Crystal Structure of μ-(Dimethylarsino)-μ-[3,3,4,4-tetrafluoro-2-(dimethylarsino)cyclobut-1-enyl(*As,C*)]-bis(tetracarbonylmanganese)

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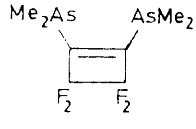
Crystals of the title compound (II) are monoclinic, space group $P2_1/n$ with cell dimensions $a = 9{\cdot}040(3)$, $b = 13{\cdot}552(4)$, $c = 18{\cdot}517(5)$ Å°, $\beta = 90{\cdot}52(2)°$ $Z = 4$. The structure was solved from diffractometer data by Patterson and Fourier methods, and refined by full-matrix least-squares techniques to R 3·6% for 1728 observed reflections.

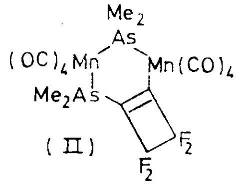
The molecule consists of two $Mn(CO)_4$ groups bridged by an $AsMe_2$ group [2·508(2) Å and 2·489(2) Å]. The ligand fragment $AsMe_2\overline{C{:}CCF_2C}F_2$ also bridges the two manganese atoms. One manganese atom is linked to the arsenic atom [2·410(2) Å] while the other is bonded through a σ bond from a carbon atom of the cyclobutene ring.

THE ligand 3,3,4,4-tetrafluoro-1,2-bis(dimethylarsino)-cyclobut-1-ene [$f_4$fars, (I)] has been shown to co-ordinate as a uni- and bi-dentate ligand, as well as a uni- and bi-ligate ligand through the $AsMe_2$ groups. By co-ordinating through the double bond as well as through both arsenic groups, tri-ligate properties are exhibited. In addition, one $AsMe_2$ group can be cleaved from the ligand and inserted into a metal–metal bond.[1]

When the compound $(f_4fars)Mn_2(CO)_8$ [where the ligand (I) bridges the Mn–Mn bond [2]] is treated under reflux with xylene, rearrangement occurs. The new product (II) was originally thought to contain the ligand (I) bonded to only one manganese atom with the Mn–Mn bond intact.[3] Though the mass spectral data indicated this to be an isomer of the starting material, the presumed structure did not explain the n.m.r. spectrum. It was therefore of interest to determine what type of rearrangement, if any, had taken place and an *X*-ray structural determination of (II) was undertaken.



(I)



(II)

EXPERIMENTAL

Heating $(f_4fars)Mn_2(CO)_3$ under reflux in xylene produced isomeric yellow monoclinic crystals of (II). Preliminary Weissenberg and precession photographs indicated the monoclinic space group $P2_1/c$. In order to obtain a more nearly orthogonal unit cell the unconventional space group $P2_1/n$ was chosen, equivalent positions $\pm(x, y, z;\ \tfrac{1}{2} - x, \tfrac{1}{2} + y, \tfrac{1}{2} - z)$.

Crystal Data.—$C_{16}H_{12}As_2F_4Mn_2O_8$, $M = 668{\cdot}0$, Monoclinic, $a = 9{\cdot}040(3)$, $b = 13{\cdot}552(4)$, $c = 18{\cdot}517(5)$ Å, $\beta = 90{\cdot}52(2)°$, $D_c = 1{\cdot}96$, $Z = 4$, $D_m = 1{\cdot}8(1)$, $U = 2268$ Å^3, $F(000) = 1296$. Space group $P2_1/n$. Mo-radiation, $\lambda = 0{\cdot}70926$ Å; $\mu(\text{Mo-}K_\alpha) = 42{\cdot}8$ cm^{-1}, $\mu(R) = 0{\cdot}43$.

A single crystal ground to a spheroid of diameter $0{\cdot}2\ \text{mm} < D < 0{\cdot}25$ mm was mounted with b approximately parallel to ϕ. Cell dimensions were obtained from a least-squares analysis of 2θ values for 12 accurately centred reflections on a computer-controlled Picker four-circle diffractometer. Errors were determined by a least-squares procedure.

