)-As(3)	2.530 (4)	S(4)-As(2)	2.368 (8)
As(1)-As*(1)	2.482 (5)	As(2)-As*(3)	2.469 (6)
As*(1)-S(6)	2.125 (10)	As*(3)-As*(2)	2.395 (7)
S(6)-As(3)	2.326 (10)	As*(2)-As(1)	2.489 (7)

Bond Angles			
As(1)-Mo(1)-As(2)	87.3 (1)	As(3)-As*(4)-S(4)	100.7 (3)
As(1)-Mo(1)-As(3)	88.5 (1)	As*(4)-S(4)-As(2)	106.4 (3)
As(2)-Mo(1)-As(3)	88.0 (1)	S(4)-As(2)-As*(3)	95.8 (2)
As(1)-As*(1)-S(6)	101.1 (3)	As(2)-As*(3)-As*(2)	101.9 (2)
As*(1)-S(6)-As(3)	111.8 (4)	As*(3)-As*(2)-As(1)	102.1 (3)
S(6)-As(3)-As*(4)	100.6 (3)	As*(2)-As(1)-As*(1)	98.0 (2)

^a Distances and angles are for the majority occupancy atoms at each of the disordered ring sites. Starred As atoms contain substantial S character.

Our prior experience with arsenic-oxygen heterocycles (arsaxanes) indicated that size-selective formation of these heterocycles could be strongly influenced by the presence of a transition-metal center capable of coordinating the heterocycles and/or their precursors; oligomer size selection occurs according to the steric and electronic requirements of the metal center.² Our present synthesis strategy uses Mo(CO)₆ as a mediator in the reaction of pentamethyl-*cyclo*-pentaarsine, *cyclo*-(CH₃As)₅, with elemental sulfur. Without Mo(CO)₆ mediation, the direct reaction of *cyclo*-(CH₃As)₅ with sulfur leads to complex mixtures of difficulty separated products. This result is consistent with that obtained in the reaction of dioxigen with arsenomethane.⁹

cyclo-Octasulfur reacts with a toluene solution of *cyclo*-(AsCH₃)₃ and Mo(CO)₆ to give transition-metal-free heterocycles. The stable heterocycles found after column chromatography are a mixture of two rings, initially separable by gross morphology of their crystalline forms and later separable by more thorough column chromatography. The two compounds, *cyclo*-(CH₃AsS)₃ (3) and *cyclo*-(CH₃AsS)₄ (4), were isolated in an approximately 3/1 ratio and are air-stable both in crystalline form and in various solvents.

Synthesis of methylarsine sulfide (methylarsathiane) by the established procedure¹⁰ and subsequent purification of the product gave two distinct crystalline forms coprecipitating in methylene chloride solution. Both NMR spectroscopy and a check on the unit-cell parameters on diffraction-grade crystals for the two forms of methylarsine sulfide confirmed the assumption that 3 and 4 are the only two tractable oligomers formed in these established reactions.

Crystal Structures of (CH₃AsS)_n (n = 3, 4). The cyclotrimer, (CH₃AsS)₃ (3), crystallizes with two independent, chemically similar molecules shown in Figure 1. The alternating As-S six-membered rings adopt the expected chair conformation of cyclohexane, with which it is isolobal. The As-S distances ranging

Table VII. Selected Bond Distances (Å) and Angles (deg) for *cyclo*-(CH₃AsS)₃ (3)

3 (Molecule A)			
As(1)-S(1)	2.256 (2)	As(2)-S(2)	2.241 (2)
As(1)-S(3)	2.251 (3)	As(3)-S(2)	2.270 (2)
As(2)-S(1)	2.262 (2)	As(3)-S(3)	2.264 (2)
S(1)-As(1)-S(3)	101.1 (1)	As(1)-S(1)-As(2)	92.8 (1)
S(1)-As(2)-S(2)	101.9 (1)	As(2)-S(2)-As(3)	94.3 (1)
S(2)-As(3)-S(3)	100.6 (1)	As(1)-S(3)-As(3)	95.2 (1)

