Novel Cleavage Product of the Reaction of a Ditertiary Arsine with Decacarbonyldimanganese: Crystal Structure of μ-(Dimethylarsino)-μ-{1—3-η-[2,3-bis(dimethylarsino)-1,1-difluoro-3-trifluoromethylallyl]-(*As, As', C, C', C''*)}bis[tricarbonylmanganese(I)]

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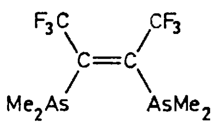
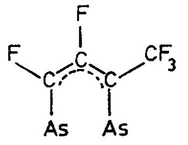
Crystals of the title compound are triclinic with $a = 9{\cdot}580$, $b = 15{\cdot}279$, $c = 9{\cdot}292$ Å, $Z = 2$, space group $P\bar{1}$. The structure was solved by the heavy-atom method from diffractometer data and refined by least-squares methods to R 7·8% (2233 observed reflections). Each manganese atom has an irregular octahedral environment which includes three *fac*-carbonyl groups. The two manganese atoms are linked by a bridging dimethylarsino-group. A further link between the two manganese atoms is provided by the substituted π-allyl ligand, $F_2C \cdots C(AsMe_2) \cdots (CF_3)CAsMe_2$. Both arsenic atoms bond to Mn(1) while the C_3-allyl system bonds symmetrically to Mn(2). Some distances are: Mn(2)–C(terminal allyl) 2·09(2) and 2·13(2), Mn(1)–As(1) 2·455(4), Mn(2)–As(1) 2·507(4), Mn(1)–As(2) 2·354(4), and Mn(1)–As(3) 2·387(4) Å. The configuration of the π-allyl ligand and significant differences in Mn–As bond lengths are discussed.

THE ligand (1) reacts with $Mn_2(CO)_{10}$ to give a novel compound of formula $[Mn_2(CO)_6As_3Me_6F_5C_4]$.[1] I.r. and ^{19}F n.m.r. data suggest that a unique fluorine-substituted π-allyl fragment (2) or (3) is present in the molecule. The presence of (2) in the molecule would indicate cleavage of a C–As bond while (3) would result from C–F bond cleavage. An example of C–As bond cleavage in a similar reaction has recently been reported.[2] Structural data on asymmetrically substituted π-allyl ligands are limited and a crystal structure analysis was undertaken in order to establish the presence of either (2) and (3) in the molecule. A preliminary report of these results has appeared.[1]


(1)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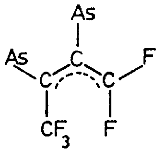
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EXPERIMENTAL

Crystal Data.—$C_{16}H_{18}As_3F_5Mn_2O_6$, $M = 717{\cdot}8$, Triclinic, $a = 9{\cdot}580(4)$, $b = 15{\cdot}279(6)$, $c = 9{\cdot}292(3)$ Å, $\alpha = 93{\cdot}07(2)$, $\beta = 119{\cdot}26(2)$, $\gamma = 82{\cdot}80(2)°$, $U = 1180{\cdot}2$ Å^3, $D_m = 2{\cdot}05$ (flotation MeI–EtI), $Z = 2$, $D_c = 2{\cdot}02$ g cm^{-3}, $F(000) = 712$. Space group $P\bar{1}$. Mo-K_α radiation (Nb filter), $\lambda = 0{\cdot}7107$ Å, μ(Mo-K_α) $= 55{\cdot}9$ cm^{-1}.

Yellow air-stable crystals were grown from methylene chloride as thin plates elongated along *a*. Preliminary Weissenberg and precession photographs were used to establish Laue symmetry $\bar{1}$. A crystal of dimensions $0{\cdot}31 \times 0{\cdot}22 \times 0{\cdot}13$ mm was mounted in a general orientation in order to minimise multiple-diffraction effects.[3]

All measurements were made with a computer-controlled Picker four-circle diffractometer equipped with scintillation counter and pulse-height analysis. Cell dimensions were obtained by the least-squares refinement of the 2θ values, (2θ > 34°) for 24 reflections which had been accurately centred. Unique intensity data were collected in two shells, $0° < 2\theta$ (Mo-$K_{\alpha1}$) $\leqslant 25°$ and $25° \leqslant 2\theta$ (Mo-$K_{\alpha1}$) $\leqslant 45°$, by the θ—2θ scan technique at a scan rate of 2·0° min^{-1}, with 2θ scan widths of 1·15 and 1·05 (extended for spectral dispersion), for inner and outer shell reflections. A background count of 10 s was made at each end of the scan range. Two standard reflections were measured every 70 reflections and the maximum deviation of any individual standard from the mean was 7·0%.

