

are also found to possess opposite signs for interactions across two and three bonds. For example,  $\alpha$  and  $\beta$  carbons of aliphatic amines bound to Ni(acac)<sub>2</sub><sup>22</sup> and Gd(fod)<sub>3</sub><sup>23</sup> show opposite signs for their contact shifts. Proton contact shifts behave similarly as seen in Ni(NH<sub>2</sub>CH<sub>3</sub>)<sub>6</sub><sup>2+</sup>.<sup>24</sup>

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## Structure of (CH<sub>3</sub>)<sub>2</sub>AsCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>As(CH<sub>3</sub>)<sub>2</sub>Mn(CO)<sub>3</sub>GeCl<sub>3</sub> in the Solid State and in Solution

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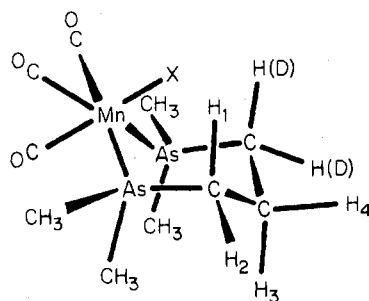
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The reaction of (CH<sub>3</sub>)<sub>2</sub>AsCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>As(CH<sub>3</sub>)<sub>2</sub>Mn(CO)<sub>3</sub>Cl with GeCl<sub>4</sub> affords *fac*-(L-L)Mn(CO)<sub>3</sub>GeCl<sub>3</sub>, **1**. The *mer* derivative is obtained from diphosMn(CO)<sub>3</sub>Br. The structure of **1** in the solid state has been determined from three-dimensional X-ray counter data. The material crystallizes in space group *P*2<sub>1</sub>/*n* with four molecules in a monoclinic cell of dimensions *a* = 8.215 (3) Å, *b* = 14.279 (7) Å, *c* = 16.787 (8) Å,  $\beta$  = 90.46 (1)°, and *V* = 1969.1 Å<sup>3</sup>. The structure was refined by full-matrix least-squares procedures to a conventional *R* factor of 8.3%. The structure of **1** consists of a slightly distorted octahedral geometry around the manganese with the chelate ring in a chair conformation such that the equatorial arsenic methyl groups are *cis* to the bulky GeCl<sub>3</sub> moiety. The chair is flattened about the As...As axis but is strongly puckered about the C...C axis. The <sup>1</sup>H NMR spectrum of **1-d**<sub>2</sub> in dichloromethane indicates that the ring is effectively locked in this solvent. The values of the <sup>3</sup>J<sub>HH</sub> coupling constants indicate strong puckering of the chelate ring about the C...C axis although the derived As-C-C-C dihedral angle is less than the solid-state value.

### Introduction

The conformations of six-membered chelate rings in metal complexes in solution have been of considerable interest in recent years.<sup>2-8</sup> In particular, using NMR techniques, it has been found that the complexes of the di(tertiary arsine) (CH<sub>3</sub>)<sub>2</sub>AsCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>As(CH<sub>3</sub>)<sub>2</sub> (L-L) of formula (L-L)-Mn(CO)<sub>3</sub>X (X = Cl, Br, I) have their chelate rings locked in a chair conformation with the axial hydrogens on the two equivalent carbon atoms pointing toward the ligand X on the metal as indicated in A.<sup>9</sup> The corresponding (L-L)M(CO)<sub>4</sub>



A

complexes undergo rapid chair  $\rightleftharpoons$  chair interconversion.<sup>2a</sup>

The locking of the ring in A is of interest because it seems that it arises because of repulsion between the ligand X on the metal and the arsenic methyl groups.<sup>10</sup> Interactions of this type are not found in rings usually studied by organic chemists so they are interesting in their own right. However it is worth noting that similar interactions could be present in the reaction intermediates of organic chemistry (replace the Mn(CO)<sub>3</sub>X moiety in A with CR<sub>2</sub>X); hence they could have an effect on reaction rates and reaction paths.

The present paper is part of a continuing study of the factors which affect chelate ring conformations.

