THE SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF [η-C₅H₅Mo(CO)₂]₂[μ-*catena*-(CH₃As)₅]. AN EXAMPLE OF A RING → CHAIN CONVERSION UPON COORDINATION

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(Received June 24th, 1982)

Summary

Pentamethylcyclopentaarsine, *cyclo*-$(CH_3As)_5$, upon combination with $[CpMo(CO)_3]_2$ ($Cp = \eta$-C_5H_5) undergoes a simple ring-opening reaction to form $[CpMo(CO)_2]_2[\mu$-*catena*$(CH_3As_5]$. This complex crystallizes in the noncentrosymmetric orthorhombic space group $Pna2_1$ [No. 33, C_{2v}^9] with a 10.901(3), b 15.279(3), c 15.985(4) Å, V 2662.51(2) Å^3, and $Z = 4$. The structure was refined to $R_F = 4.6\%$ and $R_{wF} = 4.5\%$ for 3961 reflections $|F_0| > 3\sigma(|F_0|)$. The complex possesses a near mirror plane defined by Mo(1), Mo(2), and As(3). The five arsenic atoms form an open chain (As(1) · · · As(5) 2.835(2) Å) with the terminal atoms bridging both molybdenum atoms. The Mo(1) · · · Mo(2) bond distance, 4.169(1) Å, precludes any metal–metal bonding, in accord with expectations based upon 18-electron Mo atom environments; the terminal As atoms are treated as three-electron donors. The Cp rings and CO groups adopt a mutually *trans*-configuration.

Introduction

Organocycloarsines, *cyclo*-$(RAs)_n$, combine with metal carbonyls to produce an extensive variety of coordinated homoatomic structures possessing both ring and chain configurations [3]. The diversity of observed structures, the propensity toward expansion or contraction of catenate length on reaction, and the small number of products of these reactions whose structures have been fully characterized make it difficult, if not impossible, to predict configuration and dentation of new complexes. As a part of our ongoing interest in the reactivities of *cyclo*-$(RAs)_n$ compounds, we have expanded the range of metal carbonyls studied to include cyclopentadienyl derivatives and wish now to report the synthesis and structure of $[CpMo(CO)_2]_2[\mu$-

catena(CH$_3$As)$_5$] **(1)** (Cp = η-C$_5$H$_5$). The product represents the first fully characterized example of a cyclopentaarsine undergoing an apparent simple ring-opening with coordination of the resultant chain termini [4]. Compound **1** represents a structural analog to the dimethylphosphido- and arsenido-bridged complexes, [CpMo(CO)$_2$]$_2$[μ-E(CH$_3$)$_2$]$_2$, originally reported by Hayter, in which one of the pnictogen-bonded methyl groups from each P or As atom has been replaced by a (CH$_3$As)$_3$ bridge [5, 6].

Experimental

Synthesis of [CpMo(CO)$_2$]$_2$(AsCH$_3$)$_5$ (1)

A Carius tube constructed from heavy-wall Pyrex tubing was charged with 1.0 mmol each (CH$_3$As)$_5$ (0.45 g) [18] and [CpMo(CO)$_3$]$_2$ (0.49 g) [19]. Dried toluene ($\sim$ 20 ml) was distilled from sodium/benzophenone directly into the reaction tube. After three freeze-pump-thaw cycles to thoroughly degas the contents, the tube was flame sealed and deeply immersed (horizontally) in a trough containing sand. The tube was heated at 160°C for three days, followed by a slow, two-day cooling period. While cooling, red-brown, well formed crystals were observed growing on the tube wall. After the tube stood six days undisturbed at room temperature, crystals of a size suitable for diffraction studies had formed. The tube was opened at -196°C, the contents filtered after thawing, washed with several portions of benzene, and dried in vacuo. The yield was 0.21 g. The compound is readily soluble in acetone and CHCl$_3$, insoluble in aromatic solvents, air stable when dry, and undergoes slow decomposition in solution. M.p. 217°C (d). Anal., Found: Mo, 26.89; C, 27.00; H, 3.00. C$_{19}$H$_{25}$As$_5$Mo$_2$O$_4$ calcd.: Mo, 27.09; C, 25.81; H, 2.85%. IR (CHCl$_3$): ν(CO) 1950w, 1932s, 1915vs, 1868wsh, 1846s cm^{-1}. NMR (acetone): δ(^{1}H)(CH$_3$As) 1.53(3), 1.61(3), 1.70(3), 2.01(6); (Cp) 5.28(5), 5.43(5); δ(^{13}C)(CH$_3$As) 9.76, 30.86; (Cp) 90.59, 91.15; (CO) 217.7, and 222.2 ppm.

