found in the crystal structures reported here. Of some interest is the fact that in three cases (Figure 7A,E,I) the folding of the macrocyclic ring was reversed as the Coulombic forces exceeded the strain energy induced in the ring during its inversion. Such configurations have not been found experimentally as yet.

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Supplementary Material Available: Table SI (NMR and IR data), Table SII (complete crystal data and experimental details), Tables SIII–SV (anisotropic thermal parameters), Tables SVI–SVIII (calculated H atom positions), and Table SXII (molecular mechanics parameters (11 pages); Tables SIX–SXI (observed and calculated structure factors) (32 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Center for Micro-Engineered Ceramics,
University of New Mexico, Albuquerque, New Mexico 87131,
and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405

Synthesis and Single-Crystal X-ray Structural Investigation of 1,1-Bis(pentacarbonylmanganio)-3,4-dimethylgermacyclopent-3-ene and Bis[1-(tetracarbonylferrio)-3,4-dimethylgermacyclopent-3-ene]: The First Evidence for a Puckered Ground-State Conformation in Germacyclopent-3-enes

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Received August 10, 1989

The crystal and molecular structures of 1,1-bis(pentacarbonylmanganio)-3,4-dimethylgermacyclopent-3-ene (I) and bis[1-(tetracarbonylferrio)-3,4-dimethylgermacyclopent-3-ene] (II) have been determined in the solid state by single-crystal X-ray diffraction. The yellow compound I, chemical formula $C_{16}H_{10}O_{10}Mn_2Ge$, crystallizes in the triclinic crystal system with space group $P\bar{1}$, where $a = 7.1603$ (2) Å, $b = 9.6364$ (4) Å, $c = 16.491$ (5) Å, $\alpha = 74.68$ (2)°, $\beta = 87.87$ (2)°, $\gamma = 71.90$ (2)°, and $Z = 2$; R refined to 4.0%. Orange plates of II, chemical formula $C_{20}H_{20}O_8Fe_2Ge_2$, crystallize in the triclinic crystal system with space group $P\bar{1}$, where $a = 9.949$ (3) Å, $b = 8.372$ (2) Å, $c = 7.777$ (2) Å, $\alpha = 72.41$ (1)°, $\beta = 106.77$ (1)°, $\gamma = 94.75$ (1)°, and $Z = 1$; R refined to 2.5%. The germacyclopent-3-ene rings of both molecules are severely strained and adopt a puckered ground-state conformation with puckering angles, δ, of 29.7° for I and 30.2° for II. These data provide the first evidence for a nonplanar equilibrium conformation in species containing germacyclopent-3-ene rings.

Introduction

The ground-state conformations of small ring molecules have been studied intensely for well over 20 years.[1] While cyclopentene exhibits a nonplanar ring structure,[2] the equilibrium structures of its heavier group 14 congomers are quite different, according to the literature.[3] Gas-phase, liquid-phase, and solid-state (77 K) vibrational analyses of 1,1-disubstituted silacyclopent-3-enes have been found consistent with a planar, C_{2v}, rather than a puckered, C_s, ground-state ring conformation.[4] Electron diffraction studies on these molecules have also been interpreted in terms of C_{2v} ring structures but with deviations from planarity that were largest for the 1,1-difluoride and smallest for the 1,1-dichloride.[5] Two- and three-dimensional potential energy surface calculations[6] have shown that cyclopentene, 3-phospholene, silacyclopentane, and 1,3-disilacyclobutane are puckered, whereas silacyclopent-3-ene possesses a planar ring structure. The stability of the planar ring conformation of silacyclopent-3-ene has been attributed to various effects, including an increase in stability that results from reduction of the eclipsing strain of the two CH_2 groups with the SiX_2 group due to the relatively long Si–C length compared to the C–C distance in the cyclopentene analogue. This is consistent with the planar conformation adopted by 2,5-dihydrofuran. At the same time, however, the longer Si–C bonds of silacyclopent-3-enes are also expected to result in a decrease of the C—Si—C angle and an increase the C=C—C angles if the ring remains planar. A smaller C–E–C angle is likely to become more favorable as group 14 is descended due to a reduction in stability gained from hybridization of s and p orbitals. Distortion to a puckered conformation would relieve this strain to some extent. Other explanations favoring the planar conformation have invoked interactions between vacant Si 3d orbitals and π orbitals of the double bond.[4]