Niobium-filtered Mo-K_α radiation was used for data collection. With a take-off angle of 2·1° and a scintillation counter equipped with pulse-height analysis, all reflections with $2\theta \leqslant 40°$ were measured by the θ—2θ scan technique over a base width of 2·0° in 2θ (increased to allow for dispersion effects) at 2° min^{-1}. Background counts were measured at both scan limits for 10 s. Two standard reflections were monitored after every 50 measurements.

Intensities were corrected for background variation in the standard count, and the Lorentz-polarization factor. Of the 2126 reflections measured, 1728 having a net count $>2{\cdot}3\sigma$, were considered observed. The structure was initially solved and refined by use of only 1436 reflections above a somewhat higher threshold, but final refinement was carried out for all 1728 reflections. The net intensity of the standards decreased during data collection to 83% of their initial values. No absorption corrections were made since the crystal was spherical.

Structure Determination.—Both arsenic and manganese atomic positions were derived from the unsharpened Patterson function. In the first electron-density difference map all other non-hydrogen atoms were located. Thirteen cycles of full-matrix least-squares refinement were required to refine all atomic parameters. Anisotropic thermal motion parameters for the arsenic, manganese, oxygen, and fluorine atoms were introduced only when evidence in the difference maps indicated that these additional variables were needed. All twelve hydrogen atoms were introduced and their positions refined as they became the predominant features in the difference maps. The least-squares function minimized was $\Sigma w(|F_o| - |F_c|)^2$. The final weighted and unweighted factors were R' 0·036 and R 0·034, respectively.

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[1] J. P. Crow and W. R. Cullen, *Inorg. Chem.*, 1971, **10**, 1529, 2165; F. W. B. Einstein, Anne-Marie Pilotti, and R. Restivo, *ibid.*, p. 1947; W. R. Cullen, D. A. Harbourne, B. V. Liengme, and J. R. Sams, *ibid.*, 1970, **9**, 702; 1969, **8**, 95, 1464; W. R. Cullen and D. A. Harbourne, *ibid.*, 1970, **9**, 1839; P. J. Roberts, B. R. Penfold, and J. Trotter, *ibid.*, p. 2137; W. R. Cullen, P. S. Dhaliwal, and C. J. Stewart, *ibid.*, 1967, **6**, 2256; P. J. Roberts and J. Trotter, *J. Chem. Soc.* (*A*), 1971, 1479; 1970, 3246; W. Harrison and J. Trotter, *ibid.*, 1971, 1607; F. W. B. Einstein and R. D. G. Jones, *ibid.*, p. 3359; F. W. B. Einstein and J. Trotter, *ibid.*, 1967, 824.

[2] L. Y. Y. Chan and F. W. B. Einstein, *J.C.S. Dalton*, 1973, 111.

[3] J. P. Crow, W. R. Cullen, and F. L. Hou, *Inorg. Chem.*, 1972, **11**, 2125.

The major features in the final difference map [*ca.* ±0·4(3) eÅ^{-3}] were due to anisotropy in the fluorocyclobutene ring. Small peaks near all methyl groups and three carbonyl groups indicated slight anisotropic motion or possible disorder.

TABLE 1

Final atomic parameters, with estimated standard deviations in parentheses; As and Mn ×10^5, F, O, and C ×10^4, H ×10^3. Isotropic temperature factors are ×10^3 Å^2