Collection of X-ray diffraction data

The selected crystal was sealed in an argon-purged, thin-walled glass capillary. Crystal alignment, determination of the orientation matrix and accurate cell parameters, and data collection were all carried out as previously described [7]. Details are given in Table 1.

The observed systematic absences (0, k, l: $k + l = 2n + 1$; h, 0, l: $h = 2n + 1$) indicated either the noncentrosymmetric space group *Pna2$_1$* (No. 33) or the centrosymmetric space group *Pnam* (No. 62, non-standard setting). The *E*-statistics strongly favored the noncentrosymmetric alternative, which was proved correct by the successful solution of the structure in *Pna2$_1$*; attempts to refine the structure in *Pnam* led to markedly inferior results. Empirical (ψ-scan) absorption and Lp corrections were applied to the data.

Solution and refinement of the structure

All calculations were performed on Data General computers (1200 and Nova 4) using programs contained in the XTL and SHELXTL structure solution and refinement libraries written by Syntex (Nicolet). The analytical scattering factors for neutral atoms were used [8a] and corrected for both real, Δ_f', and imaginary, Δ_f'', components of anomolous dispersion [8b]. The structure was solved using the

TABLE 1

CRYSTAL AND REFINEMENT DATA

Formula	$C_{19}H_{25}As_5Mo_2O_4$
Formula weight	883.9
Crystal system	orthorhombic
Space group	$Pna2_1$ [C_{2v}^9; No. 33]
a	10.901(3) Å
b	15.279(3) Å
c	15.985(4) Å
V	2662.5(2) Å^3
Z	4
ρ(calcd)	2.21 g cm^{-3}
Temperature	25°C
Crystal color and dimension	brown, 0.16×0.23×0.31 mm
Radiation	graphite-monochromated Mo-K_α (λ 0.71073 Å)
Diffractometer	Syntex P2$_1$
Abs. coeff.	76.3 cm^{-1}
Scan speed	3.0 (fixed) deg min^{-1}
2θ scan range, deg	3–45 deg
Scan technique	coupled θ(crystal)-2θ(counter)
Data collected	$h, k, \pm l$
Scan width	$1.8 + \Delta(\alpha_1 - \alpha_2)$ deg
Ignorance factor	0.010
Unique data	4738 reflections
Unique data with $(F_{obs})^2 > 3\sigma(F_{obs})^2$	3961
Standard reflections	3/97

direct-methods routine SOLV with $E \geqslant 1.2$. The resulting E-map provided the locations of the Mo and As atoms. The remaining nonhydrogen atoms were located from subsequent difference-Fourier syntheses. Full-matrix, least-squares refinement of the positional and anisotropic thermal parameters for all nonhydrogen atoms and with all hydrogen atoms in idealized positions with d(C–H) 0.95 Å and $B = 6.00$ led to convergence with $R_F = 6.0\%$ and $R_{wF} = 4.7\%$ for all 4638 reflections and 270 variables. Restriction of data to 3961 reflections for which $|F_0| > 3\sigma(|F_0|)$ led to $R_F = 4.6\%$, $R_{wF} = 4.5\%$, and GOF $= 1.048$. The final difference map revealed only a low-level background with the highest peak (0.69 e Å^{-3}) associated with one of the Mo atoms. The usual tests of $\Sigma w(|F_0| - |F_c|)^2$ vs. $|F_0|$, $(\sin \theta)|\lambda$, sequence number, etc. showed no unusual trends. Significantly lower residuals were obtained using the reported atomic coordinates as compared to the coordinates for the opposite enantiomorph.

Final positional parameters are collected in Table 2; anisotropic thermal parameters are listed in Table 3.