3 (Molecule B)			
As(4)-S(4)	2.264 (2)	As(5)-S(5)	2.256 (2)
As(4)-S(6)	2.255 (2)	As(6)-S(5)	2.254 (2)
As(5)-S(4)	2.266 (2)	As(6)-S(6)	2.261 (2)
S(4)-As(4)-S(6)	102.6 (1)	As(4)-S(4)-As(5)	92.8 (1)
S(4)-As(5)-S(5)	102.4 (1)	As(5)-S(5)-As(6)	93.0 (1)
S(5)-As(6)-S(6)	99.5 (1)	As(4)-S(6)-As(6)	95.2 (1)

Average Values			
As-S	2.258 (1)	As-S-As	101.4 (2)
S-As-S	93.8 (2)	S-As-S-As	81.3 (2)

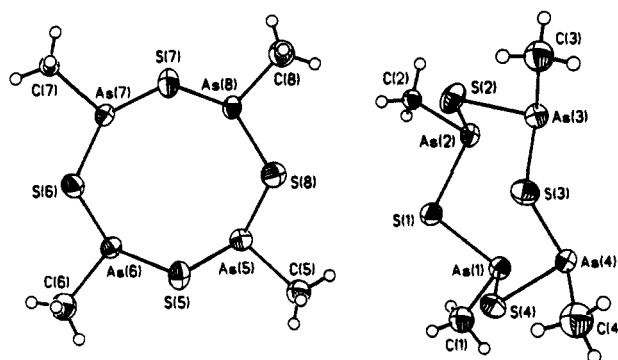


Figure 2. Molecular structure and labeling scheme for *cyclo*-(CH₃AsS)₄ (4). The two crystallographically independent molecules of 4 are shown in their correct, relative lattice positions.

from 2.241 (2) to 2.270 (2) Å (Table VII) are typical of As-S bonds found in structures of various rings and cages: Ph₂As₂S₃, 2.253 (av), Å;⁸ (PhAsS)₄, 2.262 (av), Å;¹¹ As₄S₃, 2.21 (av) Å;¹² As₄S₄, 2.237 (av) Å.¹³ The methyl groups are all equatorial. The average As-S-As angle is 93.8 (2)°, and the average S-As-S angle is 101.4 (2)°; in *cyclo*-(PhAs)₆, the average homoatomic As-As-As angle is 91.1 (1)°,¹⁴ and in *cyclo*-S₆, the average S-S-S angle is 102°.¹⁵ The average torsion angle is 81.3 (2)°.

Quite interestingly, the ring angles in the heterocycle are reversed in magnitude relative to their homocyclic analogues; the As-S-As angles are more closely similar to the homoarsenic ring (and vice versa). The reversal cannot be accounted for on electronegativity grounds, as the X-As-X and X-S-X angles for the halides AsX₃ and SX₂ increase with decreasing electronegativity.¹⁶ However, the effect is consistent with steric expectations; the endocycle angle at As increases by the removal of organic substituents at adjacent atoms (i.e., by replacing CH₃As with S), and the angle at S becomes smaller to increase the separation of methyl substituents.

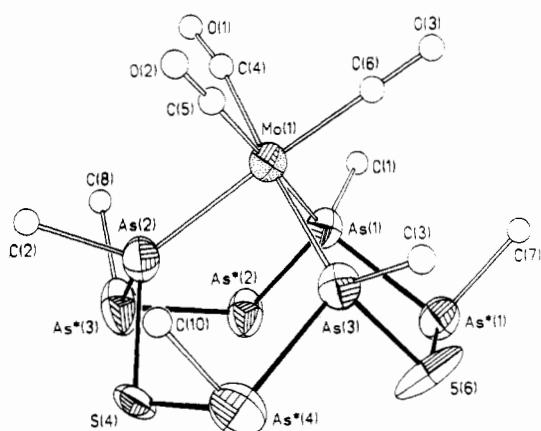
The cyclotetramer, (CH₃AsS)₄ (4), also crystallizes with two independent, chemically similar molecules shown in Figure 2.

(9) Durand, M.; Laurent, J.-P. *J. Organomet. Chem.* **1974**, *77*, 225.
 Marsmann, H. C.; Van Wazer, J. R. *J. Am. Chem. Soc.* **1970**, *92*, 3969.
 (10) Kretov, A. E.; Berlin, A. Ya. *J. Gen. Chem. USSR (Engl. Transl.)* **1931**, *1*, 411.

