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Group-6 Carbonyl Complexes of Methylarsathiane Rings, *cyclo*-$(CH_3AsS)_n$ ($n = 4-6$). Synthesis and Structural Characterization of $[Cr(CO)_5\text{-}\eta^1\text{-}cyclo\text{-}(CH_3AsS)_4]$, $[Cr(CO)_3\text{-}\eta^3\text{-}cyclo\text{-}(CH_3AsS)_5]$, and $[W(CO)_3\text{-}\eta^3\text{-}cyclo\text{-}(CH_3AsS)_6]$

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The photolysis reactions of *cyclo*-methylarsathiane, *cyclo*-$(CH_3AsS)_{3,4}$, with group-6 metal carbonyls $M(CO)_6$ (M = Cr, W) in THF give the complexes $[Cr(CO)_5\text{-}\eta^1\text{-}cyclo\text{-}(CH_3AsS)_4]$ (**1**), $[Cr(CO)_3\text{-}\eta^3\text{-}cyclo\text{-}(CH_3AsS)_5]$ (**2**), and $[W(CO)_3\text{-}\eta^3\text{-}cyclo\text{-}(CH_3AsS)_6]$ (**3**) in which the As−S ring system expands giving metal-stabilized rings of 8, 10, and 12 alternating arsenic and sulfur atoms. In this regard, *cyclo*-$(CH_3AsS)_{3,4}$ resembles *cyclo*-$(RAs)_n$ and *cyclo*-$(CH_3AsO)_4$ in its reactions with these metal carbonyls. Complexes **1** and **2** were crystallographically characterized, while the structure of **3** was deduced from ^{1}H NMR and mass spectrometry studies. In complexes **2** and **3**, the metal coordinates to both the arsenic and sulfur atoms of the ring; however, in all three complexes it shows preference for arsenic over sulfur. Bonding to sulfur occurs only when its position better accommodates octahedral symmetry at the metal atom. The main-group ring structures expand as required to fulfill the more demanding electronic and geometrical requirements of the metallic group.

Introduction

We have previously studied reactions of *cyclo*-polyarsines, *cyclo*-$(RAs)_n$,[1−10] with metal carbonyls.[11−14] West and co-workers also reported similar reactions.[15−19] One of the striking features of complexes formed from these homocyclic systems with transition-metal carbonyls is the variety of complexes containing arsenic chain and ring structures that can be derived from them.[20] The products of *cyclo*-$(RAs)_n$ reactions can be broadly classified as products with intact rings, in which the ring retains its original size or expands, products in which the rings open and bridge two metal centers, and products in which the arsenic atoms lose some or all of their organic substituents and enter the complexes as naked arsenic atoms. However, despite the isolobal similarity between *cyclo*-$(RAs)_n$ and cyclic allotropes of sulfur, their coordination chemistries are markedly different. In its reactions with organometallic reagents, *cyclo*-S_8 mainly undergoes ring opening, resulting in the formation of sulfide,[21] disulfide,[22] or chelating polysulfido[23] complexes. In stark contrast to the behavior of the cyclopnictides, only a single complex containing an intact ring of sulfur atoms has been reported, $[Ag(S_8)_2]AsF_6$.[24]

We have now extended this chemistry to the related arsenic−sulfur heterocycles *cyclo*-methylarsathiane, *cyclo*-$(CH_3AsS)_{3,4}$, a mixture of six- and eight-membered ring systems with alternating arsenic−sulfur bonds,[25] to compare the disparate chemistries of the homocyclic species to these heterocycles. In a recent paper, we showed that the rings, when opened under reducing