It might be expected that the subtle tradeoff between these opposing factors would be manifest in the ground-state conformation of *germa*cyclopent-3-enes. However, the only reported structural study of these molecules is the liquid phase vibrational analysis of 1,1-disubstituted germacyclopent-3-enes, which have been interpreted in terms of planar, C_{2v}, ring structures.[7] We now report the first solid-state single-crystal X-ray diffraction study of two classes of 1,1-dimetal-substituted germacyclopent-3-enes, which demonstrates that the ground-state ring conformation in these molecules is puckered.

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(6) Laane, J. *J. Mol. Struct.* **1985**, *126*, 99.

(7) For X = Cl, CH_3, and OCH_3: Jagodzinski, P. W.; Laane, J.; Manuel, G. *J. Mol. Struct.* **1978**, *49*, 239, Other small germanium containing heterocyclic species that have been studied include germacyclopentane (Durig, J. R.; Willis, J. N. *J. Chem. Phys.* **1970**, *52*, 6108) and alkylgermaoxacycloalkanes (Marchand, A.; Mossol, M.; Barrau, J.; Satge, J. *J. Organomet. Chem.* **1973**, *63*, 175. Marchand, A.; Forel, M. T.; Ledbedeff, M.; Valade, J. *J. Organomet. Chem.* **1971**, *26*, 69).

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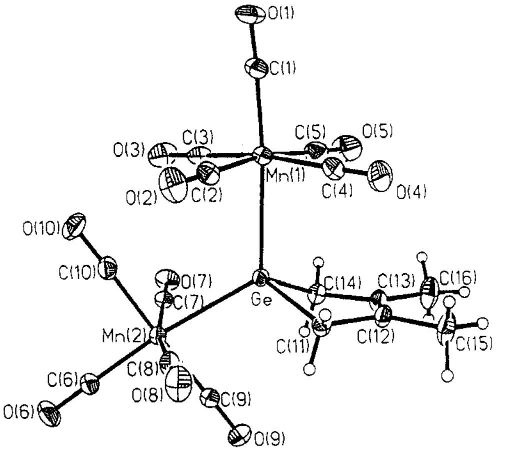
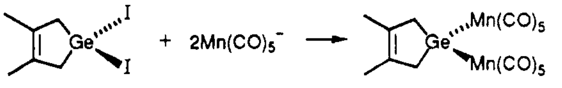


Figure 1. ORTEP plot of I. Relevant bond distances (Å): Ge–C(14) = 1.991 (4); C(14)–C(13) = 1.507 (4); C(13)–C(12) = 1.338 (6); C(12)–C(11) = 1.503 (5); C(11)–Ge = 1.980 (4); Ge–Mn(1) = 2.570 (1); Ge–Mn(2) = 2.573; C(13)–C(16) = 1.503 (7); C(12)–C(15) = 1.504 (5). Relevant bond angles (deg): C(11)–Ge–C(14) = 88.2 (2); Ge–C(14)–C(13) = 102.3; C(14)–C(13)–C(12) = 118.6 (3); C(13)–C(12)–C(11) = 117.9 (3); C(12)–C(11)–Ge = 103.1 (3); Mn(1)–Ge–Mn(2) = 120.5 (1); C(16)–C(13)–C(12) = 124.7 (3); C(15)–C(12)–C(13) = 124.8 (4).