Description of structure

The crystal is constructed of discrete, ordered units of [CpMo(CO)$_2$]$_2$[μ-catena(CH$_3$As)$_5$] (1) separated by normal Van der Waals distances. Figure 1 shows the system used to label the atoms and Figure 2 presents a stereoscopic view of the molecule. Interatomic distances and angles are provided in Table 4. The molecule

TABLE 2

POSITIONAL PARAMETERS FOR [CpMo(CO)$_2$]$_2$[μ-(CH$_3$As)$_5$] (with e.s.d.'s in parentheses)

Atom	x/a	y/b	z/c
Mo(1)	0.3130(1)	0.6233(1)	0.4075(1)
Mo(2)	0.2827(1)	0.4069(1)	0.2500
As(1)	0.2978(1)	0.4517(1)	0.4082(1)
As(2)	0.1243(1)	0.4223(1)	0.5019(1)
As(3)	−0.0265(1)	0.4023(1)	0.3910(1)
As(4)	−0.0289(1)	0.5542(1)	0.3461(1)
As(5)	0.1779(1)	0.5567(1)	0.2870(1)
Cp(1)	0.3777(13)	0.4300(14)	0.1238(9)
Cp(2)	0.4024(13)	0.3447(11)	0.1479(10)
Cp(3)	0.4700(12)	0.3474(9)	0.2186(9)
Cp(4)	0.4952(13)	0.4334(12)	0.2388(10)
Cp(5)	0.4402(12)	0.4872(10)	0.1820(14)
Cp(6)	0.2721(14)	0.6460(8)	0.5485(7)
Cp(7)	0.3394(12)	0.7173(8)	0.5211(9)
Cp(8)	0.2731(12)	0.7621(7)	0.4601(8)
Cp(9)	0.1608(12)	0.7208(8)	0.4512(9)
Cp(10)	0.1585(11)	0.6503(7)	0.5060(8)
C(1)	0.3793(11)	0.6745(8)	0.3055(9)
C(2)	0.4831(11)	0.5852(7)	0.4088(8)
C(3)	0.1248(12)	0.3870(8)	0.1944(8)
C(4)	0.2321(11)	0.2956(8)	0.3018(8)
O(1)	0.4256(10)	0.7087(7)	0.2491(7)
O(2)	0.5860(8)	0.5660(6)	0.4085(8)
O(3)	0.0367(9)	0.3706(6)	0.1586(6)
O(4)	0.2054(9)	0.2278(6)	0.3262(7)
C(11)	0.4278(13)	0.3894(8)	0.4724(9)
C(21)	0.1469(13)	0.2963(8)	0.5278(9)
C(31)	−0.1730(11)	0.4178(9)	0.4648(9)
C(41)	−0.1345(12)	0.5363(9)	0.2470(9)
C(51)	0.1455(13)	0.6336(8)	0.1905(9)
HCp(1)	0.3287	0.4477	0.0777
HCp(2)	0.3763	0.2933	0.1196
HCp(3)	0.4962	0.2979	0.2497
HCp(4)	0.5434	0.4522	0.2849
HCp(5)	0.4423	0.5493	0.1810
HCp(6)	0.2971	0.6030	0.5878
HCp(7)	0.4185	0.7333	0.5408
HCp(8)	0.3001	0.8121	0.4300
HCp(9)	0.0968	0.7377	0.4142
HCp(10)	0.0916	0.6112	0.5136
H(1)C(11)	0.5038	0.3944	0.4438
H(2)C(11)	0.4349	0.4146	0.5265
H(3)C(11)	0.4065	0.3293	0.4776
H(1)C(21)	0.0835	0.2774	0.5644
H(2)C(21)	0.1437	0.2633	0.4775
H(3)C(21)	0.2242	0.2879	0.5540
H(1)C(31)	−0.2457	0.4122	0.4324
H(2)C(31)	−0.1724	0.3743	0.5073
H(3)C(31)	−0.1706	0.4742	0.4897
H(1)C(41)	−0.1470	0.5906	0.2194
H(2)C(41)	−0.0960	0.4964	0.2097
H(3)C(41)	−0.2114	0.5132	0.2642
H(1)C(51)	0.2191	0.6419	0.1596
H(2)C(51)	0.0853	0.6074	0.1556
H(3)C(51)	0.1166	0.6886	0.2098