### Experimental Section

Hydrocarbon solvents were dried using CaH<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub> was dried using P<sub>2</sub>O<sub>5</sub>. Infrared spectra were recorded on a Perkin-Elmer 457 instrument using CO and polystyrene for calibration. NMR spectra were recorded on an extensively modified Varian HA 100 spectrometer; the ABCD spectrum was solved as previously described.<sup>2</sup> The compounds [(CH<sub>3</sub>)<sub>2</sub>As(CH<sub>2</sub>)<sub>3</sub>As(CH<sub>3</sub>)<sub>2</sub>]Mn(CO)<sub>3</sub>Cl and [(C-H<sub>3</sub>)<sub>2</sub>AsCD<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>As(CH<sub>3</sub>)<sub>2</sub>]Mn(CO)<sub>3</sub>Cl were prepared as previously;<sup>2</sup> diphosMn(CO)<sub>3</sub>Br (diphos = (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>) was prepared similarly. GeCl<sub>4</sub> was commercially available and used without further purification.

**Preparation of [(CH<sub>3</sub>)<sub>2</sub>As(CH<sub>2</sub>)<sub>3</sub>As(CH<sub>3</sub>)<sub>2</sub>]Mn(CO)<sub>3</sub>GeCl<sub>3</sub>.** A solution of (L-L)Mn(CO)<sub>3</sub>Cl (0.436 g, 1 mmol) and GeCl<sub>4</sub> (0.75 ml) in benzene (10 ml) was heated at 150° in an evacuated sealed Carius tube for 55 hr. The tube was allowed to cool, and benzene and excess GeCl<sub>4</sub> were removed on the vacuum line. The residue was then sublimed at 100° (0.1 mm) to remove any (L-L)Mn(CO)<sub>3</sub>Cl and L-L. The pure product was isolated by sublimation at 120° (0.1 mm) or recrystallized from CH<sub>2</sub>Cl<sub>2</sub>-*n*-heptane. It is essential to carry out the recrystallization under a nitrogen atmosphere with dry solvents. Crystals suitable for the X-ray crystallographic study were thus obtained. The yield of yellow [(CH<sub>3</sub>)<sub>2</sub>As(CH<sub>2</sub>)<sub>3</sub>As(CH<sub>3</sub>)<sub>2</sub>]-Mn(CO)<sub>3</sub>GeCl<sub>3</sub> was approximately 65%. Anal. Calcd for C<sub>10</sub>H<sub>18</sub>As<sub>2</sub>Cl<sub>3</sub>GeMnO<sub>3</sub>: C, 21.11; H, 3.00; Cl, 18.50. Found: C, 21.04; H, 3.18; Cl, 18.65. Infrared spectrum (CO region): 2025, 1968, 1946 cm<sup>-1</sup> (cyclohexane solution); 2023, 1951 cm<sup>-1</sup> (CH<sub>2</sub>Cl<sub>2</sub> solution); all bands strong. <sup>1</sup>H NMR (CH<sub>2</sub>Cl<sub>2</sub> solution): 1.74, 1.54 ppm (As-CH<sub>3</sub>).

The deuterated analogue (CH<sub>3</sub>)<sub>2</sub>AsCD<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>As(CH<sub>3</sub>)<sub>2</sub>-Mn(CO)<sub>3</sub>GeCl<sub>3</sub> was prepared in a similar fashion.

**Preparation of [(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]Mn(CO)<sub>3</sub>GeCl<sub>3</sub>.** An evacuated sealed Carius tube containing diphosMn(CO)<sub>3</sub>Br (0.31 g, 0.5 mmol), GeCl<sub>4</sub> (1 ml), and benzene (10 ml) was heated at 160° for 7 days. The tube was then allowed to cool, and solvent and excess GeCl<sub>4</sub> were removed on the vacuum line.

The residue was extracted with two portions of warm CH<sub>2</sub>Cl<sub>2</sub> (25 ml). The extracts were combined and evaporated to dryness to give crude diphosMn(CO)<sub>3</sub>GeCl<sub>3</sub> (0.25 g, 66%). The analytical sample was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>-*n*-heptane to give yellow crystals of

product. Anal. Calcd for  $C_{29}H_{24}Cl_3GeMnO_3P_2$ : C, 48.56; H, 3.37; Cl, 14.83. Found: C, 48.20; H, 3.48; Cl, 14.82. Infrared spectrum (CO region,  $CH_2Cl_2$  solution): 2041 (w), 1968 (s)  $cm^{-1}$ .  $^{31}P$  NMR (Varian XL-100 instrument operating in the Fourier transform mode): 1.09, 1.67 ppm (upfield from  $P_4O_6$ ); both peaks weak and broad.