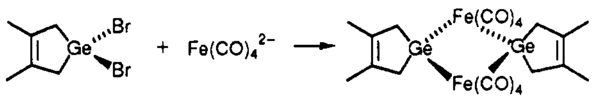
Results and Discussion

The 1,1-dimetal-substituted germacyclopent-3-enes were prepared in high yield by the metathesis reactions between 1,1-dihalo-3,4-dimethylgermacyclopent-3-ene and the appropriate transition-metal carbonylate anion, as shown in eqs 1 and 2, to



(1)

I



(2)

II

form 1,1-bis(pentacarbonylmanganio)-3,4-dimethylgermacyclopent-3-ene (I) and bis[1-(tetracarbonylferrio)-3,4-dimethylgermacyclopent-3-ene] (II). Both compounds gave satisfactory spectroscopic and elemental analysis data (see Experimental Section). The reaction of diorgano–group 14 element dihalides with Collman's reagent to form species containing four-membered metal atom rings is well-known.[8] The carbonyl stretches in the infrared spectrum observed for II are consistent with local C_{2v} symmetry about iron. Both I and II exhibit only single methylene and methyl resonances in the ^{1}H NMR spectrum, consistent with the presence of molecular mirror planes in the plane of the germacyclopent-3-ene ring and perpendicular to the ring passing through the germanium atom, bisecting the carbon–carbon double bonds. However, the spectroscopic data do not distinguish between a planar ground-state conformation of the germacyclopentene ring and a puckered ground-state conformation, which undergoes a rapid equilibration (on the NMR time scale), through a planar transition state, generating a pseudomirror plane. No change was observed upon cooling toluene solutions of either of these compounds to −90 °C.

Since there is little structural information available concerning the ground-state conformation of germacyclopent-3-enes, we carried out single-crystal X-ray diffraction studies to examine the conformations adopted by I and II in the solid state. The molecular structures of I and II are shown in Figures 1 and 2, respectively, together with the relevant bond lengths and angles.

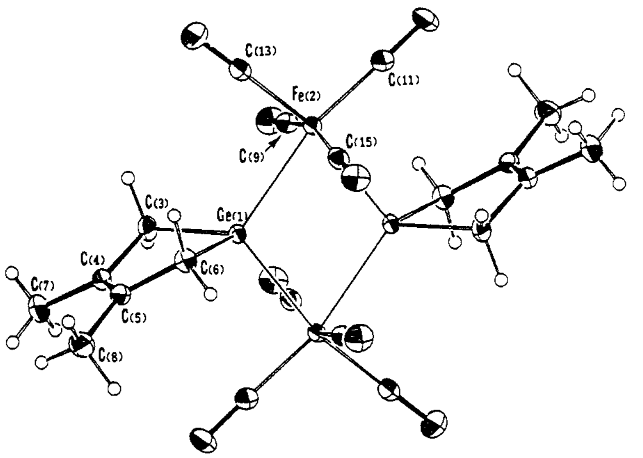
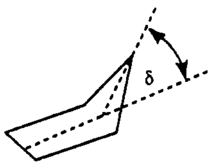


Figure 2. ORTEP plot of II. Relevant bond distances (Å): Ge–C(3) = 1.978 (2); C(3)–C(4) = 1.513 (3); C(4)–C(5) = 1.347 (3); C(5)–C(6) = 1.512 (3); C(6)–Ge = 1.973 (2); Ge(1)–Fe(2) = 2.460 (1); Ge(1)–Fe(2′) = 2.484 (1); Ge(1)–Ge(1′) = 3.000 (1); Fe(2)–Fe(2′) = 3.929 (1); C(4)–C(7) = 1.498 (3); C(5)–C(8) = 1.505 (3). Relevant bond angles (deg): C(3)–Ge(1)–C(6) = 89.0 (1); Ge(1)–C(3)–C(4) = 101.8 (1); C(3)–C(4)–C(5) = 118.3 (2); C(4)–C(5)–C(6) = 118.9 (2); Ge(1)–C(6)–C(5) = 101.7 (1); Fe(2)–Ge(1)–Fe(2′) = 105.24 (3); Ge(1)–Fe(2)–Ge(1′) = 74.76 (3); C(5)–C(4)–C(7) = 125.9 (2); C(4)–C(5)–C(8) = 125.72 (2).