Atom	*x*	*y*	*z*	*U* *
As(1)	21081(8)	22419(6)	5480(4)	
As(2)	−2246(8)	21190(6)	20472(4)	
Mn(1)	−18055(12)	33805(8)	14409(6)	
Mn(2)	16641(12)	10251(8)	14700(6)	
F(1)	−2880(6)	2824(5)	−417(3)	
F(2)	−1831(7)	4231(5)	−473(3)	
F(3)	571(6)	3378(5)	−1069(3)	
F(4)	−465(6)	1955(5)	−956(3)	
O(1)	−3100(7)	3693(5)	2893(3)	
O(2)	577(7)	4811(5)	1820(4)	
O(3)	−3725(7)	4944(5)	820(4)	
O(4)	−3835(7)	1730(5)	1046(4)	
O(5)	4002(7)	1981(5)	2365(4)	
O(6)	3781(8)	−324(5)	772(4)	
O(7)	−970(7)	328(5)	635(4)	
O(8)	1137(7)	−446(5)	2610(4)	
C(1)	−2608(9)	3560(6)	2323(5)	50(2)
C(2)	−336(9)	4275(6)	1667(4)	44(2)
C(3)	−2985(9)	4340(7)	1045(5)	47(2)
C(4)	−3079(9)	2365(7)	1197(5)	47(2)
C(5)	3112(10)	1621(6)	2019(5)	47(2)
C(6)	2965(10)	204(7)	1040(5)	63(3)
C(7)	52(9)	582(6)	938(4)	42(2)
C(8)	1326(9)	128(7)	2172(5)	56(2)
C(9)	−915(8)	3124(5)	458(4)	34(2)
C(10)	319(8)	2745(6)	146(4)	39(2)
C(11)	−1597(10)	3292(7)	−285(5)	56(2)
C(12)	−227(10)	2832(7)	−610(5)	57(2)
C(13)	−1620(12)	1239(8)	2539(6)	69(3)
C(14)	666(12)	2735(8)	2909(6)	66(3)
C(15)	3141(12)	1827(8)	−306(6)	63(3)
C(16)	3154(11)	3436(8)	795(6)	59(3)
H(131)	−212(9)	86(6)	216(5)	73
H(132)	−216(9)	167(6)	288(5)	73
H(133)	−93(9)	100(6)	290(5)	73
H(141)	110(9)	217(6)	316(5)	72
H(142)	141(9)	318(6)	279(5)	72
H(143)	−16(9)	291(6)	309(5)	72
H(151)	268(9)	137(6)	−50(5)	68
H(152)	401(10)	181(6)	−10(5)	68
H(153)	320(9)	240(6)	−59(5)	68
H(161)	269(9)	376(6)	114(5)	66
H(162)	345(8)	379(6)	35(4)	66
H(163)	400(9)	326(6)	105(5)	66

* Anisotropic thermal parameters for As and Mn (Å^2 × 10^4) and for F and O (Å^2 × 10^3), in the form: $\exp -2\pi(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)$, with parameters:

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
As(1)	335(5)	384(5)	291(5)	41(4)	5(4)	5(4)
As(2)	437(5)	340(5)	263(5)	28(4)	13(4)	44(4)
Mn(1)	368(7)	330(7)	316(7)	38(6)	10(5)	13(6)
Mn(2)	381(7)	359(7)	371(7)	48(6)	−36(5)	53(6)
F(1)	56(4)	183(7)	55(4)	16(4)	−21(3)	−24(4)
F(2)	143(6)	121(5)	61(4)	81(5)	20(4)	43(4)
F(3)	96(4)	123(5)	50(4)	40(4)	23(3)	39(4)
F(4)	94(5)	126(6)	60(4)	31(4)	−21(3)	−42(4)
O(1)	93(5)	79(5)	50(4)	21(4)	24(4)	−3(4)
O(2)	80(5)	52(4)	86(5)	−18(4)	−17(4)	3(4)
O(3)	72(4)	61(4)	68(5)	28(4)	−11(4)	5(4)
O(4)	61(4)	56(4)	98(5)	−12(4)	−6(4)	−8(4)
O(5)	67(5)	98(6)	74(5)	−26(4)	−27(4)	7(4)
O(6)	100(6)	79(6)	123(7)	40(5)	31(5)	−2(5)
O(7)	63(4)	66(5)	79(5)	−7(4)	−21(4)	−21(4)
O(8)	75(5)	83(5)	90(5)	−1(4)	−5(4)	58(5)

TABLE 2

Interatomic distances and angles

(*a*) bonded distances (Å)