Intensities for 3088 unique reflections were measured of which 2233 having $I > 2{\cdot}3\sigma(I)$ were classed observed. The values of I and $\sigma(I)$ were corrected for Lorentz and polarisation effects. No absorption corrections were applied.

Structure Solution and Refinement.—The space group was assumed to be $P\bar{1}$ and this permitted atomic positions for all the non-hydrogen atoms to be located by routine Patterson and difference-Fourier syntheses. The structure was refined by full-matrix least-squares techniques, the function minimised being $\Sigma w(|F_o| - |F_c|)^2$ and each reflection was given weight $[= 1/\sigma^2(F)]$ in terms of $\sigma(F) = \sigma(I)/(Lp)2F_o$. With anisotropic temperature factors for the manganese and arsenic atoms and individual isotropic temperature factors for the remaining non-hydrogen atoms, R was 10·2%. A difference-Fourier synthesis calculated at this stage showed peaks and troughs of electron density close to the fluorine and carbonyl group atoms, indicating anisotropic thermal motion by these atoms. Two cycles of refinement, in which all atoms except the non-carbonyl carbon atoms were allowed to vibrate anisotropically, reduced R to 8·0%.

In order to locate the hydrogen atoms a difference-Fourier synthesis was calculated using 1059 reflections having $\sin\theta/\lambda < 0{\cdot}4$. Careful examination of the region of electron density around the methyl carbon atoms indicated anisotropic thermal motion by the carbon atoms, but showed no hydrogen atom peaks significantly greater than background $[\sigma(\rho) = 0{\cdot}27$ eÅ$^{-3}]$. Several attempts were made to describe a reasonable model for the hydrogen atoms but none was successful.

Two final cycles of refinement, excluding the hydrogen atoms and with all atoms except C(13)—(16) anisotropic, reduced R to 7·8%. The maximum shift for any parameter in the last least-squares cycle was 0·07σ. The final difference map showed no unusual features and apart from

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[1] W. R. Cullen, F. W. B. Einstein, J. S. Field, and L. Mihichuk, *J. Organometallic Chem.*, 1974, **73**, C53.

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

[3] W. H. Zachariasen, *Acta Cryst.*, 1965, **18**, 705.

arsenic and manganese ' ripples ' had a maximum peak height of 0·8(3) e$Å^{-3}$. Atomic scattering factors were taken from ref. 4, and included corrections for anomalous dispersion to the manganese and arsenic atoms.[5] Programs used in the calculations are described in ref. 6.

TABLE 1

Fractional atomic co-ordinates ($\times 10^4$), with isotropic thermal parameters ($\times 10^3$). Standard deviations in this and subsequent Tables are given in parentheses as units in the least significant digit

Atom	x/a	y/b	z/c	U/Å^2
As(1)	3408(3)	3563(1)	873(3)	*
As(2)	2276(2)	1701(1)	914(3)	
As(3)	5027(2)	2329(1)	4159(3)	
Mn(1)	2324(3)	2971(2)	2478(4)	
Mn(2)	5608(4)	2511(2)	819(4)	
F(1)	3401(15)	1334(8)	−1792(15)	
F(2)	5687(14)	641(8)	−326(16)	
F(3)	7868(16)	648(9)	2735(18)	
F(4)	6734(16)	317(8)	4046(18)	
F(5)	8271(15)	1314(10)	4948(18)	
C(1)	2638(26)	3946(17)	3632(30)	
O(1)	3747(22)	4605(12)	4331(23)	
C(2)	382(27)	3389(14)	992(30)	
O(2)	−912(20)	3652(12)	37(23)	
C(3)	1663(24)	2468(15)	3672(27)	
O(3)	1147(21)	2191(12)	4440(22)	
C(4)	6880(27)	3317(15)	2080(32)	
O(4)	7775(22)	3825(12)	2846(24)	
C(5)	4862(30)	3029(16)	−1158(33)	
O(5)	4416(23)	3324(11)	−2438(22)	
C(6)	7340(26)	1970(13)	744(30)	
O(6)	8401(20)	1678(11)	555(24)	
C(7)	4097(26)	4752(12)	1661(29)	
C(8)	1697(27)	3946(17)	−1382(28)	
C(9)	671(24)	1611(16)	−1374(27)	
C(10)	2278(23)	544(13)	1747(28)	
C(11)	6682(25)	3111(15)	5501(26)	
C(12)	5390(25)	1488(14)	5868(26)	
C(13)	4729(24)	1315(13)	−212(26)	36(5)
C(14)	4493(20)	1520(11)	1124(21)	22(4)
C(15)	5747(21)	1678(11)	2675(22)	36(5)
C(16)	7106(28)	1026(15)	3532(29)	50(6)