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conditions, formed complexes of group-4 metallocenes that strictly resembled their all-sulfur analogues,[26] e.g., the metallocycles $\mathrm{Cp_2M(-S(AsCH_3)(S(AsCH_3)S-)}$, M = Ti, Zr, Hf, resemble their $\mathrm{Cp_2MS_5}$ analogues. The presence of both arsenic and sulfur in the ring system allows for the ligation of the metal atom to either or both arsenic and sulfur atoms. In earlier work, in which a mixture of the homocycles *cyclo*-$\mathrm{(CH_3As)_5}$ and $\mathrm{S_8}$ was reacted with $\mathrm{Mo(CO)_6}$, [$\mathrm{(CO)_3Mo}$[η^3-*cyclo*-$\mathrm{(CH_3As)_6S_3}$]} (**4**) was isolated.[25] Complex **4** contains a nine-membered ring with six $\mathrm{CH_3As}$ and three S units. In related work, oxygen atoms from $\mathrm{O_2}$ were inserted into the As−As bonds of *cyclo*-$\mathrm{(CH_3As)_5}$, in the presence of $\mathrm{Mo(CO)_6}$, to form methylarsaoxane, *cyclo*-$\mathrm{(CH_3AsO)_4}$,[27] which subsequently forms the ring-expansion complex [$\mathrm{Mo(CO)_3]_2}$[*cyclo*-$\mathrm{(CH_3AsO)_6}$] with exclusive bonding of the ligand through Mo−As bonds.[28] These results suggested that *cyclo*-$\mathrm{(CH_3AsS)_{3,4}}$ could serve as a polydentate ligand toward metal carbonyls and offer a means for the isolation of mixed arsenic−sulfur−metal complexes. To that end, we undertook the investigation of photolysis reactions of $\mathrm{Cr(CO)_6}$ and $\mathrm{W(CO)_6}$ in the presence of *cyclo*-$\mathrm{(CH_3AsS)_{3,4}}$, and we report here the synthesis and characterization of mononuclear chromium and tungsten complexes of *cyclo*-$\mathrm{(CH_3AsS)}_n$, [$\mathrm{Cr(CO)_5}$-η^1-*cyclo*-$\mathrm{(CH_3AsS)_4}$] (**1**), [$\mathrm{Cr(CO)_3}$-η^3-*cyclo*-$\mathrm{(CH_3AsS)_5}$] (**2**), and [$\mathrm{W(CO)_3}$-η^3-*cyclo*-$\mathrm{(CH_3AsS)_6}$] (**3**), containing 8-, 10-, and 12-membered As−S heterocycles coordinated to a metal carbonyl fragment.

Experimental Section

All experiments were carried out under an atmosphere of dry, oxygen-free dinitrogen. Chromium hexacarbonyl and tungsten hexacarbonyl (Aldrich) were sublimed prior to use. *cyclo*-$\mathrm{(CH_3AsS)_{3,4}}$ was prepared from the reaction of $\mathrm{CH_3AsCl_2}$[29] and $\mathrm{H_2S}$ in refluxing methanol. (The mixture of trimer and tetramer can be separated by crystal morphology or by column chromatography but reequilibrates in solution over a period of several days.) All reaction solvents were distilled under an atmosphere of dinitrogen from Na-benzophenone. A medium-pressure UV lamp was used for the photolysis reactions, which were carried out in a photolytic cell composed of a quartz tube fitted into an adapter having ground-joint outlets for a coldfinger and a gas inlet. The quartz tube was also equipped with a stirring bar. Cold water was allowed into the coldfinger, and the solution was constantly stirred during photolysis. IR: all products showed the expected ν(CO) bands. ^{1}H NMR spectra in $\mathrm{C_6D_6}$ and $\mathrm{CDCl_3}$ were obtained on a Bruker 250 MHz spectrometer with $\mathrm{Me_4Si}$ as an internal reference, and mass spectrometry results were obtained on VG AutospecQ or VG 7070F mass spectrometers. As has been our consistent experience, we have been unable to obtain satisfactory elemental analysis data on these and other early-transition-metal pnictides and chalcogenides.