(11) Bayer, A. *Ann. Chim. (Paris)* **1858**, *107*, 279. Shulte, C. *Ber. Dtsch. Chem. Ges.* **1882**, *15*, 1955. Nametkin, S. S.; Nekrasov, V. Z. *Anal. Chem.* **1929**, *77*, 285; *Chem. Abstr.* **1918**, *12*, 559. Kretov, A. E.; Berlin, A. Ya. *J. Gen. Chem. USSR (Engl. Transl.)* **1931**, *1*, 411. Anschütz, L.; Wirth, H. *Chem. Ber.* **1956**, *89*, 1530. Bergerhoff, G.; Namgung, H. Z. *Kristallogr.* **1979**, *150*, 209.
 (12) Whitfield, H. J. *J. Chem. Soc. A* **1970**, 1800; *J. Chem. Soc., Dalton Trans.* **1973**, 1737.
 (13) Potter, E. J.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1972**, 1347.
 (14) Rheingold, A. L.; Sullivan, P. J. *Organometallics* **1983**, *2*, 327.
 (15) Donohue, J.; Caron, A.; Goldish, E. *J. Am. Chem. Soc.* **1963**, *85*, 3748.
 (16) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Oxford University Press: Oxford, England, 1984; p 879.

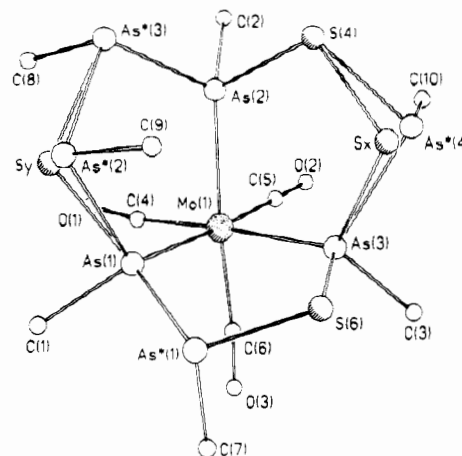
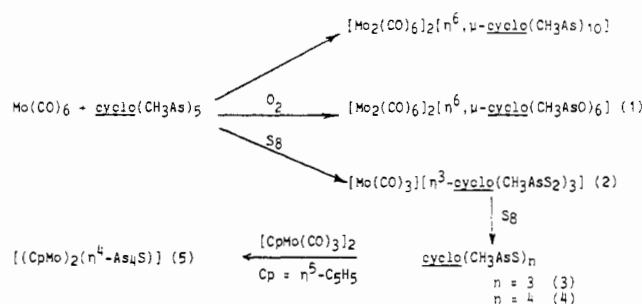
Table VIII. Selected Bond Distances (Å) and Angles (deg) for *cyclo*-(CH₃As)₄ (**4**)

4 (Molecule A)			
As(1)–S(1)	2.221 (13)	As(3)–S(2)	2.188 (22)
As(1)–S(4)	2.255 (14)	As(3)–S(3)	2.225 (12)
As(2)–S(1)	2.252 (14)	As(4)–S(3)	2.249 (13)
As(2)–S(2)	2.339 (16)	As(4)–S(4)	2.214 (17)
S(1)–As(1)–S(4)	100.1 (5)	As(1)–S(1)–As(2)	100.9 (5)
S(1)–As(2)–S(2)	103.2 (6)	As(2)–S(2)–As(3)	96.2 (6)
S(2)–As(3)–S(3)	104.9 (6)	As(3)–S(3)–As(4)	100.5 (5)
S(3)–As(4)–S(4)	103.9 (6)	As(1)–S(4)–As(4)	97.4 (6)
4 (Molecule B)			
As(5)–S(5)	2.246 (15)	As(7)–S(6)	2.248 (12)
As(5)–S(8)	2.261 (15)	As(7)–S(7)	2.264 (19)
As(6)–S(5)	2.262 (17)	As(8)–S(7)	2.219 (14)
As(6)–S(6)	2.269 (12)	As(8)–S(8)	2.279 (15)
S(5)–As(5)–S(8)	101.3 (5)	As(5)–S(5)–As(6)	98.2 (6)
S(5)–As(6)–S(6)	101.6 (6)	As(6)–S(6)–As(7)	98.1 (5)
S(6)–As(7)–S(7)	102.4 (6)	As(7)–S(7)–As(8)	95.5 (6)
S(7)–As(8)–S(8)	102.4 (6)	As(5)–S(8)–As(8)	98.5 (6)
Average Values			
As–S	2.249 (5)	As–S–As	102.5 (7)
S–As–S	98.2 (7)	S–As–S–As	106.7 (8)

**Figure 3.** Structure and labeling scheme for [Mo(CO)₃][cyclo-(CH₃As)₆S₃] (**2**). The As₆S₃ ring is disordered; starred As atoms contain substantial S character (see text and Figure 2). Thermal ellipsoids in this (and subsequent figures) are drawn by using 40% probabilities.