**Structure Analysis.** Crystal data for (L-L) $Mn(CO)_3GeCl_3$  are as follows: monoclinic,  $a = 8.215$  (3) Å,  $b = 14.279$  (7) Å,  $c = 16.787$  (8) Å,  $\alpha = 90.0$  (0)°,  $\beta = 90.46$  (1)°,  $\gamma = 90.0$  (0)°,  $V = 1969.1$  Å<sup>3</sup>,  $\rho_o = 1.92$  (2) g  $cm^{-3}$  (floatation in a methyl iodide-chloroform mixed solvent system),  $Z = 4$ ,  $\rho_c = 1.92$  g  $cm^{-3}$ , space group  $P2_1/n$ , Mo  $K\alpha_1$  radiation,  $\lambda 0.70926$  Å,  $\mu$ (Mo  $K\alpha$ ) = 62.0  $cm^{-1}$ ,  $T 21 \pm 1^\circ C$ .

The yellow air-stable crystals of the title compound are obtained as plates elongated along the  $b$  axis. A cleaved fragment, approximately needle shaped, with dimensions  $0.09 \times 0.55 \times 0.14$  mm, was selected and mounted along the needle axis for the purpose of intensity data collection.

Preliminary photographic information was collected from a different crystal specimen. Precession photographs of the  $0kl$  and  $hk0$  zones were obtained along with photographs of the reciprocal lattice layers  $h(0-3)l$  by use of equiinclination Weissenberg geometry, resulting in the assignment of monoclinic Laue symmetry. Systematically absent were reflections in the  $h0l$  zone for which  $h + l = 2n + 1$ . The space group  $P2_1/n$  was chosen so that the resultant unit cell was virtually orthogonal. The general equivalent positions used were  $x, y, z; \bar{x}, \bar{y}, \bar{z}; 1/2 - x, 1/2 + y, 1/2 - z; 1/2 + x, 1/2 - y, 1/2 + z$ .

Accurate cell dimensions were obtained from counter measurements and least-squares refinement of the  $2\theta$  values ( $2\theta > 30^\circ$ ) for 15 strong reflections centered on the Mo  $K\alpha_1$  peak ( $\lambda 0.70926$  Å). Measurements were made using a Picker Facs-1 computer-controlled diffractometer fitted with a scintillation detector employing pulse height discrimination, with the crystal  $b$  axis slightly offset with respect to  $\phi$ . Intensity data were collected in two shells  $0^\circ < 2\theta \leq 20^\circ$  and  $20^\circ < 2\theta \leq 50^\circ$  by the  $\theta-2\theta$  scan technique. A scan rate of  $2.0^\circ/min$  was used with  $2\theta$  scan widths of 0.83 and  $0.91^\circ$  for the inner- and outer-shell reflections, respectively. Background counts of 10-sec duration each were measured at the scan limits. In addition, two reflections used as standards were measured after each set of 70 reflections. The standard intensities both systematically declined by ca. 10% during data collection, the crystal appearing to undergo decomposition in the form of a surface frosting after exposure to X-rays.

Intensity measurements were obtained for 3501 unique reflections, of which 2133 were classed as observed (i.e., having  $I > 2.3\sigma(I)$  where  $\sigma(I)_{net} = [(TC) + (t_s/t_b)^2(B_1 + B_2) + (kI)^2]^{1/2}$ , where TC is the total count,  $B_1$  and  $B_2$  are the background counts,  $t_s$  is the scan time,  $t_b$  is the total background count time,  $k$  is a constant set to 0.03, and  $I$  is the net count. Intensities were corrected for Lorentz and polarization effects. Absorption corrections were not applied and could lead to a maximum error of 5% in  $F$  in extreme cases.

**Structure Elucidation and Refinement.** Examination of a Fourier synthesis generated by direct phasing and symbolic addition procedures on all data gave the positions of manganese, both arsenic atoms, and the constituents of the  $GeCl_3$  ligand. In addition, the three carbonyls were given by unresolved coordinates (i.e., carbon and oxygen atoms not resolved). Refinement of the scale and the appropriate atomic coordinates gave  $R = 0.177$  where  $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ . A subsequent electron density difference map served to locate all remaining nonhydrogen atoms; with anisotropic temperature factors for the manganese, arsenic, germanium, and chlorine atoms and isotropic temperature factors for the remaining nonhydrogen atoms  $R$  was 8.7%.