Preparation of [$\mathrm{Cr(CO)_5}$ -*cyclo*-η^1-$\mathrm{(CH_3AsS)_4}$] (1). $\mathrm{Cr(CO)_6}$ (0.880 g, 4.0 mmol) and *cyclo*-$\mathrm{(CH_3AsS)_{3,4}}$ (0.732 g, 2.0 mmol of the trimer) were charged into the photolysis cell. The cell was evacuated and back-filled with dinitrogen. THF (30 mL) was syringed into the cell, and the solution was stirred to dissolve the solids. The solution was irradiated for 3 h, and its color changed to yellow. It was transferred under dinitrogen to a Schlenk flask, and the solvent was removed under reduced pressure. Excess unreacted $\mathrm{Cr(CO)_6}$ was sublimed at about 70 °C and 5 mmHg. The solid residue was dissolved in a minimum of toluene and was loaded on an alumina column. **1** eluted as a yellow fraction with pure toluene. Yield: 0.76 g (74%). Insignificant quantities of an orange product that eluted after **1** was identified as **2** by a similar mass spectrum. Mp 140−141 °C. ^{1}H NMR (benzene-d_6): δ 2.369 (s, 3H), 1.951 (s, 3H), and 1.911 (s, 6H). MS: *m*/*z* 487.6 [0.10, $\mathrm{(CH_3AsS)_4^+}$]; 472.6 [0.25, $\mathrm{(CH_3As)_3AsS_4^+}$]; 445.7 [0.20, $\mathrm{(CH_3AsS)_3Cr(CO)^+}$]; 417.7 [0.60, $\mathrm{(CH_3AsS)_3Cr^+}$]; 365.8 [33.27, $\mathrm{(CH_3AsS)_3^+}$]; 350.7 [16.97, $\mathrm{(CH_3As)_2AsS_3^+}$]; 243.8 [40.77, $\mathrm{(CH_3AsS)_2^+}$]; 228.8 [70.96, $\mathrm{(CH_3As)AsS_2^+}$]; 211.8 [64.35, $\mathrm{(CH_3AsSAsCH_3)^+}$]; 196.8 [77.64, $\mathrm{(CH_3AsSAs)^+}$]; 181.8 [50.13, $\mathrm{(AsSAs)^+}$]; 121.9 [61.85, $\mathrm{(CH_3AsS)^+}$]; 106.9 [100, $\mathrm{AsS^+}$].

Preparation of [$\mathrm{Cr(CO)_3}$-η^3-*cyclo*-$\mathrm{(CH_3AsS)_5}$] (2). $\mathrm{Cr(CO)_6}$ (0.440 g, 2.0 mmol) and *cyclo*-$\mathrm{(CH_3AsS)_{3,4}}$ (0.366 g, 1.0 mmol of the trimer) were charged into the photolysis cell, and 20 mL of THF was added. The colorless solution changed to yellow in less than 30 min and then changed to deep yellow and finally to orange in about 6 h. The product was purified by column chromatography in a silica support loaded with toluene, and **2** eluted as an orange fraction with a toluene−THF (80:20) mixture. In the elution sequence, **2** was preceded by a much smaller yellow band identified as **1** by mass spectrometry. Removal of the solvent and recrystallization from THF/pentane afforded 0.18 g of an orange crystalline solid in 39% yield. X-ray quality crystals were grown from slow evaporation of a concentrated toluene solution. Mp 128−132 °C. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 2.401, 1.868, 1.428 (2:1:2). MS: *m*/*z* 717.7 [8.19, $\mathrm{M^+ - CO}$]; 577.7 [8.45, $\mathrm{(CH_3As)_5S_4^+}$]; 557.8 [34.90, $\mathrm{Cr(CO)_5(CH_3AsS)_3^+}$]; 501.8 [12.35, $\mathrm{Cr(CO)_3(CH_3AsS)_3^+}$]; 445.8 [51.28, $\mathrm{CrCO(CH_3AsS)_3^+}$]; 417.8 [100, $\mathrm{Cr(CH_3AsS)_3^+}$]; 402.8 [75.46, $\mathrm{Cr(CH_3\ As)_2AsS_3^+}$]; 365.8 [60.92, $\mathrm{(CH_3AsS)_3^+}$]; 350.8 [57.34,$\mathrm{(CH_3As)_2AsS_3^+}$]; 323.8 [28.03, $\mathrm{CrCO(CH_3AsS)_2^+}$]; 295.8 [47.11, $\mathrm{Cr(CH_3AsS)_2^+}$]; 280.8 [25.94, $\mathrm{Cr(CH_3As)AsS_2^+}$]; 265.8 [32.03, $\mathrm{CrAs_2S_2^+}$]; 243.9 [72.65, $\mathrm{(CH_3AsS)_2^+}$]; 213.8 [24.67, $\mathrm{As_2S_2^+}$]; 190.8 [66.59, $\mathrm{CrAsS_2^+}$]; 173.8 [52.51, $\mathrm{CrCH_3AsS^+}$]; 158.8 [56.46, $\mathrm{CrAsS^+}$]; 121.9 [52.66, $\mathrm{CH_3AsS^+}$]; 106.9 [40.58, $\mathrm{AsS^+}$].