TABLE 3

ANISOTROPIC THERMAL PARAMETERS FOR THE NON-HYDROGEN ATOMS IN $[CpMo(CO)_2]_2[\mu\text{-}(CH_3As)_5]$ (with e.s.d.'s in parentheses)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo(1)	2.42(4)	2.17(3)	2.47(4)	−0.14(3)	0.20(4)	−0.39(3)
Mo(2)	2.68(4)	2.99(4)	2.63(4)	0.50(3)	−0.22(4)	−1.06(3)
As(1)	2.61(4)	2.25(4)	2.53(4)	0.12(4)	−0.49(4)	−0.20(4)
As(2)	4.07(6)	2.96(5)	2.74(5)	−0.40(4)	0.16(5)	0.07(4)
As(3)	3.38(6)	3.64(5)	3.55(5)	−0.34(5)	0.16(5)	−0.22(5)
As(4)	2.70(5)	3.73(5)	3.21(5)	0.54(5)	0.09(4)	−0.23(4)
As(5)	2.57(5)	2.67(4)	2.20(4)	0.35(4)	−0.02(4)	−0.06(3)
Cp(1)	3.8(7)	11.3(13)	3.0(6)	1.1(8)	1.4(5)	0.2(7)
Cp(2)	4.2(7)	7.0(9)	5.1(8)	0.6(6)	0.4(6)	−3.2(7)
Cp(3)	3.6(6)	5.1(7)	6.0(8)	2.1(6)	−0.0(6)	−0.9(6)
Cp(4)	3.4(6)	10.0(11)	5.3(8)	−1.9(7)	0.3(6)	−4.3(8)
Cp(5)	5.4(9)	5.6(9)	9.2(12)	0.5(7)	4.6(9)	−0.5(8)
Cp(6)	7.1(9)	3.8(6)	2.4(5)	1.2(6)	0.4(5)	−0.7(4)
Cp(7)	4.2(7)	3.7(6)	5.8(8)	−0.0(5)	0.1(5)	−2.9(6)
Cp(8)	4.7(7)	2.2(5)	4.9(7)	0.1(5)	3.1(5)	−0.8(5)
Cp(9)	2.8(6)	4.3(6)	5.1(7)	0.9(5)	−0.0(5)	−1.0(5)
Cp(10)	3.5(6)	2.4(4)	4.4(5)	−0.5(4)	2.1(5)	−1.9(4)
C(1)	3.0(5)	4.4(6)	5.1(7)	−1.4(5)	1.1(5)	−0.4(5)
C(2)	3.1(5)	4.0(5)	4.2(6)	−1.2(4)	0.4(5)	−1.3(5)
C(3)	4.4(7)	3.8(5)	3.0(5)	0.0(5)	−0.6(5)	−1.2(4)
C(4)	3.5(6)	3.1(5)	5.2(7)	0.1(5)	−0.7(5)	−2.0(5)
O(1)	8.1(6)	7.4(5)	5.3(5)	−3.8(5)	2.3(5)	1.0(5)
O(2)	2.6(4)	5.7(5)	8.1(6)	−0.1(3)	−0.0(4)	−1.9(5)
O(3)	5.3(5)	6.8(5)	6.4(5)	0.3(4)	−3.1(5)	−2.3(4)
O(4)	7.1(6)	3.6(4)	7.6(6)	−1.4(4)	−2.1(5)	0.4(4)
C(11)	4.6(7)	4.1(6)	6.6(8)	1.8(5)	−2.5(6)	0.5(5)
C(21)	5.3(7)	4.2(6)	4.9(7)	−1.4(5)	−1.1(5)	0.9(5)
C(31)	2.7(6)	6.4(7)	5.4(7)	0.0(5)	0.9(5)	−0.0(6)
C(41)	4.9(7)	7.7(8)	3.6(6)	−0.2(6)	−1.9(6)	−0.2(6)
C(51)	5.0(7)	6.0(7)	3.8(6)	1.4(6)	0.6(5)	1.3(5)

possesses a near symmetry mirror plane defined by Mo(1), Mo(2), and As(3). This plane and other significant planes are described in Table 5. The Mo atoms are joined by a 1,5-*catena*$(CH_3As)_5$ bridge; the distances, Mo(1) $\cdots$ Mo(2) 4.169(1) and As(1) $\cdots$ As(5) 2.835(2) Å, indicate, respectively, no metal–metal bonding and little significant bonding between the As-chain termini. The coordination about each Mo atom can be described as distorted square-pyramidal (assuming one site for the Cp ring). The Mo atom environment is very similar to that found in two crystallographically independent structural studies of $[CpMo(CO)_2]_2(\mu\text{-}SPh)_2$ [9] in which the observed Mo–Mo distances are 3.940(2) and 3.916(1) Å, respectively. In compound **1** the Cp rings and CO groups adopt a mutually *trans*-configuration. The Mo(1)–As(1)–Mo(2)–As(5) rhombus is nonplanar; a dihedral angle of 140.9° relates the As(1)–Mo(1)–As(5) and As(1)–Mo(2)–As(5) planes. Although few standards of comparison for Mo–As bond distances exist, the average value, 2.627(1) Å, corresponds closely to others we have recently observed [11].