Two final cycles of refinement by full-matrix least-squares techniques (the function minimized was  $\sum w(|F_o| - |F_c|)^2$ , where  $|F_o|$  and  $|F_c|$  are the observed and calculated structure factors amplitudes) in which all noncarbonyl atoms were treated anisotropically reduced the  $R$  factor to 8.3% for all the observed data. Refinement was terminated at this point since the maximum shift/error in the atomic parameters was 0.05. For the initial refinement, constant unit weights were used; in the final stages, weights ( $=1/\sigma(F)^2$ ) were given in terms of  $\sigma(F) = \sigma(I)/(Lp)(2F_o)$ . No hydrogen atom peaks significantly above background were found in a difference synthesis using a  $(\sin \theta)/\lambda$  cutoff of  $0.4 \text{ \AA}^{-1}$  ( $\sigma(\rho) = 0.27 \text{ e \AA}^{-3}$ ).

A final electron density difference map showed no peaks greater than  $3\sigma(\rho)$ , other than those close to the heavy atoms. Atomic scattering factors were taken from ref 11 and included corrections for anomalous dispersion due to the arsenic and germanium atoms.

Table I

(a) Fractional Atomic Coordinates ( $\times 10^4$ )			
Atom	$x/a$	$y/b$	$z/c$
As(1)	-83 (2)	2521 (1)	4657 (1)
As(2)	-37 (2)	1099 (1)	3010 (1)
Ge	-231 (2)	3483 (1)	2795 (1)
Mn	1544 (2)	2422 (2)	3467 (1)
Cl(1)	-2887 (5)	3292 (3)	2870 (3)
Cl(2)	-85 (6)	4970 (3)	3105 (3)
Cl(3)	-33 (5)	3632 (3)	1494 (2)
C(1)	2674 (18)	3403 (11)	3826 (9)
O(1)	3473 (16)	4010 (9)	4058 (8)
C(2)	2905 (19)	1631 (12)	3962 (9)
O(2)	3838 (16)	1145 (9)	4260 (8)
C(3)	2720 (19)	2362 (11)	2584 (10)
O(3)	3440 (15)	2271 (9)	2003 (8)
C(4)	-878 (26)	3743 (12)	4964 (10)
C(5)	1150 (23)	2074 (18)	5598 (10)
C(6)	-2122 (17)	1830 (11)	4748 (9)
C(7)	-2040 (20)	809 (11)	4411 (10)
C(8)	-2107 (17)	783 (10)	3497 (9)
C(9)	-647 (22)	1081 (11)	1899 (9)
C(10)	1083 (21)	-83 (12)	3109 (12)

(b) Anisotropic Thermal Motion Parameters ( $\text{Å}^2 \times 10^4, \times 10^3$ for C) <sup>a</sup>						
Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
As(1)	528 (10)	477 (10)	324 (8)	-9 (8)	85 (7)	-17 (7)
As(2)	454 (10)	405 (9)	391 (9)	-23 (7)	76 (7)	-25 (7)
Ge	481 (10)	427 (10)	368 (9)	-6 (8)	40 (7)	5 (8)
Mn	337 (12)	398 (13)	336 (12)	-45 (10)	59 (9)	1 (10)
Cl(1)	459 (23)	720 (31)	744 (30)	42 (22)	58 (21)	186 (25)
Cl(2)	941 (34)	414 (24)	666 (28)	55 (24)	13 (25)	-69 (22)
Cl(3)	781 (30)	725 (31)	320 (31)	22 (24)	15 (19)	52 (20)
C(4)	157 (20)	41 (10)	64 (12)	15 (11)	33 (12)	-25 (9)
C(5)	79 (13)	182 (22)	41 (10)	23 (14)	-8 (9)	27 (12)
C(6)	52 (9)	53 (10)	56 (10)	-23 (8)	26 (8)	-15 (8)
C(7)	79 (12)	48 (11)	62 (11)	-29 (9)	26 (9)	18 (9)
C(8)	50 (9)	40 (9)	67 (11)	-17 (7)	28 (8)	-17 (8)
C(9)	118 (14)	42 (10)	39 (9)	-29 (10)	-3 (9)	-1 (8)
C(10)	83 (13)	47 (11)	112 (16)	30 (10)	9 (12)	8 (11)

(c) Isotropic Thermal Factors ( $\text{Å}^2 \times 10^3$ )			
Atom	$U$	Atom	$U$
C(1)	55 (4)	O(1)	89 (4)
C(2)	58 (4)	O(2)	88 (4)
C(3)	59 (4)	O(3)	88 (4)

<sup>a</sup> In the form  $\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12} + \dots)]$ .