Preparation of [$\mathrm{W(CO)_3}$-η^3-*cyclo*$\mathrm{(CH_3AsS)_6}$] (3). $\mathrm{W(CO)_6}$ (0.704 g, 2.0 mmol) and *cyclo*-$\mathrm{(CH_3AsS)_{3,4}}$ (0.366 g, 1.0 mmol of the trimer) were charged into the photolysis cell, and 25 mL of THF was added. The solution was photolyzed with stirring for 2 h. The color of the solution turned yellow in the first 30 min and slowly to a dark yellow orange. THF was removed under reduced pressure to leave behind a brownish-orange solid. Excess $\mathrm{W(CO)_6}$ was sublimed off under reduced pressure at about 50 °C. The solid residue was dissolved in a minimum of toluene and loaded into a silica column prepared with toluene. **3** eluted as a brown fraction with pure toluene. Yield: 0.240 g (48%). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 2.529, 2.230, 1.760 (1:1:1). MS: *m*/*z* 547.57 [0.35, $\mathrm{(CH_3AsS)_3W^+}$]; 363.72 [28.22, $\mathrm{As_2SW^+}$]; 351.83 [52.46, $\mathrm{AsS_2W(CO)^+}$]; 299.61 [100, $\mathrm{As_4^+}$]. Several attempts at growing diffraction-grade single crystals of this complex were not successful; the ones obtained diffracted too weakly to provide unit-cell data.

Crystallographic Structural Determination. Crystal data, data collection, and refinement parameters for **1** and **2** are summarized in Table 1. Microscopic examination showed that both bulk samples were morphologically pure. Crystals were mounted with epoxy cement on glass fibers. All X-ray data were collected with Siemens P4 diffractometers equiped with a graphite monochromator. Crystal quality was determined by photographic and peak-width criteria. Systematic absences in the diffraction and film data uniquely defined the space group for complex **2**. For complex **1**, the initial solution of the data set in the centrosymmetric space group *C*2/*c* proved correct based on chemically reasonable and computationally

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Table 1. Crystal, Data Collection, and Refinement Parameters for [Cr(CO)$_5$-*cyclo*-η^1-(CH$_3$AsS)$_4$] (1) and [Cr(CO)$_3$-*cyclo*-η^3-(CH$_3$AsS)$_5$] (2)

	1	2
empirical formula	$C_9H_{12}As_4CrO_5S_4$	$C_8H_{15}As_5CrO_3S_5$
fw	680.11	746.10
cryst syst	monoclinic	monoclinic
space group	*C*2/*c*	*P*2$_1$/*c*
a, Å	26.283(5)	8.762(4)
b, Å	8.4267(14)	27.69(2)
c, Å	19.926(2)	9.254(1)
β, deg	101.854(8)	99.56(2)
V, Å^3	4319.2(12)	2214(1)
Z	8	4
density (calcd), g cm^{-1}	2.092	2.238
cryst color, habit	yellow block	orange block
μ(Mo Kα), mm^{-1}	7.013	8.408
temp, °C	23(2)	24(2)
2θ scan limit, deg	4.18− 45.00	4.70−45.00
no. of reflns collected	3541	3703
no. of indep reflns	2816 (R_{int} = 0.0980)	2882 (R_{int} = 0.0520
no. of data/parameters	2816/208	2876/219
GOF	0.655	1.018
R(*F*), %^{a}	4.84	4.07
R(w*F*^{2}), %	12.17	8.43
largest diff. peak, e Å^{-3}	0.831	1.364

^{a} Quantity minimized = $R(F) = \sum\Delta/\sum(F_o)$; $R(wF^2) = \sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]^{1/2}$; $\Delta = |F_o - F_c|$.

stable refinement results. Empirical absorption corrections were applied to both **1** and **2**. Both structures were solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined with anisotropic displacement coefficients, and the hydrogen atoms were treated as idealized contributions. In **2,** atoms As(4) and S(5) are disordered over two sites in an approximately 91/9 ratio. A figure showing the disorder model is available as Supporting Information. All computer programs used are contained in the SHELXTL libraries (G. Sheldrick, Siemens XRD, Madison, WI).