* Anisotropic parameters in Table 2.

TABLE 2

Anisotropic vibrational amplitudes * ($\times 10^3$ Å^2, $\times 10^4$ Å^2 for As and Mn)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
As(1)	314(13)	338(13)	452(15)	−76(10)	237(12)	32(11)
As(2)	168(11)	362(13)	400(14)	−100(9)	176(11)	−33(10)
As(3)	221(12)	387(13)	313(13)	−85(10)	142(11)	−7(10)
Mn(1)	247(18)	378(19)	421(21)	−63(14)	227(17)	−28(16)
Mn(2)	306(19)	389(19)	506(22)	−161(15)	309(18)	−71(16)
F(1)	68(9)	78(10)	49(8)	−26(8)	42(8)	−15(7)
F(2)	60(9)	41(7)	105(11)	−17(6)	65(9)	−24(7)
F(3)	63(10)	84(11)	103(12)	29(8)	59(10)	15(9)
F(4)	66(10)	51(9)	100(12)	12(7)	48(9)	22(8)
F(5)	35(8)	101(12)	78(11)	−4(8)	−2(8)	−11(9)
C(1)	40(15)	67(18)	59(18)	−2(13)	37(14)	0(14)
O(1)	86(14)	63(13)	89(15)	−13(11)	47(12)	−21(11)
C(2)	37(15)	43(15)	62(17)	5(12)	21(14)	25(13)
O(2)	42(11)	81(14)	94(15)	8(10)	17(11)	9(12)
C(3)	38(14)	74(17)	43(15)	−26(12)	29(13)	−8(13)
O(3)	79(13)	109(15)	83(14)	−37(11)	63(12)	−1(11)
C(4)	37(15)	50(16)	86(20)	−23(12)	33(15)	−27(14)
O(4)	77(14)	93(15)	112(17)	−48(12)	60(13)	−38(13)
C(5)	74(19)	60(17)	67(19)	−28(14)	57(17)	−9(15)
O(5)	111(6)	61(12)	67(13)	−11(11)	56(13)	5(10)
C(6)	46(15)	29(12)	96(20)	−13(11)	55(15)	−21(13)
O(6)	66(12)	88(13)	145(18)	−32(10)	86(14)	−37(13)
C(7)	57(16)	23(12)	90(19)	−21(11)	46(15)	−11(12)
C(8)	47(16)	98(21)	48(16)	−10(14)	15(14)	33(15)
C(9)	29(13)	102(20)	42(15)	−10(13)	21(12)	−5(14)
C(10)	37(13)	37(13)	78(17)	−11(10)	43(13)	7(12)
C(11)	35(14)	76(17)	36(14)	−46(13)	1(12)	−18(13)
C(12)	49(15)	59(15)	39(14)	6(12)	22(12)	27(12)

* In the form: $\exp[-2\pi^2(h^2a^{*2}U_{11} + \cdots\cdot + 2hka^*b^*U_{12} + \cdots)]$.