Crystallographic computer programs used in this determination have been cited elsewhere.<sup>12</sup>

Final atomic parameters and thermal parameters are listed in Table I. Interatomic distances and angles are given in Table II and least-squares planes relevant to the discussion are given in Table III. Standard deviations in all tables are in parentheses as units in the least significant digit.

## Results and Discussion

The reaction of the chelate complex (L-L) $Mn(CO)_3Cl$  (L-L =  $(CH_3)_2AsCH_2CH_2CH_2As(CH_3)_2$ ) with  $GeCl_4$  on heating affords the new complex (L-L) $Mn(CO)_3GeCl_3$ , **1**. Similarly diphos $Mn(CO)_3Br$  affords diphos $Mn(CO)_3GeCl_3$ , **2**. To the best of our knowledge this is a new and convenient method for preparing compounds with manganese-germanium bonds.

The infrared spectrum of **1** is characteristic of a *fac* geometry as in A ( $X = GeCl_3$ ). This has been confirmed by our solid-state structural study (vide infra). The infrared spectrum of **2** has a pattern characteristic of *mer* substitution. This is confirmed by the  $^{31}P$  NMR spectrum which shows two absorptions due to two inequivalent phosphorus atoms. A *fac* geometry as in A, which is found for diphos $Mn(CO)_3Cl$ , would have equivalent phosphorus atoms.

It seems that the steric bulk of the chelated ligand is influencing the geometry of the reaction product. This has been

Table II. Interatomic Distances and Angles

(a) Distances, Å			
Mn-Ge	2.381 (3)	Ge-Cl(1)	2.218 (4)
Mn-C(2)	1.79 (2)	C(2)-O(2)	1.15 (2)
Mn-As(1)	2.416 (3)	Mn-As(2)	2.414 (3)
As(1)-C(4)	1.94 (2)	As(2)-C(9)	1.93 (1)
As(1)-C(5)	1.98 (2)	As(2)-C(10)	1.93 (2)
As(1)-C(6)	1.95 (1)	As(2)-C(8)	1.95 (1)
C(6)-C(7)	1.57 (2)	C(8)-C(7)	1.54 (2)
Mn-C(1)	1.78 (2)	Mn-C(3)	1.78 (2)
C(1)-O(1)	1.15 (2)	C(3)-O(3)	1.15 (2)
Ge-Cl(2)	2.216 (4)	Ge-Cl(3)	2.206 (5)
(b) Angles, Deg			
Mn-Ge-Cl(1)	119.8 (2)	As(1)-Mn-As(2)	91.2 (1)
Ge-Mn-C(2)	179.1 (5)	C(1)-Mn-C(3)	92.0 (7)
Mn-C(2)-O(2)	177 (2)	Cl(2)-Ge-Cl(3)	97.9 (2)
C(6)-C(7)-C(8)	112 (1)		
Mn-Ge-Cl(2)	118.2 (2)	Mn-Ge-Cl(3)	118.8 (2)
Mn-C(1)-O(1)	177 (1)	Mn-C(3)-O(3)	176 (2)
Mn-As(1)-C(4)	117.6 (6)	Mn-As(2)-C(9)	117.0 (5)
Mn-As(1)-C(5)	111.0 (6)	Mn-As(2)-C(10)	113.7 (6)
Mn-As(1)-C(6)	121.1 (4)	Mn-As(2)-C(8)	121.2 (4)
C(4)-As(1)-C(5)	104.5 (9)	C(9)-As(2)-C(10)	101.1 (8)
C(4)-As(1)-C(6)	98.2 (8)	C(9)-As(2)-C(8)	100.5 (7)
C(5)-As(1)-C(6)	102.0 (8)	C(10)-As(2)-C(8)	100.3 (7)
As(1)-Mn-C(1)	88.0 (5)	As(2)-Mn-C(3)	89.6 (5)
As(1)-Mn-C(3)	179.1 (5)	As(2)-Mn-C(1)	178.5 (5)
As(1)-Mn-Ge	90.8 (1)	As(2)-Mn-Ge	91.2 (1)
As(1)-Mn-C(2)	90.1 (5)	As(2)-Mn-C(2)	89.3 (5)
As(1)-C(6)-C(7)	113 (1)	As(2)-C(8)-C(7)	113 (1)
C(1)-Mn-C(2)	91.0 (7)	C(3)-Mn-C(2)	91.0 (7)
C(1)-Mn-Ge	88.6 (5)	C(2)-Mn-Ge	88.3 (5)
Cl(1)-Ge-Cl(2)	99.1 (2)	Cl(1)-Ge-Cl(3)	98.6 (2)