Discussion and Results

Anaerobic photolysis of THF solution of Cr(CO)$_6$ in the presence of *cyclo*-(CH$_3$AsS)$_{3,4}$ gives the complexes [Cr(CO)$_5$-η^1-*cyclo*-(CH$_3$AsS)$_4$] (**1**) and [Cr(CO)$_3$-η^3-*cyclo*-(CH$_3$AsS)$_5$] **(2)**, depending on the photolysis time and the extent of decarbonylation of the chromium hexacarbonyl. When the photolysis is performed for 2 h, the major product is **1**; when the photolysis time is increased to 6 h, **2** is the major product. Isolated samples of **1**, after a 6-h irradiation under conditions identical with those used to obtain **2** directly, were converted exclusively to **2**, as followed by NMR spectroscopy.

The structure of **1** was obtained crystallographically and is shown in Figure 1; selected bond distances and angles are given in Table 2. In **1**, the Cr(CO)$_5$ group is coordinated to the eight-membered heterocyclic arsathiane ring via an arsenic atom. The structures of both the uncoordinated and coordinated rings have the ground-state configuration of cyclooctane and crown-S$_8$. The absence of any solution or solid-state evidence for the formation of Cr(CO)$_5$ complexes of the trimer ring present in the reactant suggests that a ring opening, expansion, and closing process prior to or in conjunction with the formation of the complex exists. The largest S−As−S angle, 106.1(1)°, contains the coordinated As atom, As(4). The remaining three angles are similar and more acute. The average of the S−As−S angles (101.8(1)°) is almost identical to the average for free *cyclo*-(CH$_3$AsS)$_4$ (102.5(7)°).[25] The As−S−As bond angles vary considerably in the range 93.9(1)−103.5(1)° and do not appear to correlate with any structural feature. The wide range, therefore, is likely the result of intermolecular ("packing") forces and suggests that the As−S−As angle is easily deformed. The average As−S−As angle, 99.9(1)°, is also close to the average for free *cyclo*-(CH$_3$AsS)$_4$ (98.2(7)°). The average As−S bond distance in **1**, 2.254(3) Å, is very similar to that found in other ring and nonring As−S structures: *cyclo*-(CH$_3$AsS)$_3$, 2.258(1) Å;[25] *cyclo*-(CH$_3$AsS)$_4$, 2.249(5) Å; [25] *cyclo*-(Ph$_2$-As$_2$S$_3$), 2.253(4) and 2.252(5) Å;[30] AsS$_3^{3-}$, 2.25 Å;[31] As$_4$S$_4$, 2.21 Å;[32] The chromium environment in Cr(CO)$_5$ is essentially octahedral; the C−Cr−C bond angles are very close to 90° or 180°.

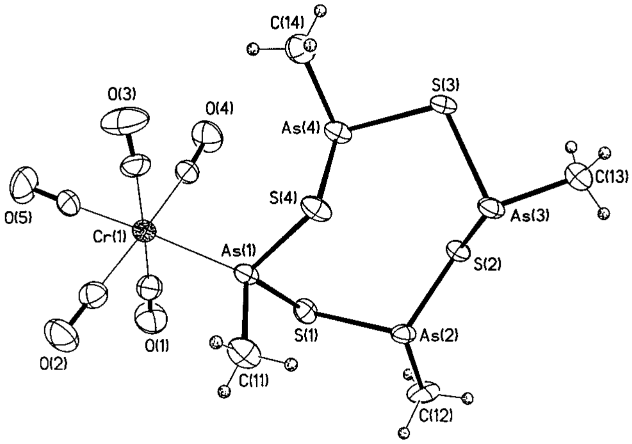

Figure 1. Molecular structure of [Cr(CO)$_5$-η^1-*cyclo*-(CH$_3$-AsS)$_4$] (**1**) drawn with 30% thermal ellipsoids.