The pentaarsenic chain shows bond distances and angles similar to those found in

TABLE 4

SELECTED INTERATOMIC DISTANCES AND ANGLES FOR $[CpMo(CO)_2]_2(CH_3As)_5$ (with e.s.d.'s in parentheses)

Distances Å

Mo(1) $\cdots$ Mo(2)	4.169(1)	Mo(1)–C(1)	1.948(13)
Mo(1)–As(1)	2.628(1)	Mo(1)–C(2)	1.944(12)
Mo(1)–As(5)	2.629(2)		
Mo(2)–As(1)	2.626(1)	Mo(2)–C(3)	1.961(13)
Mo(2)–As(5)	2.625(1)		
As(1)–As(2)	2.454(2)	Mo(2)–C(4)	1.970(12)
As(2)–As(3)	2.437(2)	As–C(av)	1.99(2)
As(3)–As(4)	2.430(2)	C–C(Cp, min)	1.35(1)
As(4)–As(5)	2.444(2)	C–C(Cp, max)	1.45(1)
As(1) $\cdots$ As(5)	2.835(2)		

Angles (deg)

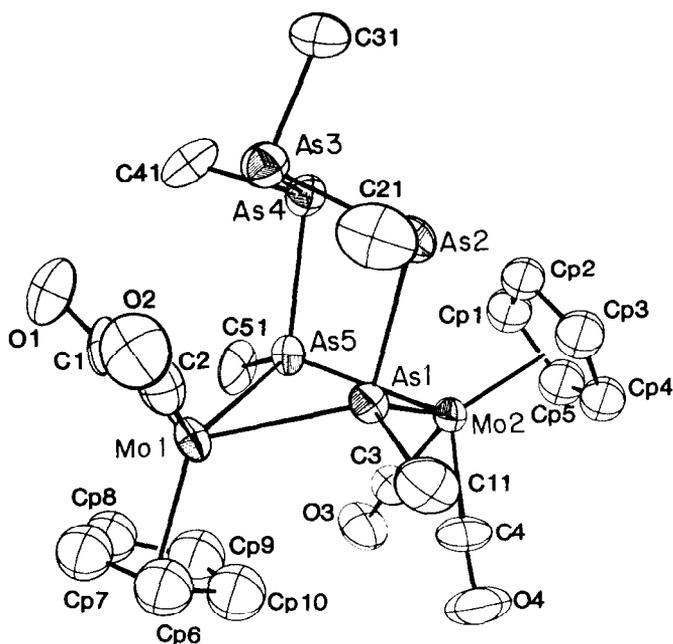|			
As(1)–Mo(1)–As(5)	65.26(4)	Mo(2)–As(1)–As(2)	119.43(6)
As(1)–Mo(2)–As(5)	65.35(4)	Mo(2)–As(5)–As(4)	118.36(6)
Mo(1)–As(1)–Mo(5)	105.04(5)	As(1)–As(2)–As(3)	99.76(5)
Mo(1)–As(5)–Mo(5)	105.02(5)	As(2)–As(3)–As(4)	95.87(6)
C(1)–Mo(1)–C(2)	77.04(51)	As(3)–As(4)–As(5)	96.85(6)
C(3)–Mo(2)–C(4)	79.12(51)	As(2)–As(1) $\cdots$ As(5)	99.49(5)
Mo–C–O(av)	175.4(12)	As(4)–As(5) $\cdots$ As(1)	98.80(5)
Mo(1)–As(1)–As(2)	103.54(6)	As–As–C(av)	98.0(4)
Mo(1)–As(5)–As(4)	103.89(6)		

Fig. 1. Labelling scheme and molecular structure for $[CpMo(CO)_2]_2[\mu\text{-}catena(CH_3As)_5]$ (**1**). Hydrogen atoms have been deleted for clarity and thermal ellipsoids are depicted at the 50% probability level.