Each adopts the crown conformation of their organic analogues, cyclooctane, (2,4,6-Me₃C₆H₂PS)₄,¹⁷ the analogous phenyl cyclooctamer (PhAsS)₄,¹⁸ and *cyclo*-S₈. As–S bond distances for **4** range from 2.188 (22) to 2.339 (16) Å (Table VIII), a larger range in comparison to that of the cyclotrimer, **3**. However, there are no significant intermolecular contacts, and the longest bond in the molecule, As(2)–S(2), is complemented by the shortest bond in the molecule, As(3)–S(2). Bond angles average 98.2 (7)° about sulfur and 102.5 (7)° about arsenic compared to 108° in *cyclo*-S₈. Both of these angles are similar to those reported in (AsPhS)₄, 96.58 (5) and 102.07 (5)°, respectively,¹⁸ and are both slightly larger than average angles found in **3**. The average torsion angle in **4**, 106.7 (8)°, is necessarily larger than that in **3** and is within the typical torsion angles found for its cyclooctane analogue but considerably larger than the 98° torsion angles in *cyclo*-S₈. As in the case of **3** and (AsPhS)₄, all four organic groups are in approximately equatorial ring positions.

In addition to the heterocycles **3** and **4**, a variety of insoluble arsenic and molybdenum sulfides are also produced in this reaction. The molybdenum sulfides constitute a small fraction of total product and proved to be intractable and rubbery. The crystalline arsenide sulfides, As₄S₄ (realgar)¹³ and As₄S₃ (dimorphite),¹² are also found in low (<5%) yields and have been identified via X-ray

**Figure 4.** Disorder model used in refining **2**. S(x) and S(y) are minor ring sites.**Scheme I**

crystallography (unit-cell data) and mass spectroscopy of individual crystals in the insoluble precipitate.¹³ Also, during initial column chromatography of the reaction mixture, trace amounts of **2** were isolated along with starting materials and the above products.

A number of modifications to the reaction conditions and stoichiometries were attempted in an effort to obtain better yields of **2**. On reduction of the reaction temperature and an increase of **1**, the presence of Mo(CO)₃(CH₃As)₆S₃ (**2**) was identified by column chromatography. Compound **2** is air-sensitive in solution; however, its crystalline form is stable for several weeks in the atmosphere.

Crystal Structure of Mo(CO)₃[cyclo-(CH₃As)₆S₃] (2**).** The structure of **2** is shown in Figures 3 and 4; a nine-membered (CH₃As)₆S₃ ring composed of six methylarsinidene units and three sulfur atoms is bound at As(1), As(2), and As(3) to a *fac*-Mo(CO)₃ group that is only slightly distorted from octahedral symmetry. Disorder in the identity of the uncoordinated As and S atoms is discussed in the Experimental Section. It may be noted that exactly this kind of disorder has been observed in other complexes of As–S ring systems.¹⁹ The composition of **2** was confirmed by mass spectrometry. The ¹H NMR data indicate the presence of both coordinated (average δ = 2.33 ppm) and uncoordinated (average δ = 1.16 ppm) methylarsinidene groups. The ring adopts the boat–chair conformation of cyclononane.²⁰ The Mo–As distances (2.564 (4), 2.546 (4), 2.530 (4) Å) (Table VI) are typical of several related complexes including [cyclo-(CH₃AsO)₆Mo(CO)₃]₂ (average Mo–As = 2.549 (1) Å).² Distances and angles within the ring are likely distorted by the disorder; nonetheless, the values reported in Table VI are within acceptable ranges for As–As and As–S bonds (distances to composite As/S atoms have intermediate values).

The appearance of **2** (and other nonisolable, but NMR-detected, congeners) in the reaction mixture leads us to a preliminary analysis of the route to heterocyclic ring formation in these systems, as summarized in Scheme I. Earlier, we reported the

(17) Lensch, C.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1984**, 2855.
 (18) Bergerhoff, G.; Namgung, H. *Z. Kristallogr.* **1979**, *150*, 209.