Table 2. Selected Bond Distances and Angles for [Cr(CO)$_5$-η^1-*Cyclo*-(CH$_3$AsS)$_4$] (1)

(a) Bond Distances (Å)

As(1)−S(1)	2.238(3)	As(1)−S(4)	2.236(3)
As(2)−S(2)	2.255(3)	As(2)−S(1)	2.267(3)
As(3)−S(2)	2.248(3)	As(3)−S(3)	2.265(3)
As(4)−S(3)	2.248(3)	As(4)−S(4)	2.278(3)
Cr(1)−As(1)	2.461(2)		

(b) Bond Angles (deg)

S(1)−As(1)−S(4)	106.11(12)	S(1)−As(1)−Cr(1)	110.40(10)
S(4)−As(1)−Cr(1)	120.34(11)	S(2)−As(2)−S(1)	101.10(12)
S(2)−As(3)−S(3)	101.87(13)	S(3)−As(4)−S(4)	98.00(12)
As(1)−S(1)−As(2)	103.52(12)	As(3)−S(2)−As(2)	93.89(13)
As(4)−S(3)−As(3)	102.05(11)	As(1)−S(4)−As(4)	99.90(12)

The ^{1}H NMR spectrum of **1** contains three sharp singlets in a 1(δ *2.369*):1(*1.951*):2(*1.911*) pattern. The most downfield resonance represents the methyl group bonded to the coordinated As atom, As(1), then the As atom most distant from the coordinated one, As(3), followed by the equivalent pair, As(2) and As(4). Up to 80 °C, no line broadening was seen that might have indicated the onset of rapid Cr(CO)$_5$ hopping to different ring sites.

The formation of **2** is accompanied by ring expansion, from 8 to 10 members, and further decarbonylation.

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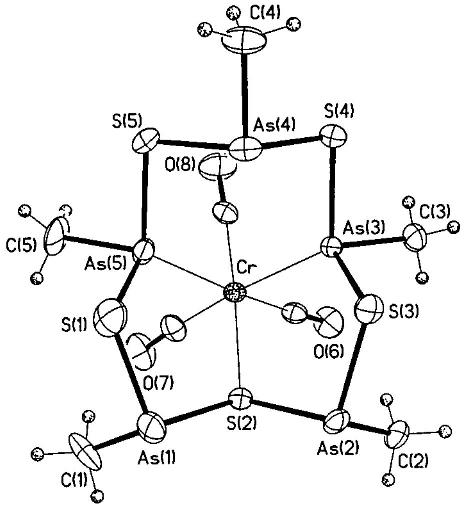

Figure 2. Molecular structure of [Cr(CO)$_3$-η^3-*cyclo*-(CH$_3$AsS)$_5$] (**2**) drawn with 30% thermal ellipsoids.

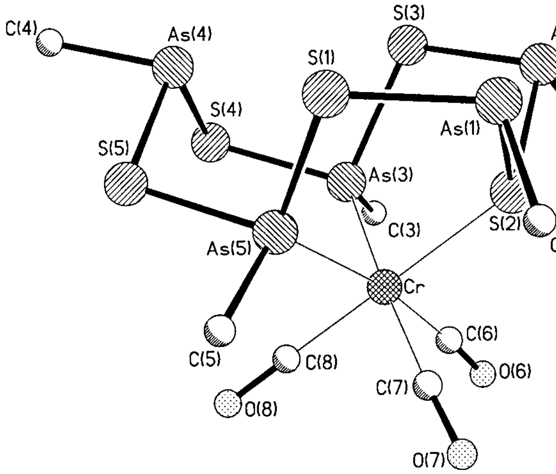

Figure 3. Side view of the molecular structure of [Cr(CO)$_3$-η^3-*cyclo*-(CH$_3$AsS)$_5$] (**2**).

Table 3. Selected Bond Distances and Angles for [Cr(CO)$_3$-η^3-*Cyclo*-(CH$_3$AsS)$_5$] (2)

(a) Bond Distances (Å)

Cr−S(2)	2.354(3)	Cr−As(5)	2.398(2)
Cr−As(3)	2.412(2)	As(1)−S(1)	2.225(4)
As(1)−S(2)	2.307(3)	As(2)−S(3)	2.217(3)
As(2)−S(2)	2.297(3)	As(3)−S(4)	2.246(3)
As(3)−S(3)	2.264(3)	As(4)−S(4)	2.228(3)
As(4)−S(5)	2.249(3)	As(5)−S(5)	2.244(3)
As(5)−S(1)	2.259(3)		

(b) Bond Angles (deg)