observed by others.<sup>4,13,14</sup> For example heating diphosMo(CO)<sub>4</sub> with triphenylphosphine affords *mer*-(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P(diphos)Mo(CO)<sub>3</sub>, yet the *fac* isomer is obtained from CH<sub>3</sub>CN.

The *fac* isomers of (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P[(CH<sub>3</sub>)<sub>2</sub>AsCH<sub>2</sub>CH(C(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)CH<sub>2</sub>As(CH<sub>3</sub>)<sub>2</sub>]Mo(CO)<sub>3</sub> are obtained from the Mo(CO)<sub>4</sub> complex in spite of the bulk of the *tert*-butyl group.<sup>4</sup> Hence the main interactions appear to be between the incoming ligand and the groups directly attached to the arsenic or phosphorus atoms in the chelate ring.

The structure of **1** is shown in Figure 1. The manganese atom has a slightly distorted octahedral geometry, with the GeCl<sub>3</sub> moiety being displaced away from the two equatorial arsenic methyl groups. The chelate ring has a chair conformation. In the corresponding (L-L)Mn(CO)<sub>3</sub>Cl, **3**, structure (A, X = Cl) the Cl is bent slightly toward the equatorial methyl groups. In (CH<sub>3</sub>)<sub>2</sub>AsCF<sub>2</sub>CHClCF<sub>2</sub>-As(CH<sub>3</sub>)<sub>2</sub>Cr(CO)<sub>4</sub>, **4**, in which the chelate ring has a chair conformation with the chlorine atom equatorial, the carbonyl group equivalent to X in A is symmetrically placed with respect to the equatorial carbonyl groups and the arsenic atoms, and it is the other trans carbonyl group which shows the greatest distortion from octahedral geometry.<sup>15</sup>

There is a noncrystallographic mirror plane (plane V) in **1**, with the result that the germanium and Cl(1) are equidistant

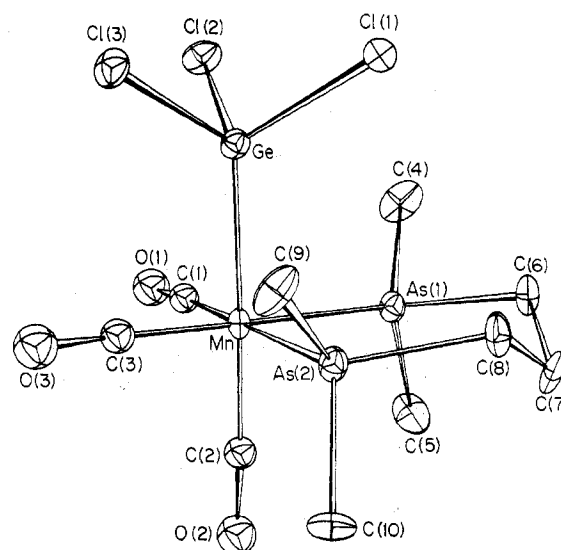


Figure 1. A view of the (CH<sub>3</sub>)<sub>2</sub>AsCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>As(CH<sub>3</sub>)<sub>2</sub>-Mn(CO)<sub>3</sub>GeCl<sub>3</sub> molecule, indicating the numbering scheme. H atoms were not located.