(19) DiVaira, M.; Innocenti, P.; Moneti, S.; Peruzzini, M.; Stoppioni, P. *Inorg. Chim. Acta* **1984**, *83*, 161.

(20) Hendrickson, J. B. *J. Am. Chem. Soc.* **1967**, *89*, 7047.

reaction of *cyclo*-(AsCH₃)₃ with molybdenum hexacarbonyl in both the absence and presence of oxygen to form [Mo₂(CO)₆]-[*cyclo*-(CH₃As)₁₀] (**10**)²¹ and [Mo₂(CO)₆][*cyclo*-(CH₃AsO)₆] (**1**),² respectively. We have repeatedly noted the facile fragmentation of *cyclo*-polyarsines under very mild conditions (even at -20 °C) in the presence of metal carbonyls, which weaken the As-As bonds by coordination and are simultaneously decarbonylated.¹ (It may be noted that neat (CH₃As)₃, when properly purified, is thermally stable above 200 °C.²²) Through a variety of low-energy, equilibrium-controlled pathways, the various (CH₃As)₃ fragments reassemble into new structures according to the electronic and steric requirements of the remaining, partially decarbonylated metal fragments. Chalcogens also provide a means for homo arsenic ring fragmentation. Controlled addition of dioxygen leads only to the formation of arsaioxanes with perfect As-O alternation and retention of a trivalent state. More complex products form in the presence of heavier chalcogens; both ring and cage structures are ultimately formed, frequently with chalcogen-chalcogen and/or As-As bonds.⁶

We believe that compound **2**, and its congeners, occur in the pathway for the formation of the arsathianes **3** and **4** and illustrate the effect that metal coordination has on ring formation. That the coordinated ring in **2** is arsenic rich suggests that the incorporation of sulfur occurs after coordination of an all-As homocatechate. In the presence of oxygen or sulfur, initial oxidation leads to a pentavalent species incapable of further coordination via the As lone pair. This is followed by a rearrangement in which the chalcogen atom inserts into an As-As bond and arsenic returns to a trivalent state. The sequence of events, coordination, oxidation, release from the metal, and rearrangement, leads to an orderly insertion of chalcogen into As-As bonds and the exclusive formation of alternating heterocycles. The inorganic molybdenum sulfides appear in the product mixture as the probable result of an excess of *cyclo*-S₈ in the reaction mixture. Only when we substantially change the reaction conditions to disfavor formation of molybdenum sulfides do we see an increase of yield for **2**. We were unable to obtain a sufficient quantity of **2** to study its reactivity independently.

We have found no evidence for the formation of metal complexes similar to **1** containing intact, coordinated arsathianes in any of our reactions with metal carbonyls. Apparently, the cyclotrimer and tetramer, **3** and **4**, are not sterically suitable ligands; compound **2** contains a nine-membered ring, and the arsaioxane complex, **1**, a twelve-membered ring. We speculate that the retention of an approximately octahedral coordination geometry (as is consistently found in group 6 complexes containing coordinated rings and chains of main-group atoms) is a prevailing effect. Also, the arsaioxane complex **1** required a ring expansion from a stable cyclotrimer precursor to a coordinated cyclohexamer, and it is reasonable to expect that such facile expansions are more difficult for arsathianes than for arsaioxanes.

In an effort to further examine the potential use of **3** and **4** as synthons, we investigated the thermal reaction of these purified heterocycles with [CpMo(CO)₃]₂ (Cp = η⁵-C₅H₅). The reaction mixture formed in toluene resulted in the isolation and identification of several products. The novel compound Cp₂Mo₂As₄S (**5**) was the first fraction to be isolated by chromatography. Subsequent fractions revealed two diarsenic-bridged cyclopentadienylmolybdenum carbonyl dimers, [CpMo(CO)₂]₂(η²,μ-As₂) (**7**)²³ and [CpMo(CO)]₂(η²,μ-As₂)₂ (**8**),²⁴ isolated in minor quantities (<5% yield) and identified by spectroscopic means. Compounds **7** and **8** and a compound similar to **5**, namely Cp₂Mo₂As₅ (**6**),²⁵ have been reported previously as the products