S(2)−Cr−As(5)	92.47(9)	S(2)−Cr−As(3)	92.21(8)
As(5)−Cr−As(3)	98.38(6)	S(1)−As(1)−S(2)	103.35(11)
S(2)−As(2)−S(3)	101.81(10)	S(4)−As(3)−S(3)	98.88(11)
S(4)−As(3)−Cr	122.30(8)	S(3)−As(3)−Cr	114.73(9)
S(4)−As(4)−S(5)	103.79(12)	S(5)−As(5)−S(1)	100.41(14)
S(5)−As(5)−Cr	121.26(11)	S(1)−As(5)−Cr	116.94(11)
As(1)−S(1)−As(5)	103.78(14)	As(2)−S(2)−Cr	117.40(11)
As(1)−S(2)−Cr	116.74(11)	As(2)−S(3)−As(3)	104.09(11)
As(1)−S(2)−As(1)	96.33(10)	As(4)−S(4)−As(3)	97.40(11)
As(5)−S(5)−As(4)	99.04(12)		

Ring expansion is well-known for the homocyclic arsines in reactions with metal carbonyls[11] in which the preferred ring size is dictated by the metallic group and the extent of decarbonylation. The structure of **2** was crystallographically determined as shown in Figures 2 and 3; selected bond distances and angles are given in Table 3. The chromium atom is coordinated to the heterocyclic ring through two arsenic atoms and one sulfur atom in such a way that there are two or three atoms in the ring between any two coordinated atoms. There are three spacer atoms between the two coordinated arsenic atoms and two between the coordinated sulfur and arsenic atoms. To allow simultaneous coordination to three atoms of the same ring, the ring is highly puckered and resembles the ground-state, boat−chair−boat (BCB) conformation of cyclodecane.[33] The structure of the ring in this complex is not unprecedented, as it closely resembles the homoatomic ring in the dinuclear complex [Mo$_2$(CO)$_6$-η^6-*cyclo*-(CH$_3$As)$_{10}$] (**5**).[11]

The structure of the rings in **2** and **5** are very similar, yet **2** is a mononuclear complex and **5** is dinuclear. In a BCB conformation, it would be sterically impossible for the chromium atom to maintain its octahedral environment if the number of spacer atoms was fewer than two. The side view of **2** in Figure 3 clearly shows that the metal-coordinated atoms S(2), As(3), and As(5) have a symmetry related set of three atoms: S(1), S(3), and As(4). If this ring configuration was to form a dinuclear complex similar to **5**, the second chromium atom would be constrained to coordinate to two sulfur and one arsenic atom. No evidence for dinuclear coordination was observed, despite an initial 2:1 Cr(CO)$_6$/arsathiane ratio indicating the considerable preference of arsenic over sulfur as a coordination site.

The S−As−S bond angles of the decamer ring in **2** are more acute at the coordinated arsenic atoms, As(3) and As(5) (98.9(1)° and 100.4(1)°), than at the uncoordinated arsenic atoms, As(1), As(2), and As(4), whose values fall in the narrow range of 101.8(1)−103.8(1)°. In a similar manner, the As−S−As bond angle for the coordinated sulfur, S(2) (96.33(10)°), is closer to bond angles for S(4) and S(5) (97.40(11)° and 99.04(12)°) but much more acute than the angles for S(1) and S(3) (103.78(14)° and 104.09(11)°). The As−S−As and the S−As−S bond angles are found to be considerably smaller than the C−C−C bond angles in cyclodecane (av. 116.7°)[33] but slightly larger than in [Mo$_2$(CO)$_6$ -η^6-cyclo(CH$_3$As)$_{10}$] (96.1°).[11] The average As−S bond distance for **2**, 2.253(3) Å, is very close to that of **1** and other As−S ring and nonring structures.[22,30−32] A slight elongation of the As−S bonds (2.307(3) and 2.297(3) Å) for the coordinated sulfur, S(2)−As(1) and S(2)−As(2), is observed. In general, the bond distances and angles in **2** do not show dramatic deviations from the uncoordinated ligand due to either the expansion of the ring or the ligation to the metal fragment. The chromium-atom coordination environment deviates only slightly from octahedral.