Both molecules crystallize with a significantly puckered germacyclopent-3-ene ring: the puckering angles, δ, defined below are 29.7° for I and 30.2° for II.



We have considered the possibility that the molecular structure of these species may be influenced by intermolecular crystal packing forces. Indeed we note that, in I, there is a relatively short intermolecular distance between the oxygen atoms of two carbonyl ligands, O(3)–O(3′) = 2.788 Å, which is on the order of the sum of their van der Waals radii (see Figure 2S of the supplementary material). However, we believe that this interaction does not affect the germacyclopentene ring conformation in I. There are no unusual intermolecular interactions in the solid-state structure of II. The structural features of the germacyclopent-3-ene rings of both molecules are very similar. The bond lengths within the rings are approximately as expected on the basis of covalent radii values[9] with Ge–C bonds averaging 1.99 Å in I and 1.98 Å in II. The angles within the germacyclopent-3-ene rings of these two molecules, however, are severely distorted and are all substantially smaller than the values expected on the basis of pure sp^3 and sp^2 hybridization. The C–Ge–C angles are exceptionally small, 88.2° for I and 90.0° for II. The most notable feature of these two structures is the striking similarity of the conformations of the two germacyclopent-3-ene rings *irrespective* of the nature of the transition-metal carbonylate substituents on germanium.

Intramolecular interactions between the sterically demanding [$\mathrm{Mn(CO)_5}$] groups in I are apparent from the large Mn(1)–Ge–Mn(2) angle (120.5°) and the staggered orientation of the carbonyl ligands. In contrast, the Fe–Ge–Fe angle of II (105°) is less than the tetrahedral angle by virtue of the dimeric nature of this molecule. The relatively short nonbonded Ge–Ge distance (3.00 Å) in II is probably a consequence of the attempt to retain tetrahedral geometry about germanium in the four-membered Ge–Fe–Ge–Fe ring. The angles about iron are severely distorted, but these distortions are analogous to the distortions previously noted[10] for the [$(\mu\text{-ER}_2)\mathrm{Fe(CO)_4}$]$_2$ (E = Ge, Sn) structural type:

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[8] Marks, T. J.; Newman, A. R. *J. Am. Chem. Soc.* **1973**, *95*, 769. Cornwell, A. B.; Harrison, P. G. *J. Chem. Soc., Dalton Trans.* **1975**, 2017. Cornwell, A. B.; Harrison, P. G.; Richards, J. A. *J. Organomet. Chem.* **1976**, *108*, 47.

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Table I. Summary of the Experimental Details for the X-ray Diffraction Studies of I and II

	I	II
empirical formula	$C_{16}H_{10}O_{10}Mn_2Ge$	$C_{20}H_{20}O_8Fe_2Ge_2$
T, °C	20	−155
a, Å	7.1603 (2)	9.947 (3)
b, Å	9.6364 (4)	8.372 (2)
c, Å	16.491 (5)	7.777 (2)
α, deg	74.68 (2)	72.41 (1)
β, deg	87.87 (2)	106.77 (1)
γ, deg	71.90 (2)	94.75 (1)
V, Å^3	992.91	591.26
space group	$P\bar{1}$	$P\bar{1}$
Z	2	1
linear abs coeff, mm^{-1}	17.632	37.289
R	0.0406	0.0262
R_w	0.0397	0.0248

a reduced *cis*–Ge–Fe–Ge angle (74.6°), an enlarged *cis*–OC–Fe–OC angle (100.9°) and a reduced *trans*-OC–Fe–CO angle (162°).

