Articles

Mixed Arsenic−Sulfur Metallacyclic Complexes. Synthesis and Structures of $(\eta^5\text{-Cp})_2M(-SCH_3AsSCH_3AsS-)$ (M = Ti, Zr, Hf) and $(\eta^5\text{-Cp*})_2Zr(-SCH_3AsS-)$

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The sodium-reduced form of the mixed trimer and tetramer of *cyclo*-methylarsathiane, *cyclo*-$(CH_3AsS)_{3,4}$ (**1**), in THF reacts at room temperature with the metallocene dichlorides of group 4 elements to give the metallacycle complexes $(\eta^5\text{-Cp})_2M(-SCH_3AsSCH_3AsS-)$ (M = Ti (**2**) Zr (**3**) Hf (**4**)) and $(\eta^5\text{-Cp*})_2Zr(-SCH_3AsS-)$ (**5**). All four complexes were crystallographically characterized. The structures of **2**−**4** are isomorphous, consisting of a cyclohexane-like six-membered MS_3As_2 ring in a chair conformation with two η^5-Cp rings on the metal atoms in pseudo-equatorial and -axial positions and the methyl groups on arsenic in equatorial positions. These complexes have the same molecular structure as the all-sulfur metallacycles Cp_2MS_5 (M = Ti, Zr, Hf). Complex **5**, containing Cp* groups forms a four-membered metallacycle similar to $Cp*_2TiS_3$. However, the related titanocene all-sulfur analogue possesses a puckered "butterfly" ring, while the ring in **5** is nearly planar and similar to the all-arsenic complexes $Cp_2M(RAs)_3$ (M = Ti, Zr). The methyl group on the arsenic atom on **5** is above the plane of the ring, causing an inequivalency of the Cp* groups.

Introduction

While the transition-metal chemistry of the homocycles and homocatenates of groups 15 and 16, e.g., *cyclo*-$(RAs)_n$ and *cyclo*-S_8, has been studied in some detail, comparatively little attention has been given to the transition-metal derivatives of the mixed group 15/16 heterocycles of the heavier pnicogens, e.g., *cyclo*-$(RAsO)_n$, *cyclo*-$(RAsS)_n$, and *cyclo*-$(RSbS)_n$. The reactivity of homocyclic *cyclo*-polyarsines is complex; products are obtained by ring-size retention, ring-size expansion, and the formation of RAs chains longer and shorter than the parent ring system.[1] On the other hand, the chemistry of sulfur is dominated by the formation of metallacyclic polysulfides in a variety of geometries.[2−9] However, only a single example is known of a *cyclo*-polysulfur−metal complex in which a ring (S_8 in this case) is maintained in the complex,[10] unlike the case for *cyclo*-polyarsines, *cyclo*-$(RAs)_n$, which can be found as cyclic ligands in some products of reactions with metal carbonyls.[11,12]

Previous work done in this laboratory on reactions of *cyclo*-methylarsaoxane, *cyclo*-$(CH_3AsO)_n$, with a variety of organometallic reagents has shown the arsaoxane to be an effective oxygen-transfer agent toward early, oxophilic metals, leading to the formation of a variety of oxo−metal clusters[13a] and tetrahedrane analogue clusters with M_3As, M_2As_2, and MAs_3 frameworks.[13b] This work prompted us to extend this investigation to the sulfur analogue of arsaoxane, *cyclo*-methylarsathiane, *cyclo*-$(CH_3AsS)_n$.[14] The *cyclo*-methylarsathiane **1** is a heterocyclic oligomer, usually obtained as a mixture of trimer and tetramer, containing alternating methylated trivalent arsenic and sulfur atoms.

In this paper we compare the structures of complexes of the heterocyclic arsathiane to those formed by the homocyclic *cyclo*-$(RAs)_n$ and *cyclo*-S_8. Even though *cyclo*-polyarsines and *cyclo*-polysulfur are isolobally related, their complexes with transition metals are varied in both structure and reactivity, and it would be of special interest to investigate how the mixed ring systems behave toward early-transition-metal reagents. Thus, we have undertaken the study of reactivities of

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cyclo-$(CH_3AsS)_n$ toward transition-metal reagents and are reporting here the synthesis and X-ray crystal and molecular structures of four novel mixed arsenic−sulfur complexes of group 4 metallocenes, $Cp_2M(-SCH_3AsSCH_3AsS-)$ ($Cp = C_5H_5$; M = Ti (**2**), Zr (**3**), Hf **(4)**) and $[Cp^*{}_2Zr(-SAsCH_3S-)]$ ($Cp = C_5Me_5$; **5**). The group 4 metallocene polychalcogenide metallacycles have been shown to be extremely valuable as reagents in the preparation of novel main-group heterocycles.[4] In a subsequent paper, we will describe additional complexes formed by group 6 carbonyls and cyclopentadienyl derivatives in which ring systems remain intact.