TABLE 5

LEAST-SQUARES PLANES FOR $[CpMo(CO)_2]_2[\mu\text{-}(CH_3As)_5]$ (with e.s.d.'s in parentheses)

Atom	dev (Å)	Atom	dev (Å)
Plane I $-0.24140X - 0.8220Y - 0.5278Z + 0.98201 = 0$			
As(1) [a]	0.008(1)	As(3)	1.531(1)
As(2) [a]	$-0.008(1)$	C(11)	$-0.054(13)$
As(4) [a]	0.008(1)	C(51)	$-0.084(13)$
As(5) [a]	$-0.008(1)$		
Plane II $-0.4670X + 0.5648Y - 0.6804Z + 0.6467 = 0$			
Mo(1) [a]	0.000	As(2)	$-1.778(1)$
Mo(2) [a]	0.000	As(4)	0.1824(1)
As(3) [a]	0.000	As(5)	1.439(1)
As(1)	$-1.389(1)$	C(31)	0.007(13)
Plane III $0.8066X - 0.0536Y - 0.5887Z + 1.5925 = 0$			
Mo(1) [a]	0.000	As(5) [a]	0.000
As(1) [a]	0.000		
Plane IV $0.8593X + 0.4769Y - 0.1858Z - 4.8743 = 0$			
Mo(2) [a]	0.000	As(5) [a]	0.000
As(1) [a]	0.000		
Dihedral angles (°)			
I/II	94.18	II/III	90.36
I/III	79.51	II/IV	90.35
I/IV	118.57	III/IV	140.93

[a] These atoms were used in calculating the planes.

the cyclic precursor, *cyclo*-$(CH_3As)_5$ (2). In 1, the average As–As distance (excluding the As(1) $\cdots$ As(5) distance) is 2.441(2) Å, while in 2 the average is 2.428(5) Å [12]. Further comparisons can be found in *cyclo*-$(PhAs)_6$ where the average As–As
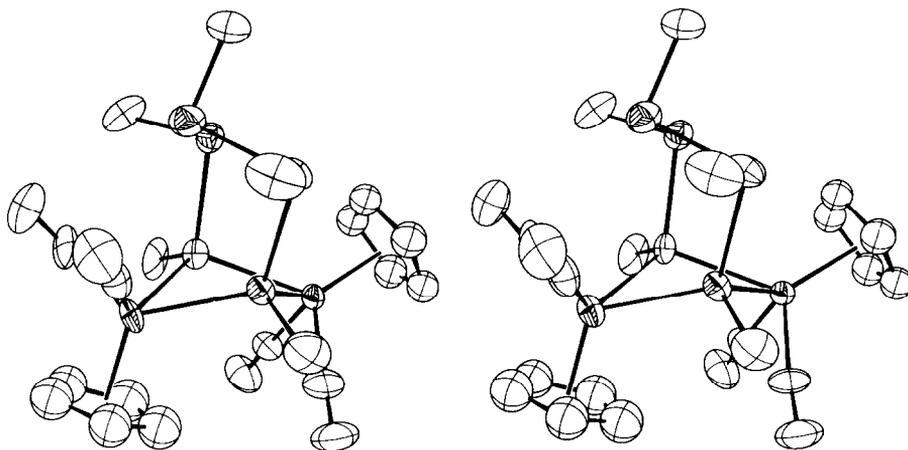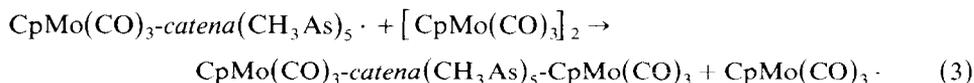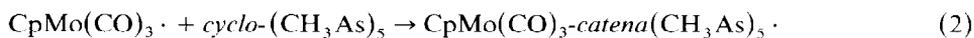

Fig. 2. A stereoscopic view of 1.