On the basis of these data, we believe that eclipsing CH_2–GeX_2–CH_2 interactions are important in 1,1-disubstituted germacyclopent-3-ene rings containing sterically demanding germanium substituents and that, as a result, the ground-state conformation is puckered rather than planar. Although the angles within the puckered germacyclopent-3-ene rings of I and II are distorted, molecular models show that they are significantly less distorted than if the rings were planar. Furthermore, since in solution both I and II each exhibit only one type of methylenic proton resonance in their ^{1}H NMR spectra at room temperature, which is unchanged when cooled to −90 °C, whether or not these molecules adopt a planar ring conformation or undergo a rapid degenerate puckered $\rightleftharpoons$ puckered interconversion in solution is still in question. At this stage, the electronic effects of the germanium substituents on the ring conformation in germacyclopent-3-enes are not clear. A larger data base is required to draw unambiguous conclusions. We are currently preparing variously substituted germacyclopent-3-enes to measure the ring strain, eclipsing interactions, and electronic effects in these molecules. The reaction chemistry of these species will be the subject of future publications.[11]

Experimental Section

a. Syntheses of I and II. All manipulations were carried out under an atmosphere of dry nitrogen. All solvents were distilled from sodium benzophenone ketyl and stored under dry nitrogen. 1,1-Dibromo- and 1,1-diiodo-3,4-dimethylgermacyclopent-3-ene[12] and $NaMn(CO)_5$[13] were prepared by literature procedures, and $Na_2Fe(CO)_4$·dioxane was purchased from Aldrich Chemical Co. Both I and II were prepared by a similar procedure.

I. To a suspension of an excess of $NaMn(CO)_5$ (2.18 g; 0.01 mol) in 50 mL of *n*-pentane was slowly added a solution containing 3.50 g of 1,1-diiodo-3,4-dimethyl-germacyclopent-3-ene in 40 mL of *n*-pentane. The initial clear solution became slightly yellow during the addition. After the mixture was stirred for 3 h, a fine white precipitate had been produced. The stirrer was stopped, and the solution was filtered and washed with two 10-mL portions of *n*-pentane. The washings were combined and the volatile components removed in vacuo to give a pale yellow crystalline solid. ^{1}H NMR spectroscopy showed this crude material to be pure I, in a yield of 1.50 g (87% based on germanium starting material). Crystals suitable for X-ray diffraction were grown by cooling a saturated (room-temperature) solution of I in *n*-pentane to −30 °C for 18 h. ^{1}H NMR data (250.13 MHz, 20 °C, C_6D_6): CH_2, s, br, 2.44 ppm, 4 H; CH_3, s, br, 1.82 ppm, 6 H. ^{13}C NMR data (62.9 MHz, 20 °C, C_6D_6): CH_3, 18.8 ppm; CH_2, 38.7 ppm; *C*Me, 133.1 ppm; *C*O, 214.9 and 211.7 ppm. IR data (ν(CO), cm^{-1}): 2100, m; 2067, m; 2032, s, br; 1950, sh. Anal. Calcd for $C_{16}H_{10}O_{10}Mn_2Ge$: C, 35.30; H, 1.85. Found: C, 35.03; H, 2.07.