Experimental Section

All experiments were performed under a dry dinitrogen atmosphere, either by standard Schlenk line techniques or in a Vacuum Atmospheres glovebox. Cp_2TiCl_2, Cp_2ZrCl_2, and Cp_2HfCl_2 were purchased from Aldrich and used without further purification. Cp^*ZrCl_2 was synthesized by the literature method.[15] Sodium powder was obtained as a sodium dispersion in mineral oil (Alfa Products). THF, toluene, and hexanes were distilled from Na/benzophenone and transferred to the glovebox without exposure to air. NMR spectra were recorded on a Bruker AM250 (250 MHz) spectrometer. Chemical shifts are reported as ppm downfield of internal TMS. Melting points were obtained using Mel-Temp Laboratories devices. Mass spectra were performed on VG 7070 and Nicolet FT2000 instruments. No elemental analysis data are included. We have obtained data from two laboratories, but, as has been our frequent experience with some classes of transition-metal pnictides and chalcogenides, the results were inconsistent. Others have noted similar difficulties.[32] All bulk samples were crystalline and found to be morphologically pure.

Synthesis of the *cyclo*-Methylarsathianes *cyclo*-$(CH_3AsS)_{3,4}$ (1). Methylarsine dichloride, synthesized by the reduction of sodium methyl arsonate with sulfur dioxide in concentrated HCl,[16] was taken in hot methanol and treated with hydrogen sulfide gas to give **1** as an air-stable crystalline solid in 67% yield. ^1H NMR spectra in $CDCl_3$ give two singlets at 1.99 and 1.89 ppm for the trimer and the tetramer, respectively, in a relative abundance of ca. 2:3. MS ([% I_{rel}, ion] *m/z*): [0.32, $(CH_3AsS)_4{}^+$] 487.83; [0.73, $(CH_3)_3As_4S_4{}^+$] 472.9; [100, $(CH_3AsS)_3{}^+$] 365.8; [16.28, $(CH_3)_2As_3S_3{}^+$] 350.7; [6.18, $(CH_3)_2As_3S_2{}^+$] 318.8; [79.85, $(CH_3AsS)_2{}^+$] 243.8; [64.30, $CH_3As_2S_2{}^+$] 228.8; [16.85, $CH_3AsSAsCH_3{}^+$] 211.9; [10.14, CH_3AsSAs^+] 196.8; [12.97, CH_3AsS^+] 121.9; [14.18, AsS^+] 106.8.

Synthesis of $Cp_2Ti(-SCH_3AsSCH_3AsS-)$ (2). *cyclo*-$(CH_3AsS)_{3,4}$ (0.366 g, 1.0 mmol of trimer) and sodium powder (0.05 g, 2.17 mmol) in 10 mL of THF were stirred at room temperature for 3 h to give a white slurry. Cp_2TiCl_2 (0.250 g, 1.0 mmol) in 10 mL of THF was slowly added to the white slurry. The solution turned dark purple. The reaction mixture was stirred at room temperature for 18 h and then filtered by a glass frit and the THF removed under reduced pressure. The dark purple residue was washed with about 45 mL of mixed hexanes and then extracted into 120 mL of toluene in 10 mL batches. The toluene extract was then filtered by a fine glass frit, and the toluene was removed under reduced pressure. The resulting dark purple solid was dissolved in 20 mL of a hot toluene/hexane mixture (1:1) and the solution cooled slowly. On standing overnight, purple crystals of **2** were obtained in 56% yield. ^1H NMR (benzene-d_6): 5.934 (singlet, 10H) and 1.910 (singlet, 6H). Mp: 181−184 °C. MS [%I_{rel}, ion] *m/z*): [32.61, AsS^+] 106.7; [18.29, $CpTi^+$] 112.8; [10.42, CH_3AsS^+] 121.9; [52.74, $CpTiS^+$] 144.9; [80.72, Cp_2Ti^+] 178.0; [11.36, Cp_2TiS^+] 209.9; [62.58, $Cp_2TiS_2{}^+$] 241.9; [100, $CpTiS_2As^+$] 251.8; [63.47, $CpTiS_2AsCH_3{}^+$] 266.8; [90.72, $Cp_2TiS_2As^+$] 316.9; [22.56, $Cp_2TiS_2CH_3As^+$] 331.9; [16.61, M^+] 453.8.