TABLE 3

Bond lengths (Å)

Mn(1)–As(1)	2·455(4)	Mn(1)–As(2)	2·354(4)
Mn(2)–As(1)	2·507(4)	Mn(1)–As(3)	2·387(4)
Mn(1)–C(1)	1·70(3)	Mn(2)–C(4)	1·79(3)
Mn(1)–C(2)	1·75(3)	Mn(2)–C(5)	1·80(3)
Mn(1)–C(3)	1·77(3)	Mn(2)–C(6)	1·79(2)
Mn(2)–C(13)	2·09(2)	Mn(2)–C(15)	2·13(2)
Mn(2)–C(14)	2·07(2)		
C(1)–O(1)	1·16(3)	C(4)–O(4)	1·16(3)
C(2)–O(2)	1·15(3)	C(5)–O(5)	1·15(3)
C(3)–O(3)	1·17(3)	C(6)–O(6)	1·15(2)
As(1)–C(7)	1·99(2)	As(2)–C(14)	2·02(2)
As(1)–C(8)	1·99(2)	As(3)–C(11)	1·97(2)
As(2)–C(9)	1·93(2)	As(3)–C(12)	1·97(2)
As(2)–C(10)	1·97(2)	As(3)–C(15)	1·99(2)
C(13)–C(14)	1·38(3)	C(13)–F(2)	1·33(2)
C(14)–C(15)	1·39(3)	C(16)–F(3)	1·34(3)
C(15)–C(16)	1·45(3)	C(16)–F(4)	1·36(3)
C(13)–F(1)	1·40(2)	C(16)–F(5)	1·34(3)

TABLE 4

Bond angles (°)

As(1)–Mn(1)–As(2)	82·8(1)	As(2)–Mn(1)–C(3)	94·2(7)
As(1)–Mn(1)–As(3)	84·3(1)	As(3)–Mn(1)–C(1)	93·0(7)
As(1)–Mn(1)–C(1)	89·6(7)	As(3)–Mn(1)–C(2)	171·4(8)
As(1)–Mn(1)–C(2)	89·6(7)	As(3)–Mn(1)–C(3)	91·8(7)
As(1)–Mn(1)–C(3)	175·3(8)	C(1)–Mn(1)–C(2)	93·0(11)
As(2)–Mn(1)–As(3)	81·3(1)	C(1)–Mn(1)–C(3)	93·1(10)
As(2)–Mn(1)–C(1)	170·8(7)	C(2)–Mn(1)–C(3)	94·2(10)
As(2)–Mn(1)–C(2)	92·0(8)		
As(1)–Mn(2)–C(4)	84·1(7)	C(4)–Mn(2)–C(14)	137·3(10)
As(1)–Mn(2)–C(5)	82·2(7)	C(4)–Mn(2)–C(15)	100·2(10)
As(1)–Mn(2)–C(6)	167·7(7)	C(5)–Mn(2)–C(6)	91·5(11)
As(1)–Mn(2)–C(13)	109·8(5)	C(5)–Mn(2)–C(13)	93·6(9)
As(1)–Mn(2)–C(14)	86·5(5)	C(5)–Mn(2)–C(14)	121·6(9)
As(1)–Mn(2)–C(15)	92·5(5)	C(5)–Mn(2)–C(15)	160·1(9)
C(4)–Mn(2)–C(5)	98·2(11)	C(6)–Mn(2)–C(13)	81·0(8)
C(4)–Mn(2)–C(6)	86·3(10)	C(6)–Mn(2)–C(14)	105·8(8)
C(4)–Mn(2)–C(13)	162·9(10)	C(6)–Mn(2)–C(15)	96·9(9)
Mn(1)–C(1)–O(1)	176(2)	Mn(2)–C(4)–O(4)	175(2)
Mn(1)–C(2)–O(2)	178(2)	Mn(2)–C(5)–O(5)	177(2)
Mn(1)–C(3)–O(3)	175(2)	Mn(2)–C(6)–O(6)	173(2)
Mn(1)–As(1)–Mn(2)	111·8(1)	C(9)–As(2)–C(10)	100·3(10)
Mn(1)–As(1)–C(7)	111·2(6)	C(9)–As(2)–C(14)	109·5(8)
Mn(1)–As(1)–C(8)	112·3(6)	C(10)–As(2)–C(14)	98·7(7)
Mn(2)–As(1)–C(7)	112·2(6)	Mn(1)–As(3)–C(11)	118·7(7)
Mn(2)–As(1)–C(8)	112·1(8)	Mn(1)–As(3)–C(12)	116·6(6)
C(7)–As(1)–C(8)	96·3(10)	Mn(1)–As(3)–C(15)	107·5(5)
Mn(1)–As(2)–C(9)	122·3(7)	C(11)–As(3)–C(12)	99·9(9)
Mn(1)–As(2)–C(10)	119·5(6)	C(11)–As(3)–C(15)	106·1(8)
Mn(1)–As(2)–C(14)	104·0(5)	C(12)–As(3)–C(15)	107·2(8)
F(1)–C(13)–F(2)	101(2)	C(13)–C(14)–C(15)	122(2)
F(1)–C(13)–C(14)	119(2)	As(3)–C(15)–C(14)	114(2)
F(2)–C(13)–C(14)	127(2)	As(3)–C(15)–C(16)	113(2)
As(2)–C(14)–C(13)	122(2)	C(14)–C(15)–C(16)	121(2)
As(2)–C(14)–C(15)	115(2)		
C(15)–C(16)–F(3)	119(2)	F(3)–C(16)–F(4)	102(2)
C(15)–C(16)–F(4)	114(2)	F(3)–C(16)–F(5)	105(2)
C(15)–C(16)–F(5)	113(2)	F(4)–C(16)–F(5)	102(2)