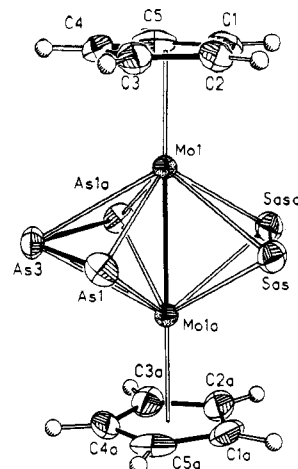


Figure 5. Molecular structure and labeling scheme for [(CpMo)₂(As₄S)] (**5**). Sas is a 50/50 S/As composite atom resulting from the 2-fold rotational disorder produced by an axis through As(3) and the midpoint of the Sas-Sas(a) vector.

Table IX. Selected Bond Distances (Å) and Angles (deg) for [(CpMo)₂(As₄S)] (**5**)^a

Bond Distances			
Mo(1)-As(1)	2.531 (1)	Mo(1)-C(1)	2.339 (10)
Mo(1a)-As(1)	2.539 (1)	Mo(1)-C(2)	2.330 (8)
Mo(1)-As(3)	2.743 (1)	Mo(1)-C(3)	2.330 (8)
Mo(1a)-As(3)	2.744 (1)	Mo(1)-C(4)	2.336 (8)
Mo(1)-Sas	2.555 (2)	Mo(1)-C(5)	2.320 (11)
Mo(1a)-Sas	2.558 (1)	Sas-Sas(a)	2.237 (3)
Mo(1)-Mo(1)-Mo(1a)	2.683 (1)		
Bond Angles			
As(1)-As(3)-As(1a)	107.3 (1)	Mo(1)-As(3)-Mo(1a)	58.5 (1)
Mo(1)-As(1)-Mo(1a)	63.9 (1)	Mo(1)-Sas-Mo(1a)	63.3 (0)

^aSas is a 50/50 sulfur/arsenic composite atom.

of the reaction between [CpMo(CO)₃]₂ and *cyclo*-(AsCH₃)₃.

The formation of **7** and **8**, even in small quantities, suggests that under the reaction conditions the arsathianes experience some degree of "scrambling" with the extrusion of sulfur. However, despite a careful search for their presence, no evidence was found for the formation of dinuclear CpMo polysulfur complexes, which are known in a variety of structural forms.²⁶ Since these reactions were conducted with the Mo dimer as the limiting reagent, it appears that, in a competitive environment, arsenic, even if it has to lose its organic substituent (as occurred to form **7** and **8**), is preferred over sulfur as a ligating element.

The compounds **5** and **6** are in a special class of main-group transition-metal "triple-decker-sandwich" compounds consisting of Cp ring outer decks and a middle deck of main-group atoms from groups 15 and 16. Scherer and co-workers have also reported phosphorus-containing triple-decker-sandwich compounds of group 6 cyclopentadienides and very recently one containing a hexaarsabenzene ring.²⁷ Sacconi and co-workers have also synthesized compounds containing P₃ and As₃ rings in a similar fashion.²⁸ Other triple-decker-sandwich compounds are known for a number of transition-metal cyclopentadienides with organic rings²⁹ and with carboranes.³⁰

- (21) Rheingold, A. L.; Fountain, M. E.; DiMaio, A.-J. *J. Am. Chem. Soc.* **1987**, *109*, 141.
 (22) Rheingold, A. L. In *Homoatomic Rings, Chains and Macromolecules of the Main-Group Elements*; Rheingold, A. L., Ed.; Elsevier: Amsterdam, 1977; p 385.
 (23) Sullivan, P. J.; Rheingold, A. L. *Organometallics* **1982**, *1*, 1547.
 (24) DiMaio, A.-J.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1987**, 404.

- (25) Foley, M. J.; Sullivan, P. J.; Rheingold, A. L. *J. Am. Chem. Soc.* **1982**, *104*, 4727.
 (26) Tremel, W.; Hoffmann, R.; Jemmis, E. D. *Inorg. Chem.* **1989**, *28*, 1213.
 (27) (a) Scherer, O. J.; Schwall, J.; Wolmershäuser, G.; Kaim, W.; Gross, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 363. (b) Scherer, O. J.; Sitzmann, H.; Wolmershäuser, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 351. (c) Scherer, O. J.; Swarowsky, M.; Wolmershäuser, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 405. Scherer, O. J.; Sitzmann, H.; Wolmershäuser, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 212.
 (28) DiVaira, M.; Midollini, S.; Sacconi, L. *J. Am. Chem. Soc.* **1979**, *101*, 1757. Dapporto, P.; Sacconi, L.; Stopponi, P.; Zanobini, F. *Inorg. Chem.* **1981**, *20*, 3843. Bianchini, C.; DiVaira, M.; Meli, A.; Sacconi, L. *J. Am. Chem. Soc.* **1981**, *103*, 1448.