Synthesis of $Cp_2Zr(-SCH_3AsSCH_3AsS-)$ (3). Route A. Cp_2ZrCl_2 (0.438 g, 1.5 mmol), *cyclo*-$(CH_3AsS)_{3,4}$ (0.366 g, 1.0 mmol of trimer), and magnesium (0.150 g, 6.17 mmol) were loaded in a 50 mL Schlenk flask, and 30 mL of THF was added. The flask was equipped with a magnetic stirring bar, fitted with a condenser and a gas adapter, and was brought to reflux temperature. The colorless solution turned very slowly to light yellow and then to deep yellow. The reaction was refluxed for 20 h. The yellow reaction mixture was Schlenk-filtered while still hot to give a clear yellow solution. The THF was stripped off under reduced pressure. The residue was extracted with 40 mL of toluene, and the extract was then filtered and the toluene removed. Initial ^1H NMR spectra indicated the presence of another product in addition to **3**. Green crystals of this material, $Cp_2Zr(\mu\text{-}S)_2ZrCp_2$,[17] (**6**), identified by NMR (benzene-d_6 6.29 ppm) and by the crystallographic unit cell, were isolated from the toluene solution by fractional crystallization in low yield. After separation of **6**, a concentrated toluene solution gave crystals of **3** in 35% yield; mp 140 °C ^1H NMR (benzene-d_6): 6.04 (s, 10H), 1.53 (6H). MS [% I_{rel}, ion] *m/z*): [34.87, SAs^+] 106.9; [6.00, CH_3AsS^+] 121.9; [35.86, $CpZrS^+$] 186.9; [18.51,$CpZrS_3{}^+$] 250.9; [37.21, $CpZrS_2As^+$] 293.8; [100, $Cp_2ZrS_2As^+$] 358.9; [22.97, $Cp_2ZrS_2AsCH_3{}^+$] 373.9; [2.16, $M^+ - S$] 464.8.

Route B. A solution of *cyclo*-$(CH_3AsS)_{3,4}$ (0.366 g, 1.0 mmol of trimer) and sodium powder (0.070 g, 3.0 mmol) in 20 mL of THF was stirred at room temperature for 3 h to form a white slurry. Cp_2ZrCl_2 (0.298 g, 1.0 mmol) was added to the slurry and the mixture stirred for 15 h. The resulting yellow solution was filtered through a C-porosity glass frit. The THF was removed under reduced pressure to leave a glassy yellow residue, which was extracted into 70 mL of toluene, in 10 mL batches, until the wash was almost clear. The toluene solution was concentrated and allowed to evaporate slowly. Yellow crystals of **3** were isolated in 40% yield.

Synthesis of $Cp_2Hf(-SCH_3AsSCH_3AsS-)$ (4). A solution of *cyclo*-$(CH_3AsS)_{3,4}$ (0.55 g, 1.5 mmol of trimer) and sodium powder (0.071 g, 3.0 mmol) in 20 mL of THF was stirred at room temperature for 3 h to give a white slurry. To the white slurry was added Cp_2HfCl_2 (0.57 g, 1.5 mmol). The solution turned yellow immediately. The reaction mixture was stirred for 6 h and was then filtered through a glass frit. The THF was removed under reduced pressure to leave a glassy yellow residue, which was extracted with 20 mL of a hot hexanes/toluene mixture (1:1) and filtered through a medium-porosity glass frit. The hexanes/toluene mixture on standing for 5 days gave microcrystals of **4** in 19.3% yield. X-ray-grade crystals were grown by pentane diffusion into a concentrated THF solution. ^1H NMR (toluene-d_8): 6.032 (s, 10H), 2.020 (s, 6H). MS [% I_{rel}, ion] (*m/z*): [100, AsS^+] 106.8; [94.5, CH_3AsS^+] 196.8; [47.6, HfS^+] 211.8; [68.9, $CH_3As_2S_2{}^+$] 228.7; [27.3, $CpHf^+$] 243.7; [74.4, $(CH_3)_2As_3S_2{}^+$] 318.7; [15.5, Cp_2HfS_2As+] 448.8; [0.9, $Cp_2HfS_2AsCH_3{}^+$] 463.8; [1.0, $M^+ - CH_3$] 572.8.