from the arsenic atoms and the equatorial methyl groups. The orientation of the GeCl<sub>3</sub> group is such as to minimize these interactions which are probably responsible for the orientation of the chair conformation of the six-membered ring.<sup>16</sup> It is also this interaction which is probably responsible for the displacement of the GeCl<sub>3</sub> group and for the appreciable flattening of the chair conformation such that the angle between the As(1)As(2)Mn and As(1)As(2)C(8)C(6) planes is 168°. In **3** the corresponding angle is 149°, and in **4**, 142°. This flattening is reflected in the dihedral angle MnAs(1)C(6)C(7) which is 41.5° (55° average in **3** and 59° average in **4**).<sup>10,15</sup>

The flattening of the chelate ring by bulky axial substituents on the metal was predicted by Gollgoly and Hawkins.<sup>17</sup>

In an "isolated" CoNH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>, (Co(tn)), ring the CoNCC dihedral angle is calculated to be ~68°;<sup>18</sup> in [Cl<sub>4</sub>Co(tn)]<sup>-</sup> calculations predict ~61° for the same angle.<sup>19</sup> In other six-membered ring systems the YCCY dihedral angle is 69° in 1,4-dithiane (Y = S), 37° in 1,4-dioxane (Y = O), and 55° in cyclohexane (Y = C).<sup>20</sup>

Contact shift measurements<sup>8</sup> on the paramagnetic nickel(II) complex Ni(*ms*-NH<sub>2</sub>CH(CH<sub>3</sub>)CH<sub>2</sub>CH(CH<sub>3</sub>)NH<sub>2</sub>)(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup> indicate flattening of the six-membered ring about the N-N axis, and <sup>3</sup>J<sub>PtH</sub> coupling constants reveal the ring in Pt(II) complexes of (CH<sub>3</sub>)<sub>2</sub>AsCH<sub>2</sub>CH(C(CH<sub>3</sub>)<sub>3</sub>)CH<sub>2</sub>As(CH<sub>3</sub>)<sub>2</sub> is also flattened.<sup>3</sup> Neither of these techniques can be used to establish the folding about the As-As axis of **1** in solution. However, as will be seen below, <sup>3</sup>J<sub>HH</sub> couplings do give conformational information.

The flattening in **1** opens up the endocyclic MnAsC angles to 121° although it does not greatly affect the other angles

Table III

(a) Mean Planes <sup>a</sup>						
Planes	<i>l</i>	<i>m</i>	<i>n</i>	<i>p</i>	<i>x</i>	
I: Mn, As(1), As(2)	-0.628	0.621	-0.469	1.352	0.0	
II: As(1), As(2), C(6), C(8)	-0.456	0.716	-0.529	1.505	86.3 <sup>b</sup>	
III: C(6), C(7), C(8)	0.998	0.061	-0.029	1.878	0.0	
IV: As(1), As(2), C(1), C(3)	-0.633	0.619	-0.465	1.326	23.4 <sup>b</sup>	
V: Mn, Ge, C(2), C(7)	0.019	-0.584	-0.812	6.717	3.4	
(b) Dihedral Angles, Deg						
I-II	11.8	II-III	66.7	II-V	89.9	

<sup>a</sup> Equations are in the form  $lX + mY + nZ + p = 0$ , with reference to an orthogonal system of axes (*X*, *Y*, *Z*) with *X* along the *a* axis, *Y* in the *ab* plane, and *Z* along the *c*\* axis. <sup>b</sup> These values indicate that the atoms do not form a truly coplanar group.

around the arsenic atoms.<sup>21</sup> For example the MnAsC<sub>eq</sub> angles in **1** are 117°, the same as **3**, as are the equivalent angles in **4**. The CH<sub>3</sub>AsCH<sub>3</sub> angles in all three compounds are correspondingly smaller than the tetrahedral value. These results are of interest in view of the difference in ring flattening between **1** and **3** and it seems likely that interactions with substituents on C(8) and C(6) contribute significantly to the repulsive forces.

The remainder of the chelate ring in **1**, the three-carbon fragment, is strongly puckered with respect to the As(1)-As(2)C(8)C(6) plane (113.3°), resulting in a dihedral angle for AsCCC of ~77°. This is greater than in **3** (71°) or **4** (63°). The endocyclic AsCC angles are similar (~118°) in all three compounds so apparently the flattening of one end of the ring is simply compensated by puckering at the other.