As(1)–Mn(2)	2·410(2)	C(7)–O(7)	1·130(8)
As(1)–C(10)	1·901(7)	C(8)–O(8)	1·138(10)
As(1)–C(15)	1·927(11)	C(9)–C(10)	1·361(10)
As(1)–C(16)	1·928(10)	C(9)–C(11)	1·519(11)
As(2)–Mn(1)	2·489(2)	C(10)–C(12)	1·485(11)
As(2)–Mn(2)	2·508(2)	C(11)–C(12)	1·516(12)
As(2)–C(13)	1·965(10)	C(11)–F(1)	1·336(10)
As(2)–C(14)	1·967(11)	C(11)–F(2)	1·342(10)
Mn(1)–C(1)	1·810(9)	C(12)–F(3)	1·343(10)
Mn(1)–C(2)	1·844(9)	C(12)–F(4)	1·366(10)
Mn(1)–C(3)	1·831(9)	C(13)–H(131)	0·98(8)
Mn(1)–C(4)	1·847(9)	C(13)–H(132)	0·99(8)
Mn(1)–C(9)	2·027(7)	C(13)–H(133)	0·96(8)
Mn(2)–C(5)	1·837(9)	C(14)–H(141)	0·98(8)
Mn(2)–C(6)	1·809(10)	C(14)–H(142)	0·94(8)
Mn(2)–C(7)	1·852(9)	C(14)–H(143)	0·86(9)
Mn(2)–C(8)	1·808(10)	C(15)–H(151)	0·82(8)
C(1)–O(1)	1·162(9)	C(15)–H(152)	0·88(8)
C(2)–O(2)	1·134(9)	C(15)–H(153)	0·94(8)
C(3)–O(3)	1·134(9)	C(16)–H(161)	0·88(8)
C(4)–O(4)	1·133(9)	C(16)–H(162)	0·99(8)
C(5)–O(5)	1·135(9)	C(16)–H(163)	0·92(8)
C(6)–O(6)	1·144(10)		

(*b*) Bond angles (°)

As(2)–Mn(1)–C(1)	85·3(3)	Mn(2)–As(1)–C(16)	119·4(3)
As(2)–Mn(1)–C(2)	86·5(3)	C(10)–As(1)–C(15)	101·6(4)
As(2)–Mn(1)–C(3)	176·8(3)	C(10)–As(1)–C(16)	101·9(4)
As(2)–Mn(1)–C(4)	87·3(3)	C(15)–As(1)–C(16)	101·5(5)
As(2)–Mn(1)–C(9)	93·2(2)	Mn(1)–As(2)–Mn(2)	127·15(5)
C(9)–Mn(1)–C(1)	177·9(4)	Mn(1)–As(2)–C(13)	104·9(3)
C(9)–Mn(1)–C(2)	91·5(4)	Mn(1)–As(2)–C(14)	107·7(4)
C(9)–Mn(1)–C(3)	89·8(4)	C(13)–As(2)–C(14)	98·1(5)
C(9)–Mn(1)–C(4)	84·5(4)	Mn(2)–As(2)–C(13)	106·3(3)
C(1)–Mn(1)–C(2)	90·0(4)	Mn(2)–As(2)–C(14)	108·7(4)
C(1)–Mn(1)–C(3)	91·7(4)	Mn(1)–C(1)–O(1)	178·5(8)
C(1)–Mn(1)–C(4)	93·9(4)	Mn(1)–C(2)–O(2)	178·4(15)
C(2)–Mn(1)–C(3)	92·3(4)	Mn(1)–C(3)–O(3)	177·9(8)
C(2)–Mn(1)–C(4)	172·4(4)	Mn(1)–C(4)–O(4)	178·6(8)
C(3)–Mn(1)–C(4)	94·1(4)	Mn(2)–C(5)–O(5)	179·2(10)
As(1)–Mn(2)–As(2)	90·91(5)	Mn(2)–C(6)–O(6)	179·3(16)
As(1)–Mn(2)–C(5)	88·2(3)	Mn(2)–C(7)–O(7)	177·9(8)
As(1)–Mn(2)–C(6)	89·8(3)	Mn(2)–C(8)–O(8)	178·7(12)
As(1)–Mn(2)–C(7)	88·9(3)	Mn(1)–C(9)–C(10)	141·2(6)
As(1)–Mn(2)–C(8)	179·1(10)	C(10)–C(9)–C(11)	90·0(6)
As(2)–Mn(2)–C(5)	89·4(3)	As(1)–C(10)–C(9)	131·8(6)
As(2)–Mn(2)–C(6)	177·6(3)	As(1)–C(10)–C(12)	132·2(6)
As(2)–Mn(2)–C(7)	83·3(3)	C(9)–C(10)–C(12)	95·9(6)
As(2)–Mn(2)–C(8)	88·3(3)	C(9)–C(11)–C(12)	88·4(7)
C(5)–Mn(2)–C(6)	92·9(4)	C(9)–C(11)–F(1)	116·0(7)
C(5)–Mn(2)–C(7)	172·1(4)	C(9)–C(11)–F(2)	116·1(8)
C(5)–Mn(2)–C(8)	91·2(4)	F(1)–C(11)–F(2)	105·5(8)
C(6)–Mn(2)–C(7)	94·5(4)	C(10)–C(12)–C(11)	85·6(7)
C(6)–Mn(2)–C(8)	91·0(4)	C(10)–C(12)–F(3)	117·7(7)
C(7)–Mn(2)–C(8)	91·6(4)	C(10)–C(12)–F(4)	115·0(8)
Mn(2)–As(1)–C(10)	112·1(3)	F(3)–C(12)–F(4)	105·4(8)
Mn(2)–As(1)–C(15)	117·8(4)		