Synthesis of $Cp^*{}_2Zr(-SCH_3AsS-)$ (5). A solution of *cyclo*-$(CH_3AsS)_{3,4}$ (0.366 g, 1.0 mmol) and sodium powder (0.051 g, 2.2 mmol) in 20 mL of THF was stirred at room temperature for 3 h. To the white slurry that formed was added $Cp^*{}_2ZrCl_2$ (0.393 g, 1.0 mmol). The reaction mixture turned light orange and then deeper orange over a 12 h period. The orange mixture was filtered through a glass frit and the THF stripped under reduced pressure. A reddish orange residue was obtained, which was extracted into 40 mL of toluene and filtered through a glass frit. The toluene was removed under reduced pressure, and the residue was dissolved in a hot hexanes/toluene mixture (1:1) and left standing. On slow

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Table 1. Crystal, Data Collection, and Refinement Parameters for 2−5

	2	**3**	**4**	**5**
empirical formula	$C_{12}H_{16}As_2S_3Ti$	$C_{12}H_{16}As_2S_3Zr$	$C_{12}H_{16}As_2HfS_3$	$C_{21}H_{33}AsS_2Zr$
fw	454.1	497.5	584.76	515.73
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/n$
a, Å	8.738(2)	8.907(3)	8.847(1)	9.500(2)
b, Å	12.555(2)	12.740(4)	12.682(3)	17.852(3)
c, Å	29.723(4)	29.936(9)	29.838(6)	13.403(5)
β, deg	94.21(1)	94.02(4)	94.17(2)	95.39(2)
V, Å^3	3252(3)	3389(2)	3339(1)	2262.9(8)
Z	8	8	8	4
D_{exptl} (calc), g cm^{-3}	1.855	1.950	2.327	1.514
cryst color and habit	deep red plate	yellow block	yellow block	deep red block
abs coeff, mm^{-1}	4.764	4.876	10.539	2.124
temp, K	296	296	298	296
2θ scan range, deg	4.0−48.0	4.0−45.0	4.2−45.0	4.6−50.0
no. of rflns collected	5176	5638	5923	4672
no. of indep rflns	5067	5538	4357	3921
N_o/N_v	7.0	8.0	15.0	17.34
GOF	0.90	1.24	0.744	0.771
$R(F)$, %[a]	3.68	4.95	5.43	4.70
$R_w(F)$, %	4.22	5.91		
$R_w(F^2)$, %			12.14	12.26
diff peak (min, max), e Å^{-3}	0.92, −0.47	1.55, −0.58	1.69, −0.99	0.78, −0.48

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

evaporation, deep red crystals of **5** formed in 73% yield. Mp: 204−206 °C. ^{1}H NMR (benzene-d_6): 1.858 (s, 15H), 1.810 (s, 15H), 1.335 (s, 3H). MS ([% I_{rel}, ion]): [17.63, M$^+$] 514.05; [100, M$^+$ − CH$_3$] 499.08; [24.06, M$^+$ − 2CH$_3$] 484.88; [19.34, M$^+$ − 3CH$_3$] 468.8; [6.22, M$^+$ − 3CH$_3$ − As] 394.09; [47.92, M$^+$ − 4CH$_3$ − As] 378.98; [35.16, M$^+$ − 5CH$_3$ − As)] 364.88; [11.97, M$^+$ − 5CH$_3$ − AsS] 333.77; [14.48, M$^+$ − 6CH$_3$ − AsS] 318.77; [22.56, Cp*$^+$] 135.11; [16.46, Cp*$^+$ − 2CH$_3$] 105.05; [24.37, Zr$^+$] 91.04.

Crystallographic Structural Determination. Crystal data, data collection, and refinement parameters are summarized in Table 1. All samples were mounted with epoxy cement on glass fibers. A Siemens P3 diffractometer with Mo Kα radiation and a conventional scintillation detector was used to collect data. Preliminary photographic work showed that all four complexes belonged to the monoclinic crystal system, and systematic absences in the diffraction data were uniquely consistent with the reported space groups. The structures were solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. Semiempirical absorption corrections were applied to **2**−**4** but not to **5** because there was a less than 10% variation in the integrated ψ-scan intensities. The asymmetric units of **2**−**4** are isomorphous; each contains two independent but chemically equivalent molecules. The carbon atoms in the cyclopentadienyl rings of **4** were fixed as rigid planar groups to conserve data. All non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were treated as idealized contributions. All software and sources of the scattering factors are contained in either the SHELXTL PLUS (4.2) or the SHELXTL (5.3) program libraries (G. Sheldrick, Siemens XRD, Madison, WI).