distance is 2.456(5) Å [13], and in gaseous As_4, 2.44 Å [14]. The complex $[Fe(CO)_3]_2(AsCH_3)_4$ also contains a chain of As atoms. In comparison to the more uniform distribution of As–As bond distances in **1**, the four-membered chain in the Fe complex shows significant alteration; while the 1–2 and 3–4 As–As bond lengths are similar, 2.543(7) Å, the 2–3 As–As bond is significantly shorter, 2.391(7) Å [15]. In **1**, the average As–As–As angle is 97.49(5)° which is somewhat smaller than the average found in **2**: 101.8(3)° [12]. The As-atom chain in **1** and the As-atom ring in **2** are similarly arranged with a single atom elevated from a nearly planar tetraarsenic base (see Table 5). In **1** the out-of-plane As atom is displaced by 1.531(1) Å, and in **2** by 1.252 Å, in keeping with the more acute angles found in **1**. Compounds **1** and **2** differ significantly in the arrangement of methyl groups. Whereas a near mirror plane exists in **1**, the arrangement of organic substitution in **2** is devoid of symmetry.
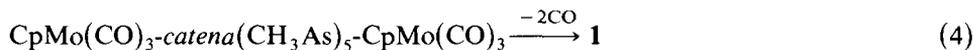
Discussion

West has demonstrated that in the mass spectrum of complexes containing intact, coordinated $(CH_3As)_5$ rings, a large m/e 450 peak $(CH_3As)_5^+$ is observed along with a complete fragmentation pattern of **2**; in complexes with opened rings, fragmentation patterns associated with $(CH_3As)_5$ are absent [3]. In both $[Mn(CO)_4)]_2(CH_3As)_5$ [4] and **1**, patterns attributable to *cyclo*-$(CH_3As)_5$ are absent. Since the $CpMo(CO)_2$ and $Mn(CO)_4$ groups are also isoelectronic, it is likely the two complexes have similar structures.

If the As-atom termini can be considered three-electron donors (the extreme case in which all As(1)–As(5) bonding is excluded), the Mo atoms exist in 18-electron environments, and no Mo–Mo bonding is expected. In $[Fe(CO)_3]_2(AsCH_3)_4$, the $Fe(CO)_3$ group has one fewer electron than $CpMo(CO)_2$, and the presence of an Fe–Fe bond is indicated: Fe–Fe 2.680(7) [4,15]. The presence of a metal–metal bond slightly lengthens the As $\cdots$ As distance: 2.835(2) in **1** as compared to 2.888(7) in $[Fe(CO)_3]_2(AsCH_3)_4$ [15].

From studies [6] of the thermolysis reactions involved in the formation of the dimethylarsenido-bridged complex, $[CpMo(CO)_2]_2[\mu\text{-}(CH_3)_2As]_2$, insight into the reaction pathway leading to the formation of **1** is provided. Since under the conditions used to prepare **1**, the cyclopentaarsine starting material is thermally stable [16], the likely initial event is the homolytic cleavage of the Mo–Mo bond (eq. 1) [17]. Metal–metal bond cleavage is followed by attack of the metal-centered radicals at the As–As ring bond leading to ring opening and transfer of the radical site from Mo to As (eq. 2). An intermediate is formed, $[CpMo(CO)_3]_2[catena\text{-}(CH_3As)_5]$, in which each terminal As atom is a one-electron donor as required to restore an 18-electron Mo-atom environment (eq. 3). Panster and Malisch have shown that similar one-electron As-donor complexes readily lose CO, an event accompanied by the conversion of a one-electron donor to a three-electron bridging ligand (eq. 4) [6].

$$[CpMo(CO)_3]_2 \rightarrow 2\,CpMo(CO)_3 \cdot \tag{1}$$

$$CpMo(CO)_3 \cdot + cyclo\text{-}(CH_3As)_5 \rightarrow CpMo(CO)_3\text{-}catena(CH_3As)_5 \cdot \tag{2}$$

$$CpMo(CO)_3\text{-}catena(CH_3As)_5 \cdot + [CpMo(CO)_3]_2 \rightarrow$$

$$CpMo(CO)_3\text{-}catena(CH_3As)_5\text{-}CpMo(CO)_3 + CpMo(CO)_3 \cdot \tag{3}$$

$$CpMo(CO)_3\text{-}catena(CH_3As)_5\text{-}CpMo(CO)_3 \xrightarrow{-2CO} \mathbf{1} \qquad (4)$$

In support of the radical nature of the proposed mechanism is the observation that traces of O_2 severely inhibit formation of **1**, a result similar to that observed by Poë et al. [17].

Acknowledgements

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