Crystal Structure of $Cp_2Mo_2(\eta^2, \mu-As_3)(\eta^2, \mu-AsS)$ (5). The structure of **5** is shown in Figure 5; a crystallographic 2-fold rotational axis passes through As(3) and the midpoint of the Sas-Sas(a) bond. The overall structure is that of a triple-decker sandwich in which the middle deck contains one sulfur and four arsenic atoms; deviations from planarity for these five atoms is less than their esd's. The outer decks are Cp rings that are also coplanar. The middle deck is divided into two units: a μ, η^2-As_3 group and a μ, η^2-AsS group. The As-S distance between these groups is very long (2.961 (2) Å) (Table IX) indicating, at best, a weakly bonded interaction. The As_3 group is allylic with an As-As distance of 2.374 (1) Å, which is intermediate between recognized single- and double-bond ranges,¹ and the As-As-As angle is 107.3 (1)°. The crystallographically imposed symmetry creates disorder in the AsS group such that both atoms are 50/50

As/S composites; these are labeled Sas. Although possibly affected by this disorder, the As-S (Sas-Sas(a)) distance is short (2.237 (3) Å) and indicative of a bond order fractionally greater than 1. The distances of the atoms of these groups to Mo are very similar for the 1,3-atoms of the allylic group (2.539 (1) Å) and the AsS composite atoms (2.558 (1) Å); the distance to the central allylic As atom is considerably longer (2.744 (1) Å).

Recently, this class of triple-decker sandwiches has been the subject of two theoretical studies with particular emphasis on structures containing a group 15 or 16 central ring.³¹ In **6**, the middle layer is also distorted, but to a lesser degree, and in the all-P analogue to **6**, $Cp_2Cr_2P_3$,^{27a} the central is undistorted. Treme et al.^{31b} have postulated that the central As_3 ring distortion from an ideal D_{3h} configuration is due to a second-order Jahn-Teller distortion. On the basis of their calculations, they predicted that as more electronegative atoms are placed in the ring these atoms would have a tendency to be more "isolated", with ring-ring bonds lengthening and eventually becoming nonexistent. Compound **5** conforms to these expectations. Conversely, less electronegative elements should favor higher symmetry. The substitution of S for As increases the cluster electron count to 28, making it iso-electronic to $Cp_2Mo_2As_5^-$.

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Supplementary Material Available: Tables of complete crystallographic data, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates (12 pages); listings of observed and calculated structure factors (47 pages). Ordering information is given on any current masthead page.

- (29) [Cp_2Ni_2]⁺: Werner, H.; Salzer, A. *Synth. Inorg. Met.-Org. Chem.* **1972**, *2*, 239. Salzer, A.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 930. $Cp_2V_2C_6R_6$: Duff, A. W.; Jonas, K.; Goddard, R.; Kraus, H.-J.; Kruger, C. *J. Am. Chem. Soc.* **1983**, *105*, 5479. $Cp_2Co_2C_6R_6$: Jonas, K. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 295. $Cp_2Cr_2C_6H_6$: Lamanna, W. M.; Gleason, W. B.; Britton, D. *Organometallics* **1987**, *6*, 1583. Lamanna, W. M. *J. Am. Chem. Soc.* **1986**, *108*, 2096. $Cp_2Ru_2Cp^*$: Kudinov, A. R.; Rybinskaya, M. L.; Struchkov, Yu. T.; Yanovskii, A. I.; Petrovskii, P. V. *J. Organomet. Chem.* **1987**, *336*, 187.
- (30) Siebert, W.; Renk, T.; Kingberger, K.; Bochmann, M.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 779. Siebert, W.; Rothermel, W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 333. Edwin, J.; Bochmann, M.; Bohm, M. C.; Brennan, D. E.; Geiger, W. E.; Kruger, C.; Pebler, J.; Pritzkow, H.; Siebert, W.; Swiridoff, W.; Wade, H.; Weiss, J.; Zennick, U. *J. Am. Chem. Soc.* **1983**, *105*, 2582. Beer, D. C.; Miller, V. R.; Sneddon, L. G.; Grimes, R. N.; Mathew, M.; Palenic, G. *J. Am. Chem. Soc.* **1973**, *95*, 3046. Grimes, R. N.; Beer, D. C.; Miller, V. R.; Sneddon, L. G.; Weiss, R. *Inorg. Chem.* **1974**, *13*, 1138. Herberich, G. E.; Hessner, B.; Huttner, G.; Zsolnar, L. *J. Am. Chem. Soc.* **1983**, *105*, 5479. Wade, H.; Pritzkow, H.; Siebert, W. *Chem. Ber.* **1985**, *118*, 729. Kuhlman, T.; Pritzkow, H.; Zenneck, U.; Siebert, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 965.