Results and Discussion

Arsathiane complexes of group 4 metals were prepared by first opening the *cyclo*-methylarsathiane ring using sodium to give the disodium methylarsine sulfide chain (scheme 1, eq 1). This was then reacted with the metallocene dichloride at room temperature (eq 2). The salt formation is complete in 3−4 h. A 1:2 molar ratio of *cyclo*-(CH$_3$AsS)$_{3,4}$ and sodium was used; the use of excess sodium was avoided to prevent the reduction of the ring into smaller fragments, such as Na$_2$S and Na$_2$(CH$_3$As)$_n$. That the major products isolated were the six-membered metallacycles indicates the absence of extensive fragmentation. Additionally, the presence of only metal−sulfur bonding in these complexes, with no evidence for metal−arsenic bonding, suggests that cleavage and reduction occur to form exclusively sulfur-terminated anionic chains. This may be explained by sulfur's better ability to accommodate negative charge. The values of m and n in Scheme 1 are unspecified but are related by $m + 1 = n$, and the product of Na reduction is undoubtedly a mixture of catenated oligomers. From this mixture the fragments suitable for complexation are removed and are replenished by equilibria relating the remaining components of the mixture. Obviously, the products are sulfur-enriched relative to **1**, but the absence of uncharacterized bands during chromatographic separation suggests that the unaccounted-for arsenic may have formed immobile polyarsine catenates. In all cases, unchromatographable insoluble residues were observed.

Scheme 1

$$\underset{\mathbf{1}}{cyclo\text{-}(CH_3AsS)_{3,4}} + Na \xrightarrow[\text{3 h/room temp}]{\text{THF}} Na_2(S)_n(CH_3As)_m \tag{1}$$

$$Na_2(S)_n(CH_3As)_m + Cp_2MCl_2 \xrightarrow{\text{THF}} Cp_2M(-SCH_3AsSAsCH_3S-) \tag{2}$$

$$M = Ti\ (\mathbf{2}),\ Zr\ (\mathbf{3}),\ Hf\ (\mathbf{4})$$

$$Na_2(S)_n(CH_3As)_m + Cp^*{}_2ZrCl_2 \xrightarrow{\text{THF}} \underset{\mathbf{5}}{Cp^*{}_2Zr(-SCH_3AsS-)} \tag{3}$$

$$cyclo\text{-}(CH_3AsS)_{3,4} + Cp_2ZrCl_2 + Mg \xrightarrow[\text{20 h}]{\text{THF/reflux}} \underset{\mathbf{3}}{Cp_2Zr(-SCH_3AsSAsCH_3S-)} + \underset{\mathbf{6}}{Cp_2Zr(\mu\text{-}S)_2ZrCp_2} \tag{4}$$

We also explored the effects of reversing the order of reduction and salt formation. As shown in eq 4, the

Table 2. Selected Bond Distances (Å) and Angles (deg) for $Cp_2MS_3(MeAs)_2$ (M = Ti, Zr, Hf)

	2 (Ti)		**3** (Zr)		**4** (Hf)	
	molecule A	molecule B	molecule A	molecule B	molecule A	molecule B
			Distances (Å)			
M−S(1)	2.412(4)	2.417(4)	2.520(4)	2.504(5)	2.499(5)	2.497(5)
M−S(3)	2.422(4)	2.417(4)	2.519(4)	2.526(4)	2.483(6)	2.479(5)
S(1)−As(1)	2.232(4)	2.240(3)	2.240(4)	2.237(4)	2.221(6)	2.246(7)
S(3)−As(2)	2.231(4)	2.236(4)	2.240(4)	2.226(4)	2.230(7)	2.252(2)
S(2)−As(1)	2.267(4)	2.266(4)	2.261(4)	2.293(5)	2.258(7)	2.254(7)
S(2)−As(2)	2.258(4)	2.267(4)	2.257(5)	2.249(5)	2.265(6)	2.260(6)
M−Cent1	2.069	2.076	2.204	2.205	2.192	2.181
M−Cent2	2.074	2.077	2.202	2.204	2.181	2.180
			Angles (deg)			
S(1)−M−S(3)	94.8(1)	94.8(1)	96.3(1)	96.6(2)	96.2(2)	96.5(2)
M−S(1)−As(1)	108.9(1)	109.4(1)	106.8(2)	106.4(2)	106.8(2)	106.8(2)
M−S(3)−As(2)	108.9(1)	109.6(1)	107.0(2)	106.1(2)	106.9(2)	107.5(2)
As(1)−S(2)−As(2)	98.7(1)	100.5(1)	101.2(2)	98.9(2)	98.7(2)	101.2(2)
S(1)−As(1)−S(2)	101.7(1)	102.5(1)	102.1(2)	101.9(2)	102.1(2)	102.2(2)
S(2)−As(2)−S(3)	101.6(1)	101.6(1)	102.9(2)	102.3(2)	102.1(3)	102.5(2)
Cent(1)−M−Cent(2)	131.4	131.7	130.7	129.8	130.6	129.9
Cent(1)−M−S(1)	110.8	110.6	101.8	110.7	110.3	109.8
Cent(2)−M−S(3)	101.4	102.3	111.3	102.1	101.1	101.0
Cent(1)−M−S(3)	110.5	109.7	101.6	111.3	110.3	111.3
Cent(2)−M−S(1)	101.7	101.4	109.6	101.2	102.3	103.1