RESULTS AND DISCUSSION

Final co-ordinates and thermal factors are listed in Tables 1 and 2. Tables 3 and 4 give the bond lengths and angles; errors were estimated by the least-squares

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[4] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[5] ' International Tables for *X*-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1965, 3.3.

[6] F. W. B. Einstein and R. D. G. Jones, *Inorg. Chem.*, 1972, **11**, 395.

procedure and include both correlation effects and cell dimension errors. Important non-bonded contacts are shown in Table 5. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21114 (20 pp., 1 microfiche).*

TABLE 5

Shortest non-bonded distances (Å) of various types

Type	Atoms	Distance
(*a*) Intramolecular		
Mn ··· Mn	Mn(1) ··· Mn(2)	4·108
Mn ··· As	Mn(2) ··· As(3)	3·443
Mn ··· F	Mn(2) ··· F(1)	3·01
	Mn(2) ··· F(2)	3·00
	Mn(2) ··· F(3)	3·35
Mn ··· C	Mn(2) ··· C(16)	3·14
As ··· As	As(2) ··· As(3)	3·087
As ··· F	As(2) ··· F(1)	3·19
	As(3) ··· F(5)	3·05
As ··· C	As(1) ··· C(5)	2·88
	As(1) ··· C(14)	3·15
	As(2) ··· C(2)	2·98
	As(3) ··· C(14)	2·85
F ··· F	F(1) ··· F(2)	2·11
	F(2) ··· F(3)	2·58
	F(3) ··· F(4)	2·10
F ··· O	F(3) ··· O(6)	2·90
F ··· C	F(1) ··· C(9)	2·81
	F(1) ··· C(14)	2·40
	F(2) ··· C(6)	2·59
O ··· C	O(5) ··· C(8)	3·23
C ··· C	C(1) ··· C(2)	2·55
	C(4) ··· C(6)	2·45
	C(4) ··· C(15)	3·02
	C(5) ··· C(13)	2·85
	C(6) ··· C(13)	2·53
	C(6) ··· C(15)	2·95
(*b*) Intermolecular ($\leqslant$3·5 Å)		
F ··· F	F(1) ··· F(4$^{\rm I}$)	3·17
	F(2) ··· F(2$^{\rm I}$)	2·74
F ··· O	F(1) ··· O(3$^{\rm II}$)	3·32
F ··· C	F(2) ··· C(13$^{\rm I}$)	3·16
O ··· O	O(1) ··· O(5$^{\rm III}$)	3·25
O ··· C	O(5) ··· C(1$^{\rm II}$)	3·32
	O(6) ··· C(2$^{\rm IV}$)	3·32

Roman superscripts refer to the following transformation of the co-ordinates of the second atom:

I $-x, -y, -z$

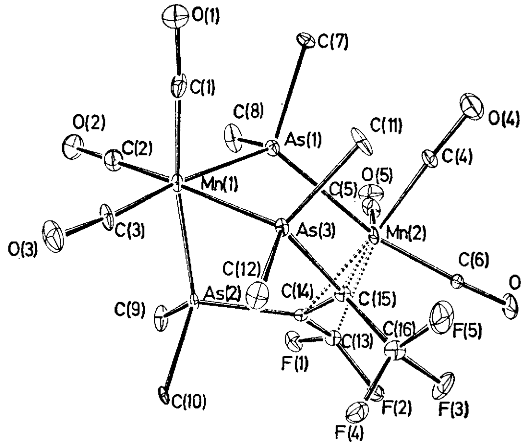
II $x, y, z-1$

III $x, y, 1+z$

IV $1+x, y, z$

The crystal structure consists of discrete, monomeric $Mn_2(CO)_6(AsMe_2)_3C_4F_5$ molecules; the Figure gives a perspective view of the molecule and shows the labelling of the atoms. The geometry around both manganese atoms is irregular octahedral. Mn(1) has three *cis*-arsenic atoms and three carbonyl carbon atoms within its inner co-ordination sphere. The inner co-ordination sphere around Mn(2) includes seven atoms: the bridging arsenic, three carbonyl, and three allyl carbon atoms, C(13)—(15). The allyl carbon atoms occupy two adjacent octahedral sites and form part of an asymmetrically substituted π-allyl system (3), which is linked to Mn(1) *via* two manganese–arsenic bonds. Mn(1), As(2), C(14), C(15), and As(3) thus form a five-membered ring. Distortion from ideal octahedral geometry around Mn(1) is reflected in the large C–Mn(1)–C angles (mean 93·4°), and can be mainly attributed to non-bonding repulsions between ligand orbitals which receive electron density from the metal *via* π back donation.[7] The C_3 allyl ligand appears to control departures from ideal octahedral geometry around Mn(2). For example, the small C(4)–Mn(2)–C(6) angle [86(1)°] is probably forced by the short C(6) ··· C(13) non-bonded contact (2·53 Å) while no such steric restriction is imposed on the position of C(5) [C(5) ··· C(13) 2·85 Å, C(5)–Mn(2)–C(4) 98(1)°].

A variety of data exists for the configuration of π-allyl groups co-ordinated to a transition metal: [{(π-C_3H_5)PdCl}$_2$] (ref. 8), [(π-C_3H_4Me)Ni(diphos)Br] (ref. 9), [(π-C_3H_4Me)(CO)$_2$($C_{12}H_8N_2$)Mo(NCS)] (ref. 10), and [(π-C_3H_5)$_2$Ru(PPh$_3$)$_2$] (ref. 11) typically include π-allyl ligands which are symmetrically co-ordinated (metal–terminal-carbon and carbon–carbon distances equal). The complexes [(π-C_3H_4Me)(PPh$_3$)PdCl] (ref. 12) and [(π-C_3H_5)$_2$RhCl] (ref. 13) provide examples of asymmetrically co-ordinated allyl ligands and have been interpreted as σπ-allyl systems.[14] Other workers[15] have suggested that substitution on one terminal carbon atom should provide the most favourable conditions for an asymmetrical π-allyl structure. In the present molecule the metal–terminal-carbon distances [Mn(2)–C(13) 2·09(2), Mn(2)–C(15) 2·13(2) Å] differ only at the 1σ level. Moreover, the C–C distances [C(13)–C(14) 1·38(3), C(14)–C(15) 1·39(3) Å] are clearly equal within the quoted σ, and fall in the range of C–C distances (1·33—1·49 Å)[10,16] previously reported. The metal–



View of one molecule down *c** showing the labelling of the atoms. Atoms are shown with 12% probability thermal ellipsoids

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

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central-carbon distance [2·07(2) Å] is shorter but not significantly so and the angle subtended at the central carbon atom [C(13)–C(14)–C(15) 122(2)°] has the expected value.

Table 6 gives the equation of the plane through the C_3-allyl carbons, C(13)—(15), and selected distances of atoms from this plane. The allyl group comprising atoms C(13)—(16), As(1), As(2), F(1), and F(2) is distinctly non-planar; atoms F(2) and C(16) show the maximum deviations from the three-carbon plane (I) (−0·910 and −1·073 Å), in a direction away from the manganese atom. F(1) and the arsenic atoms are displaced from the C_3-allyl plane (I) towards the metal. In the nickel [9] and palladium [12] methylallyl complexes the out-of-plane displacement (0·26 and 0·5 Å) of the 2-substituted methyl carbon atom is towards the metal. We suggest that steric interactions between bulky substituents (in particular the CF_3 group) will contribute to deviations from planarity in (3). The short F(2) · · · F(3) non-bonded contact (2·58 Å) indicates this. Dihedral angles between the C_3-allyl plane and the equatorial and vertical mean planes which include Mn(2) are given in Table 6.