The ^{1}H NMR spectrum of **2** consists of three sharp singlets in a 2(δ *2.401*):1(*1.868*):2(*1.428*) ratio. Again, the most downfield resonance represents the methyl groups attached to the two symmetry-equivalent coordinated As atoms, As(3) and As(5), the middle signal to the unique As atom, As(4), and the upfield signal to the equivalent pair of uncoordinated As atoms, As(1) and As(2). There is no evidence of dynamic behavior up to 80 °C.

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(33) Hilderbrandt, R. L.; Wieser, J. D.; Montgomery, L. K. *J. Am. Chem. Soc.* **1973**, *95*, 8598.

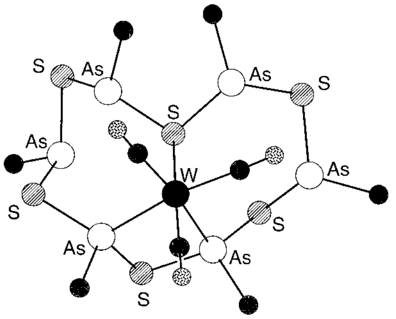

Figure 4. Proposed structure for [W(CO)$_3$-η^3-*cyclo*-(CH$_3$-AsS)$_6$] (**3**) based on an MM2 minimization.

Further expansion of the *cyclo*-(CH$_3$AsS)$_n$ ring occurs in the synthesis of [W(CO)$_3$-η^3-*cyclo*-(CH$_3$AsS)$_6$] (**3**), which was identified by its ^{1}H NMR spectrum and mass spectrum. The mass spectrum establishes the presence of the cyclohexamer. Samples removed at shorter irradiation times showed the presence of only **3** as the product; no evidence was found for tungsten analogues of either **1** or **2**, suggesting that these products are not sufficiently kinetically protected to accumulate in solution. The ^{1}H NMR spectrum of **3** in CDCl$_3$ shows three sharp singlets: one downfield (coordinated AsCH$_3$) methyl-group resonance at 2.52 ppm and higher-field (uncoordinated AsCH$_3$) methyl-group resonances at 2.23 and 1.76 ppm in a 1:1:1 ratio. These NMR assignments are consistent with those found in **1** and **2**. This would require coordination of the W(CO)$_3$ group to a 12-membered ring through two arsenic atoms and one sulfur atom in the MM2-idealized arrangement proposed in Figure 4. There are two coordinated arsenic atoms, two sets of two uncoordinated arsenic atoms, one coordinated sulfur atom, and five uncoordinated sulfur atoms in the ring. Surprisingly, the only pattern that satisfies the apparent mirror-plane symmetry requires W(CO)$_3$ coordination to adjacent As atoms in the ring.

Conclusions

cyclo-(CH$_3$AsS)$_{3,4}$ resembles *cyclo*-(RAs)$_n$ and *cyclo*-(CH$_3$AsO)$_4$ but is unlike *cyclo*-S$_8$ in its reactions with group-6 metal carbonyls as it also forms ring-expansion complexes. However, the possibility of both arsenic and sulfur coordination makes it a more versatile ligand than the homocyclic arsine or its oxygenated derivative. In the oxygen analogue, the metal atom is coordinated to the ring through the arsenic atoms exclusively, as opposed to **2** and **3** in which the sulfur atoms of the ring participate in the coordination to the metal in addition to the arsenic atoms. Bonding to sulfur occurs only as often as is necessary to maintain an ideal octahedral symmetry at the metal atom. *cyclo*-(CH$_3$AsS)$_{3,4}$ tends to form mononuclear complexes, while the all-arsenic and the oxygenated analogues form dinuclear complexes. When the metal loses more than one carbonyl group, it coordinates to more than one atom in the ring, which leads to the expansion of the ring to allow the metal to maintain its octahedral structure. When a larger metal atom is used, as when tungsten replaces chromium, the ring expands further. Hence, it is the metal that dictates the size of the ring and the atoms in the ring to which the metal coordinates. The more accommodating main-group ring rearranges itself both in terms of size and spatial orientation to conform to the demands of the metal.

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Supporting Information Available: Tables of crystallographic data, atomic coordinates, bond distances and angles, and thermal parameters for **1** and **2**, NMR spectrum of **3**, and disorder model for **2** (13 pages). Ordering information is given on any current masthead page.

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