Table II

a. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for I

atom	*x*	*y*	*z*	*U*(eq)
Ge	2503 (1)	9870 (1)	7639 (1)	33 (1)
Mn(1)	4255 (1)	7580 (1)	7071 (1)	40 (1)
C(1)	5478 (6)	6067 (4)	6586 (3)	54 (2)
O(1)	6215 (5)	5163 (3)	6252 (2)	85 (2)
C(2)	6107 (5)	8556 (4)	6752 (2)	50 (1)
O(2)	7288 (4)	9120 (4)	6574 (2)	80 (2)
C(3)	2666 (5)	8681 (4)	6120 (2)	49 (1)
O(3)	1701 (4)	9352 (4)	5531 (2)	78 (1)
C(4)	5608 (6)	6674 (4)	8104 (3)	58 (2)
O(4)	6476 (5)	6105 (4)	8733 (2)	86 (1)
C(5)	2295 (6)	6785 (5)	7507 (3)	63 (2)
O(5)	1101 (6)	6268 (4)	7771 (3)	100 (2)
Mn(2)	1800 (1)	12583 (1)	6689 (1)	36 (1)
C(6)	1149 (6)	14575 (4)	6105 (2)	51 (1)
O(6)	742 (5)	15815 (3)	5747 (2)	83 (1)
C(7)	−327 (5)	12205 (4)	6292 (2)	43 (1)
O(7)	−1634 (4)	11977 (3)	6054 (2)	63 (1)
C(8)	4063 (6)	12466 (4)	7232 (2)	50 (1)
O(8)	5448 (4)	12395 (4)	7585 (2)	77 (1)
C(9)	376 (6)	13065 (4)	7582 (2)	49 (1)
O(9)	−529 (5)	13400 (4)	8119 (2)	77 (1)
C(10)	3240 (5)	11977 (4)	5823 (2)	50 (1)
O(10)	4109 (5)	11654 (4)	5275 (2)	78 (1)
C(11)	3763 (6)	9630 (4)	8738 (2)	44 (1)
C(12)	2791 (5)	8645 (4)	9350 (2)	46 (1)
C(13)	1052 (5)	8596 (4)	9111 (2)	46 (1)
C(14)	164 (5)	9536 (4)	8250 (2)	43 (1)

b. Fractional Coordinates and Isotropic Thermal Parameters (Å^2) for II[a]

atom	*x*	*y*	*z*	B_{iso}
Ge(1)	8510.6 (2)	5206.0 (2)	8787.1 (2)	10
Fe(2)	9696.9 (3)	2576.0 (3)	10891.3 (3)	11
C(3)	6711 (2)	5744 (2)	9097 (3)	15
C(4)	5948 (2)	6720 (2)	7114 (3)	15
C(5)	6366 (2)	6521 (2)	5691 (3)	15
C(6)	7576 (2)	5346 (2)	6138 (3)	15
C(7)	4769 (2)	7821 (3)	6924 (4)	23
C(8)	5741 (2)	7391 (3)	3638 (3)	22
C(9)	9165 (2)	3240 (2)	12588 (3)	15
O(10)	8825 (2)	3652 (2)	13668 (2)	21
C(11)	10902 (2)	970 (2)	12620 (3)	18
O(12)	1642 (2)	9954 (2)	3720 (3)	29
C(13)	8144 (2)	1337 (2)	10298 (3)	16
O(14)	7164 (2)	574 (2)	9919 (2)	27
C(15)	10315 (2)	2618 (2)	8923 (3)	15
O(16)	10714 (2)	2607 (2)	7691 (2)	21
H(1)	620 (3)	468 (4)	952 (4)	25 (6)
H(2)	674 (3)	637 (3)	991 (4)	21 (5)
H(3)	724 (3)	421 (3)	605 (3)	16 (5)
H(4)	815 (3)	581 (3)	532 (4)	18 (5)
H(5)	514 (4)	855 (5)	773 (5)	43 (7)
H(6)	413 (3)	721 (4)	737 (4)	28 (6)
H(7)	433 (4)	847 (4)	570 (5)	40 (7)
H(8)	498 (3)	805 (4)	342 (4)	27 (6)
H(9)	650 (4)	817 (5)	312 (5)	47 (7)
H(10)	543 (4)	665 (4)	296 (5)	38 (7)

[a] Fractional coordinates are ×10^4 for non-hydrogen atoms and ×10^3 for hydrogen atoms. B_{iso} values are ×10. Isotropic values for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