reaction of *cyclo*-$(CH_3AsS)_{3,4}$ with Cp_2ZrCl_2 was carried out in the presence of magnesium metal in refluxing THF (eq 4). In this case, Mg does not react directly with the arsathiane to open the ring but, rather, initially reduces Cp_2ZrCl_2 to form "Cp_2ZrMg", which then becomes the ring-opening agent. Besides the formation of **3**, the previously known disulfide bridging dimer $Cp_2Zr(\mu\text{-}S)_2ZrCp_2$[17] (**6**) was isolated as a minor product and identified by its ^1H NMR spectrum and by its X-ray crystallography unit-cell parameters.

Depending on the metallic fragment, either four- or six-membered rings are formed. There appears to be thermodynamic control of ring size in both the homoatomic and heteroatomic metal complex systems. Despite widely ranging reaction conditions, starting materials, and stoichiometries, the cyclohexameric metallocene polysulfur complexes Cp_2MS_5 (M = Ti, Zr, Hf) are, in all but one instance,[39] the sole product,[18−29] and for the all-organoarsenic complexes of the same metals, only the four-membered metallacycles $Cp_2M(RAs)_3$ are known.[30,31] Similarly, with Cp* groups the only known group 4 all-sulfur complexes are cyclotetrameric $Cp^*_2MS_3$,[32,33] and the only all-arsenic complex, $Cp^*_2Zr(RAs)_3$,[30] is also a cyclotetramer.

Complexes **2**−**4** crystallize in isomorphous settings and are structurally nearly identical. The structure of **2** is shown in Figure 1, and the visually indistinguishable structures of **3** and **4** are contained in the Supporting Information. These complexes have a cyclohexane-like, six-membered MS_3As_2 ring in a chair conformation with the Cp rings on the metal atoms in pseudo-equatorial and -axial positions. The methyl groups on the arsenic atoms are in equatorial positions to avoid 1,3-interactions. They are structurally very similar to the isolobally analogous Cp_2MS_5 complexes. Selected bond distances and angles for **2**−**4** are given in Table 2. A comparison of the bond distances and angles for the Cp_2MS_2 fragment in **2**−**4** to those for the analogous Cp_2MS_5 complexes is given in Table 3. The metal ions adapt the familiar pseudo-tetrahedral, bent-sandwich configuration. The Cent−M−Cent bond angles for the three complexes **2**−**4** fall in the narrow range 129.8−131.7°, and these values are very close to those reported for the polysulfide complexes Cp_2MS_5 for the same metals (Ti, 133.7; Zr, 131.3; Hf, 131.5°).[26,27,29] The S−M−S bond angles (average 94.8(2), 96.4(2), 96.3°(2)°) are also nearly identical with those reported for the all-sulfur complexes (94.6(1), 97.8(1), 96.8(1)°). The [Cent-,M,Cent] plane bisects the [S,M,S] plane at nearly perpendicular dihedral angles of 89.6 (**2**), 89.9 (**3**), and 89.6° (**4**). The M−S−As bond angles (106.1(2) −109.6-

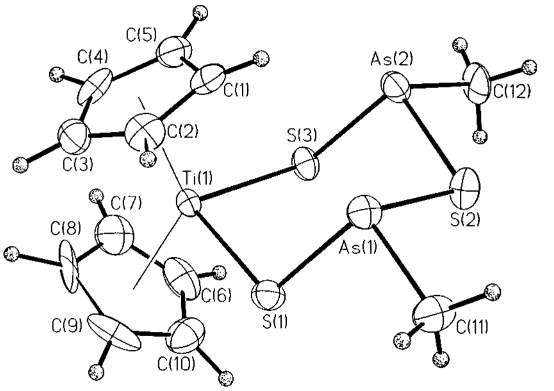

Figure 1. Molecular structure of $Cp_2TiS_3(CH_3As)_2$ (**2**) drawn with 35% thermal ellipsoids. One of the two crystallographically independent, but chemically identical, molecules is shown.