(*c*) Methyl bond angles (°)

	C(13)	C(14)	C(15)	C(16)
As(1)–C–H(1)	106(5)	102(5)	109(6)	110(6)
As(1)–C–H(2)	105(5)	112(5)	95(6)	110(5)
As(1)–C–H(3)	96(5)	95(6)	104(5)	108(5)
H(1)–C–H(2)	123(5)	110(7)	129(8)	119(7)
H(1)–C–H(3)	128(7)	113(8)	114(7)	99(7)
H(2)–C–H(3)	94(5)	123(8)	103(7)	109(7)

(*d*) Important non-bonded distances (Å)

(i) Non-hydrogen distances (⩽3·2 Å)

O(1) ··· F(4^{I})	3·16	O(2) ··· F(3^{III})	3·00
O(1) ··· O(8^{II})	3·12	O(2) ··· O(8^{IV})	3·16
O(2) ··· F(2^{III})	3·04	O(7) ··· O(7^{V})	3·08

(ii) Hydrogen distances (⩽2·9 Å)

H(132) ··· F(3^{I})	2·84	H(151) ··· O(7^{V})	2·78
H(133) ··· O(3^{VI})	2·78	H(161) ··· O(8^{IV})	2·76
H(141) ··· F(1^{VII})	2·78	H(162) ··· O(3^{III})	2·78

TABLE 2 (*Continued*)

Roman numeral superscripts refer to the following equivalent positions, relative to the reference molecule at x, y, z:

I	$x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$	V	$-x, -y, -z$
II	$-x - \frac{1}{2}, y + \frac{1}{2}, \frac{1}{2} - z$	VI	$-x - \frac{1}{2}, y - \frac{1}{2}, \frac{1}{2} - z$
III	$-x, 1 - y, -z$	VII	$\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$
IV	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$		

Final atomic parameters are listed in Table 1, bond distances, angles, and intermolecular contacts in Table 2. The two arsenic and manganese atoms definitely are not planar, while the calculated mean planes (Table 3) also show the cyclobutene ring to be non-planar. Figure 1 shows a drawing of the molecule and Figure 2 a unit-cell packing diagram. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20877 (4 pp.).*

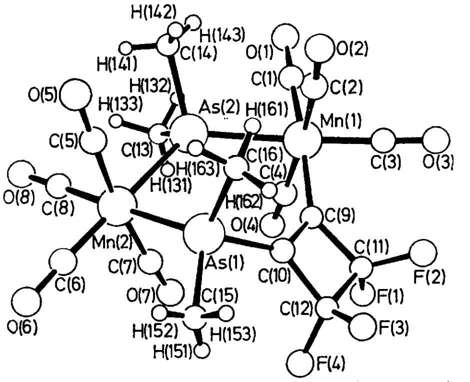

FIGURE 1 Diagram of molecule (II) showing the atom numbering system used in the analysis