TABLE 6

(*a*) Mean planes. Equations are in the form $lx + my + nz + p = 0$ where x, y, z are orthogonal Å co-ordinates, with X along the a axis, Y in the ab plane, and Z along the c^* axis

	l	m	n	p	χ^2
Plane (I): C(13)—(15)	0·0715	0·9695	−0·2344	−2·2322	0·0
Plane (II): As(1), Mn(2), C(5), C(6)	−0·5347	−0·7541	−0·3813	6·1938	2142·4 †
Plane (III): As(1), Mn(2), C(4), C(6)	0·3322	0·5113	−0·7926	−3·3427	1234·2 †
Plane (IV): Mn(2), C(4), C(5)	0·8657	−0·4934	−0·0848	−2·8136	0·0

(*b*) Dihedral angles (°): (I)–(II) 133, (I)–(III) 45, (I)–(IV) 114

(*c*) Selected distances (Å) of atoms from C_3-allyl plane (I):

C(16) −1·073, F(1) 0·278, F(2) −0·910, F(3) −1·410, F(4) −2·263, F(5) −0·872, As(2) 0·162, As(3) 0·582, Mn(2) 1·613

† The atoms used to define these planes show statistically significant deviations from planarity.

Previously reported Mn–As distances fall in the range 2·392—2·508 Å.[17] The Mn–As distances in this molecule show significant differences: Mn(2)–As(1) 2·507(4) > Mn(1)–As(1) 2·455(4) > Mn(1)–As(3) 2·387(4) > Mn(1)–As(2) 2·354(4) Å. Similar trends are also shown by the angles around as As(1)—(3), *e.g.* Mn(1)–As(1)–Mn(2) 111·8(1) > Mn(1)–As(3)–C(15) 107·5(5) > Mn(1)–As(2)–C(14) 104·0(5); C(7)–As(1)–C(8) 96·3(10) < C(11)–As(3)–C(12) 99·9(9) < C(9)–As(2)–C(10) 100·3(10)°. Furthermore the As–C(Me) bond lengths show a definite (though not significant) trend; mean values are As(1)–C(Me) 1·99 > As(3)–C(Me) 1·97 > As(2)–C(Me) 1·95 Å. Assuming that the electron-withdrawing effects of atoms C(14), C(15), Mn(1), and Mn(2) follow the order C(14) > C(15) > Mn(1), Mn(2) the foregoing trends are consistent with Bent's rule,[18] which states that atomic p character concentrates in orbitals directed toward electronegative substituents. Certainly application of this rule [18] would appear valid as there can be little or no π back bonding between the metal and arsenic atoms. The significant difference in the Mn–As(bridge) bond lengths can in part be accounted for by non-bonding repulsions between As(1) and ligands within the inner co-ordination sphere around Mn(2). The 'extra' crowding brought about by the presence of the C_3-allyl ligand is reflected in the shortest As(1) · · · C non-bonded contacts [As(1) · · · C(5) 2·88, As(1) · · · C(14) 3·15 Å, see Table 5].

The Mn(1)–C(O) (1·75—1·77 Å) and the Mn(2)–C(O) distances (1·79—1·80 Å) do not differ significantly but the systematically longer Mn(2)–C(O) bond lengths are noteworthy. Possible explanations would include non-bonded repulsions with other ligands bonded to Mn(2); (the allyl ligand, unlike say ethylene, has little or no π back-bonding properties and does not compete with the carbonyl groups for metal d_π electron density).[19] Steric hindrance and a short F(2) · · · F(2′) intermolecular contact (2·74 Å) may play a role in determining the rather small F(1)–C(13)–F(2) angle [101(2)°]. This work provides the first X-ray diffraction data on a difluoromethylene group which includes a π-allyl carbon, (approximately sp^2 hybridised). The C–F bond lengths fall in the range 1·33—1·40 Å and are not significantly different from the values [20] reported for C(sp^2)–F and C(sp^3)–F distances. Remaining distances and angles within the molecule are as expected. Apart from the short F(2) · · · F(2′) intermolecular contact the packing of the molecules shows no unusual features (see Table 5 for intermolecular contacts <3·5 Å).

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