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Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for the Cp_2MS_2 Fragment in $Cp_2MS_3(CH_3As)_2$[a] and Cp_2MS_5[29] (M = Ti, Zr, Hf)

		Cp_2TiS_5[29]	$Cp_2TiS_3(MeAs)_2$[a] (**2**)	Cp_2ZrS_5[29]	$Cp_2ZrS_3(MeAs)_2$[a] (**3**)	Cp_2HfS_5[29]	$Cp_2HfS_3(MeAs)_2$[a] (**4**)
M−S(1)	A	2.448(1)	2.412(4)	2.544	2.520(4)	2.523(2)	2.499(5)
	B		2.417(4)		2.504(5)		2.497(5)
M−S(3)	A	2.422(1)	2.422(4)	2.526(1)	2.519(4)	2.501(2)	2.483(6)
	B		2.417(4)		2.526(4)		2.479(5)
M−Cent(1)	A	2.066	2.069	2.216	2.204	2.190	2.192
	B		2.076		2.205		2.181
M−Cent(2)	A	2.071	2.074	2.206	2.202	2.188	2.181
	B		2.077		2.204		2.180
Cent−M−Cent	A	133.7	131.4	131.3	130.7	131.5	130.6
	B		131.7		129.8		
S(1)−M−S(2)	A	94.6	94.8	97.8	96.3	96.8	96.2

[a] This work.

(1)°) are more open than the As−S−As bond angles at the unique sulfur at the foot of the chair (98.7(1)−101.2(2)°).

The average Ti−S bond distances in complex **2**, Cp_2TiS_5,[26−28] and $Cp_2Ti(-S_2AsCH_3S_2-)$[34] are almost identical. So are the As−S bond distances in **2** and $Cp_2Ti(-S_2AsCH_3S_2-)$, which are also very close to the average values of **3**−**5** and *cyclo*-$(CH_3AsS)_3$ and *cyclo*-$(CH_3AsS)_4$ (average 2.258(1) and 2.249(4) Å).[14] Likewise, the S−Ti−S bond angles for these three complexes fall in the narrow range 94.4(1)−95.6(1)°.

Variable-temperature NMR studies have shown that the Cp_2MS_5 complexes are engaged in chair-to-chair ring flipping. At low temperatures, the axial and equatorial Cp rings are resolved as two distinct resonances, which coalesce to a single peak at higher temperatures. The methyl-group resonances remain magnetically equivalent and appear as singlets at all temperatures. Complexes **2**−**4** behave similarly to the all-sulfur complexes. However, the activational free energies ($\Delta G^{\ddagger}$, kJ mol^{-1} in toluene) for the arsenic−sulfur complexes **2** (64.9), **3** (39.5), and **4** (46.0) are all about 10 kJ mol^{-1} lower than those found for the pentasulfido complexes: M = Ti (76.3),[20,32,37] Zr (48.6),[32] and Hf (58.0).[32] Clearly, the inclusion of two CH_3As units in the metallacycle substantially reduces the ring inversion barrier. Rauchfuss has suggested that lone-pair−lone-pair and lone-pair−substituent repulsions play a major role in determining inversional barriers.[38]

The barriers to ring flipping for **2** are much higher in THF; the doublet pattern was maintained up to 325 K, whereas the coalescence temperature in toluene was at 289 K. Even small quantities of THF, as originally carried from the syntheses to the NMR samples, strongly inhibit ring flipping.

Complex **5** has a nearly planar ZrS_2As ring with inequivalent Cp* rings (see Table 4 and Figure 2). The inequivalency of the Cp* rings, also observed in the NMR spectrum, is caused by the methyl group on the arsenic atom being to one side of the ZrS_2As ring. The As−S bond distances (2.254(2) and 2.247(2) Å) are comparable to distances found in the six-membered metallocycles **2**−**4** and in uncoordinated *cyclo*-$(CH_3AsS)_{3,4}$. The Zr−S bond distances (2.506(2) and 2.509(2) Å) are similar to those values found for **3** (2.520(4), 2.519(4), 2.504(5), and 2.526(4) Å). The S−Zr−S bond angle in **5** (87.53(7)°) is smaller than that found for **2**−**4** by about 7−10° due to the presence of the bulkier Cp* ligand in **5**, in addition to the smaller metallacycle ring size. The S−As−S bond angle (100.84(7)°) is typical and similar to other similar bond angles found for **2**−**4**, which range from 101.6(1) to 102.9(2)°.

Table 4. Selected Bond Distances and Angles for $Cp^*_2Zr(-SCH_3S-)$ (5)

(a) Bond Distances (Å)			
Cent(1)−Zr	2.271(8)	S(1)−As	2.254(2)
Cent(2)−Zr	2.278(7)	S(2)−As	2.247(2)
Zr−S(1)	2.509(2)	S(2)−Zr	2.506(2)
As···Zr	3.245(1)		
(b) Bond Angles (deg)			
Cent(1)−Zr−Cent(2)	133.9(1)	S(1)−As−S(2)	100.84(7)
Cent(1)−Zr−S(1)	105.0(3)	Zr−S(1)−As	85.69(6)
Cent(2)−Zr−S(1)	107.4(3)	Zr−S(2)−As	85.91(6)
Cent(1)−Zr−S(2)	105.9(3)	S(1)−Zr−S(2)	87.53(7)
Cent(2)−Zr−S(2)	107.3(3)	S(1)−As−C(1)	101.2(3)
S(2)−As−C(1)	102.7(3)		