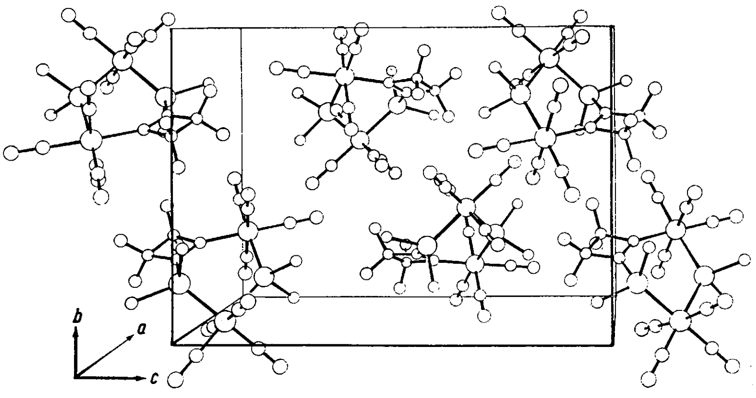

FIGURE 2 Unit-cell packing diagram

Atomic scattering factors for manganese and the anomalous scattering factors for arsenic and manganese were from ref. 4, those for hydrogen from ref. 5, while those for all other atoms were from ref. 6.

RESULTS AND DISCUSSION

The asymmetric unit of the monoclinic unit cell contains one molecule. Each molecule contains two manganese atoms in a distorted octahedral environment; each is linked to four carbonyl groups and one bridging dimethylarsino-group. The portion of the ligand (I) from which the one dimethylarsino-group was separated, also bridges the manganese atoms, completing the octahedral environment. The arsenic atom attached to the original ligand bonds to one manganese atom while the carbon, from the point of previous attachment of the bridging $AsMe_2$ group, σ bonds to the other manganese atom. The Mn–Mn bond in the isomer $(f_4fars)Mn_2(CO)_8$,[2] from which this compound was made, was broken by insertion of a bridging $AsMe_2$ group, to give Mn ··· Mn 4·475 Å.

TABLE 3

Equations of selected mean planes (in the form $Ax' + By' + Cz' + D = 0$) and χ^2 [$\Sigma p^2/\sigma^2(p)$, where p is the distance (Å) of the atom normal to the plane]. Co-ordinates (Å) are orthogonalized such that: x' is parallel to a, y' is in ab plane, 90° from a, and z' is perpendicular to ab plane. Distances of atoms from the planes are given in square brackets

	A	*B*	*C*	*D*	χ^2
Plane (1): C(9)—(12)	0·411	0·911	−0·047	−3·482	9·21
[C(9) −0·009, C(10) 0·010, C(11) 0·014, C(12) −0·014]					
Plane (2): As(1), Mn(1), C(9)—(12)	0·392	0·920	−0·016	−3·522	64·83
[As(1) 0·000, Mn(1) −0·001, C(9) 0·031, C(10) 0·007, C(11) 0·024, C(12) −0·052]					
Plane (3): As(1), Mn(1), C(9)—(11)	0·396	0·918	−0·0055	−3·535	8·07
[As(1) 0·000, Mn(1) 0·000, C(9), 0·017, C(10) −0·008, C(11) −0·007, C(12) −0·083]					

The significant differences between chemically similar bonds and angles are those involving only manganese and arsenic atoms. Many of the other observed differences are at or lower than the possibly significant level.

Each of the three Mn–As bonds differ. One [As(1)–Mn(2) 2·410(2) Å] is within the range reported in

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other structural studies [2·389(2)—2·403(2) Å] [2,7] while two others, involving As(2), are unusually long [2·489(2) and 2·507(2) Å]. These differences are also reflected in As(2)–C(Me) distances, which are slightly longer than those for As(1). There is also an increase in the Mn(1)–As(2)–Mn(2) angle and a reduction in the C(Me)–As(2)–C(Me) angle, relative to As(1). This may be explained by assuming electron withdrawal from As(1) by the tetrafluorocyclobutene ring, thus reducing its effective radius.

Manganese–carbonyl bond distances [1·810(9)—1·852(9) Å] are within the expected range, as are the C–O distances,[8] the carbonyl groups being linear. The environment of the central manganese atoms deviates only slightly from a perfect octahedron such as to increase the carbonyl–carbonyl and decrease the carbonyl–arsenic contact distances.

Within the cyclobutene ring the double-bond [1·361(10) Å] and three single-bond distances [1·485(11)—1·519(11) Å] are within the expected range. C(10) is displaced toward C(11) slightly more than would be expected in order to accommodate the shorter double-bond distance and resulting angle change. The Mn(1)–C(9)–C(10) angle [141·2(6)°] is somewhat greater than the expected 135°. This, coupled with the 'statistical' non-planarity within the ring, is consistent with appreciable Mn(1)–C(9) π-bonding.

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