II. A solution of 1.205 g (0.0038 mol) of 1,1-dibromo-3,4-dimethylgermacyclopent-3-ene in 20 mL of diethyl ether was added to a rapidly stirred suspension containing 1.570 g (0.005 mol) of $Na_2Fe(CO)_4$·dioxane in 80 mL of diethyl ether. The reaction mixture turned deep green with formation of a white precipitate and was stirred at room temperature for 2 h. The mixture was filtered, the solid residue washed with two 10-mL portions of diethyl ether, and the volatile component removed in vacuo. During removal of the solvent, white crystals formed in the green solution. When all of the volatile components had been removed, a light green solid remained. The crude product was then dissolved in the minimum volume of *n*-pentane at room temperature, filtered, and cooled to −30 °C. After

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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 °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. ^{1}H NMR data (250.13 MHz, 20 °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 °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: (ν(CO), cm^{-1}): 2046, s; 2005, s, br; 1975, s, br. Anal. Calcd for $C_{20}H_{20}O_8Fe_2Ge_2$: 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 °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 e/Å^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 geniostat 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 °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°/min) continuous θ-2θ 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 e/Å^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.

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Arsenic–Sulfur Heterocycle Formation via Metal Coordination. Synthesis and Molecular Structure of *cyclo*-$(CH_3AsS)_n$ (n = 3, 4), $[(CO)_3Mo][\eta^3$-*cyclo*-$(CH_3As)_6S_3]$, and the Triple-Decker-Sandwich Complex $[\eta^5\text{-}(C_5H_5)_2Mo_2(\eta^2,\mu\text{-}As_3)(\eta^2,\mu\text{-}AsS)]$

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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 $Mo(CO)_6$, 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) Å, b = 10.189 (2) Å, c = 12.925 (4) Å, α = 75.25 (2)°, β = 70.09 (2)°, γ = 89.54°, V = 1056.4 (5), Å^3, Z = 4, $R(F)$ = 4.97%;, $(CH_3AsS)_4$, orthorhombic, $Pn2_1a$, a = 11.495 (3) Å, b = 30.624 (5) Å, c = 8.276 (2) Å, V = 2913.2 (10) Å^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, $[(CO)_3Mo]$[*cyclo*-$(CH_3As)_6S_3]$, which contains a nine-membered ring of three $(CH_3As)_2S$ units coordinated exclusively through As to a *fac*-$Mo(CO)_3$ group. The complex has been structurally characterized: monoclinic, $P2_1/c$, a = 10.551 (3) Å, b = 10.819 (3) Å, c = 22.407 (6) Å, β = 90.33°, V = 2557.7 (10) Å^3, Z = 4, $R(F)$ = 8.43%. Unlike the case for arsaoxanes, $(RAsO)_n$, which have demonstrated ligand properties, no evidence was found for the formation of coordinated arsathianes in reactions with either $Mo(CO)_6$ or $[CpMo(CO)_3]_2$ (Cp = η^5-C_5H_5). However, reactions of the arsathianes with $[CpMo(CO)_3]_2$ lead to the formation of several naked arsenic clusters, only one of which contains sulfur: $[CpMo(CO)_2]_2(\eta^2,\mu\text{-}As_2)$ and $[CpMo(CO)_2]_2(\eta^2,\mu\text{-}As_2)_2$ are obtained in low yields. The sulfur-containing product, $Cp_2Mo_2(\eta^2,\mu\text{-}As_3)(\eta^2,\mu\text{-}AsS)$, is a triple-decker sandwich possessing a planar middle deck composed of an allylic As_3 group and an $As\overset{\cdots}{-}S$ group: monoclinic, $C2/c$, a = 11.668 (2) Å, b = 11.273 (3) Å, c = 12.881 (4) Å, β = 119.63 (2)°, V = 1472.7 (4) Å^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 *homo*atomic 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 arsaoxane ring system, *cyclo*-$(CH_3AsO)_4$, which subsequently combined with $Mo(CO)_6$ to form the ring-expansion complex $[Mo(CO)_3]_2$[*cyclo*-$(CH_3AsO)_6]$ (**1**).[2] Complex **1** contains a highly puckered 12-membered ring of alternating As and O atoms facially coordinated to two $Mo(CO)_3$ groups to form, overall, a flattened

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

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