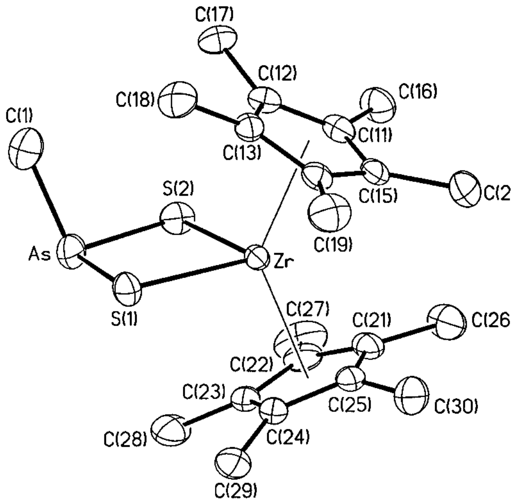

Figure 2. Molecular structure of $Cp^*_2ZrS_2(CH_3As)$ (**5**) drawn with 40% thermal ellipsoids.

The two acute M−S−As bond angles (85.69(2) and 85.91(6)°) could be the result of a long-range interaction (Zr···As = 3.245(2) Å) between the zirconium and arsenic atoms. Such transannular interactions are also cited for similar phosphorus and arsenic complexes.[30,31,35] This interaction can be explained in terms of frontier orbital interaction using the Ballhausen−Dahl model for the bent metallocenes.[36] This interaction brings the

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oppositely located zirconium and arsenic atoms closer and forces the sulfur atoms away, causing them to have more acute angles than would be expected in the absence of such interaction. The crystal structure of the analogous all-sulfur complex $Cp^*_2ZrS_3$ is not reported in the literature, although the compound is known,[32] but the structure of the titanium analogue $Cp^*_2TiS_3$ has been reported.[33] It has a nonplanar TiS_3 ring with the central sulfur atom significantly displaced in the direction of one Me_5C_5 ring and the dihedral angle between the two planes defined by [S,Ti,S] and [S,S,S] is 49.0°. In contrast to this, in **5,** the ZrS_2As ring is almost planar, and the dihedral angle between the related two planes defined by [S(1),Zr,S(2)] and [S(1),As(1),S(2)] is 1.9°. The all-arsenic complexes $Cp_2Ti(AsPh)_3$,[31] $Cp_2Zr(AsCH_3)_3$,[30] and $Cp^*_2Zr(AsTol)_3$[30] all have nearly planar MAs_3 rings, similar to the case for **5**.

The preparative routes for $Cp_2Zr(-SCH_3AsSCH_3AsS-)$ (**3**) and $Cp^*_2Zr(-SCH_3AsS-)$ (**5**) are similar, but the resulting ring sizes are different. This ring-size contraction is likely the result of increasing the steric bulk of the Cp ring and its electron-donating capacity to the metal, but this differentiation is not observed for the *cyclo*-polyarsines. Both $Cp^*_2ZrCl_2$ and Cp_2ZrCl_2 give the four-membered-ring complexes Cp_2(or Cp^*_2)$Zr(RAs)_3$ with *cyclo*-$(TolAs)_6$;[31] $M(RAs)_5$ complexes for the *cyclo*-polyarsines have not been reported. For the all-sulfur complexes, MS_3 complexes are known, but only for Cp*.[32,33] These results do not allow a clear distinction to be made between electronic and steric effects in determining ring size. Both factors would appear to be important. When substituents exist on the ring atoms attached to the metal atom, as found in the all-arsenic complexes, the ring is forced to be flat and limited to four members, regardless of the substitution on the Cp ring.

We have shown in this work that the metallacycles formed from *cyclo*-$(CH_3AsS)_{3,4}$ in reactions with group 4 metallocenes have structures closely similar to those of complexes formed from *cyclo*-S_8 or its salts with the same metals. We have also found that while the six-membered metallacycles have the chairlike conformation of cyclohexane, the four-membered rings are planar, as were also the all-arsenic complexes formed from *cyclo*-polyarsines.

Supporting Information Available: Tables of crystallographic data, atomic coordinates, bond distances and angles, and thermal parameters for **2**−**5** and ORTEP diagrams of **2** (molecule B), **3** (molecules A and B), and **4** (molecules A and B) (41 pages). Ordering information is given on any current masthead page.

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