The Mn-Ge bond (2.381 (3) Å) may be compared with values found for the Fe-Ge bond of 2.438 (4) Å ( $[(\pi\text{-C}_5\text{H}_5)\text{Co}(\text{CO})]_2(\text{GeCl}_2)_2\text{Fe}(\text{CO})_4$ ),<sup>22</sup> 2.36 Å ( $(\text{Cl}_2\text{Ge})[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ ),<sup>23</sup> and 2.28 (1) Å ( $(\pi\text{-C}_4\text{H}_4)(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{GeCl}_2\text{Me})$ ).<sup>24</sup> One would expect a somewhat longer Mn-Ge bond in comparable situations; presumably the presence of three chlorine atoms leads to significant shortening. The Ge-Cl distances are unexceptional.<sup>22</sup>

The NMR spectrum of **1-d**<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>AsCD<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-As(CH<sub>3</sub>)<sub>2</sub>Mn(CO)<sub>3</sub>GeCl<sub>3</sub>, in dichloromethane, although not of the highest quality owing to low solubility, consists of an ABCD pattern for the -CH<sub>2</sub>CH<sub>2</sub>- fragment, part of which is hidden under the arsenic methyl resonances. Using the numbering shown in A (X = GeCl<sub>3</sub>) the spectrum can be analyzed to afford the following chemical shifts and coupling constants:  $\delta_1$  312.5,  $\delta_2$  339.9,  $\delta_3$  352.0,  $\delta_4$  300.2 Hz upfield from internal CH<sub>2</sub>Cl<sub>2</sub>;  $J_{12} = -13.60$ ,  $J_{13} = 12.37$ ,  $J_{14} = 2.45$ ,  $J_{23} = 1.45$ ,  $J_{24} = 5.80$ ,  $J_{34} = -14.83$  Hz.

The values of  $J_{13}$  and  $J_{24}$  indicate that the ring is effectively locked in a chair conformation.<sup>2b</sup> Since the solid-state conformation is as shown in Figure 1, this is taken to be the locked conformation found in solution.<sup>16</sup> The "R value"<sup>20,25</sup>  $(J_{13} + J_{24})/(J_{14} + J_{23})$  is 4.66 which indicates a strongly puckered chair about the CH<sub>2</sub>-CD<sub>2</sub> axis.  $\psi$ , the dihedral angle in the AsCCC fragment, can be calculated from the "R value" and is ~68° which is smaller than the solid-state value of ~77°. In similar studies on **3** the "R value" gave ~68° for  $\psi$  in better agreement with the solid-state angle of 71°.<sup>2b,10</sup> It seems that these calculations are less reliable at high dihedral angle.<sup>20</sup>

The chemical shifts of H<sub>3</sub> and H<sub>4</sub> are in the usual relative positions; i.e., the axial proton is upfield of the equatorial. In the case of H<sub>1</sub> and H<sub>2</sub> this situation is reversed and the axial proton H<sub>1</sub> is downfield of H<sub>3</sub>. A similar downfield shift of the axial hydrogen was found in the "locked" complex **3** and its bromo and iodo derivative (A; X = Cl, Br, I). It was also

found in one of the two "locked" isomers of (CH<sub>3</sub>)<sub>2</sub>AsCH<sub>2</sub>CH(C(CH<sub>3</sub>)<sub>3</sub>)CH<sub>2</sub>As(CH<sub>3</sub>)<sub>2</sub>Mn(CO)<sub>3</sub>X<sup>2b</sup> and appears to be due to an interaction between the group X and the axial H.<sup>26</sup>

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**Registry No.**  $[(\text{CH}_3)_2\text{As}(\text{CH}_2)_3\text{As}(\text{CH}_3)_2]\text{Mn}(\text{CO})_3\text{GeCl}_3$ , 56804-75-2;  $[(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_5)_2]\text{Mn}(\text{CO})_3\text{GeCl}_3$ , 56804-76-3;  $[(\text{CH}_3)_2\text{As}(\text{CH}_2)_3\text{As}(\text{CH}_3)_2]\text{Mn}(\text{CO})_3\text{Cl}$ , 41660-26-8; diphosMn(CO)<sub>3</sub>Br, 19195-72-3; GeCl<sub>4</sub>, 10038-98-9.

**Supplementary Material Available.** Table IV, a listing of structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.50 for photocopy or \$2.50 for microfiche, referring to code number AIC50238Q-12-75.

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