- (31) (a) Jemmis, E. D.; Reddy, A. C. *Organometallics* **1988**, *7*, 1561. (b) Tremel, W.; Hoffmann, R.; Kertesz, M. *J. Am. Chem. Soc.* **1989**, *111*, 2030.

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Synthesis of Icosahedral Boranes Containing Bismuth

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The first bismaboranes, 1,2-EBiB₁₀H₁₀ (E = P, As, Sb, Bi), have been prepared and characterized. The compound 1,2-Bi₂B₁₀H₁₀ has also been characterized by a single-crystal X-ray structure determination (space group $P\bar{1}$, $a = 12.174$ (1) Å, $b = 14.070$ (2) Å, $c = 12.135$ (1) Å, $\alpha = 91.07$ (0)°, $\beta = 99.51$ (0)°, $\gamma = 106.70$ (0)°, $Z = 8$). Two-dimensional (¹¹B-¹¹B) NMR studies have been used to assign boron nuclei to specific resonances. The anion B₁₁H₁₁Bi⁻ was prepared from B₁₁H₁₄⁻, BiCl₃, and *n*-butyllithium. While these compounds decompose slowly at room temperature in solution, in the solid state they are surprisingly stable to heat.

Introduction

Boron cage compounds incorporating one or two group 15 elements are known for all the elements of this group with the exception of bismuth.¹⁻⁴ Carboranes containing the heavy element lead have been known for several years. While the compound 1,2,3-SnC₂B₉H₁₁ could be sublimed at 250 °C under vacuum, the

related 1,2,3-PbC₂B₄H₆ was found to decompose at room temperature under vacuum.^{5,6} Recently reported syntheses of R₂Bi-BiR₂ derivatives indicate that these compounds are thermally unstable as well as air sensitive.⁷ The easy thermal decomposition of organolead compounds is well-known.

Despite this unfavorable background information, we have investigated the syntheses of several icosahedral bismaboranes containing one or two bismuth atoms in the cage structure. In this paper, we report the preparation and characterization of these

- (1) Todd, L. J. In *Metal Interactions in Boron Clusters*; Grimes, R. N., Ed.; Plenum: New York, 1982, pp 145-171. (b) Todd, L. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., et al., Eds.; Pergamon Press: New York, 1982; Vol. I, pp 543-553.
- (2) Little, J. L. *Inorg. Chem.* **1979**, *18*, 1598.
- (3) Hanusa, T. P.; Roig de Parisi, N.; Kester, J. G.; Arafat, A.; Todd, L. J. *Inorg. Chem.* **1987**, *26*, 4100 and references therein.
- (4) Arafat, A.; Baer, J.; Huffman, J. C.; Todd, L. J. *Inorg. Chem.* **1986**, *25*, 3757.

- (5) Rudolph, R. W.; Voorhees, R. L.; Cochoy, R. E. *J. Am. Chem. Soc.* **1970**, *92*, 3351.
- (6) Wong, K. S.; Grimes, R. N. *Inorg. Chem.* **1977**, *16*, 2053.
- (7) Calderazzo, F.; Poli, R.; Pelizzi, G. *J. Chem. Soc., Dalton Trans.* **1984**, 2365.
- (8) Little, J. L.; Pao, S. S.; Sugathan, K. K. *Inorg. Chem.* **1974**, *13*, 1752.