X-Ray Crystallographic Determination of the Molecular Structures of π-Cyclopentadienyl-[1-hydroxy-2,3,4,5-tetrakis(trifluoromethyl)phosphole-1-oxide]cobalt and Tricarbonyl-η^4-[1-pentafluorophenyl-2,3,4,5-tetrakis(trifluoromethyl)thiophen]manganese †

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The organometallic derivatives $[Co(\pi\text{-}C_5H_5)(C_4F_6)_2PO(OH)]$ (1) and $[Mn(CO)_3(C_4F_6)_2SC_6F_5]$ (2) which resulted from the interaction of hexafluorobut-2-yne with metal complexes have been studied by *X*-ray diffraction and shown to contain non-planar $(CF_3)_4C_4X$ heterocycles with non-bonding metal–heteroatom separations. The absence of an Mn–S bond in (2) leads to the formulation of a zwitterion structure formally involving a sulphonium derivative with a Mn(−1) species. Crystals of (1) are orthorhombic with $a = 9{\cdot}353(7)$, $b = 9{\cdot}893(7)$, $c = 17{\cdot}923(10)$ Å, space group $P2_12_12_1$, and $Z = 4$. Crystals of (2) are triclinic with $a = 7{\cdot}889(6)$, $b = 11{\cdot}737(8)$, $c = 12{\cdot}195(9)$ Å, $\alpha = 91{\cdot}45(10)$, $\beta = 69{\cdot}71(10)$, $\gamma = 81{\cdot}55(9)°$, space group $P\bar{1}$ and $Z = 2$. Intensity data were collected on a four-circle diffractometer, and the structures solved by Fourier methods; least-squares refinements converged at R 6·3% over 1922 reflections for (1) and 4·5% over 3229 reflections for (2).

X-RAY diffraction characterization of tricarbonylthiophenchromium,[1] tricarbonyl(*N*-methylpyrrole)chromium,[2] and tricarbonyl(tetraphenylarsole)manganese[3] has demonstrated that these compounds contain planar five-membered rings and have metal–heteroatom bonds.

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† Reprints not available.

[1] M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, 1965, **4**, 1306.

[2] G. Huttner and O. S. Mills, *Chem. Ber.*, 1972, **105**, 301.

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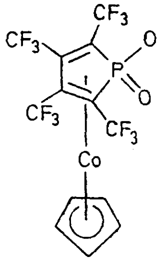
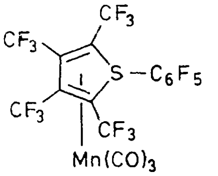
Recent chemical and crystallographic investigations have established that heterocyclic complexes can be obtained by reaction between electrophilic acetylenes and transition-metal derivatives.[4,5] Thus, reaction between hexafluorobut-2-yne and $[Co(\pi\text{-}C_5H_5)(PF_3)_2]$ and $[\{Mn(CO)_4SC_6F_5\}_2]$ leads to the organometallic compounds $[Co(\pi\text{-}C_5H_5)(C_4F_6)_2PO(OH)]$ (1) and $[Mn(CO)_3(C_4F_6)_2SC_6F_5]$ (2) which contain $(CF_3)_4C_4X$ heterocycles.[4] Our structural investigations show that in the complexes these heterocyclic ligands are non-planar, with non-bonding metal–heteroatom separations.



(1)



(2)

EXPERIMENTAL

Crystallographic Data.—(1), $C_{13}H_6CoF_{12}O_2P$, $M = 512{\cdot}1$, Orthorhombic, $a = 9{\cdot}353(7)$, $b = 9{\cdot}893(7)$, $c = 17{\cdot}923(10)$ Å, $U = 1658{\cdot}4$ Å^3, $Z = 4$, $D_c = 2{\cdot}05$, $F(000) = 1000$. Mo-K_α radiation, $\lambda = 0{\cdot}71069$ Å, $\mu(\text{Mo-}K_\alpha) = 13{\cdot}2$ cm^{-1}. Space group $P2_12_12_1$ (D_2^4, No. 19) by systematic absences.

Crystals are orange needles. The crystal used for intensity measurements had dimensions *ca.* $0{\cdot}4 \times 0{\cdot}2 \times 0{\cdot}2$ mm. Four-circle diffractometer data (Zr filter): 2519 independent reflections in the range $\theta < 29°$ measured; analysis based on the 1922 intensities having $I > 3\sigma(I)$. The final least-squares weighting scheme was $w^{-1} = 1 + 0{\cdot}0016(F_o - 10)^2$. The final discrepancy index was R 6·3%.

(2), $C_{17}F_{17}MnO_3S$, $M = 662{\cdot}1$, Triclinic, $a = 7{\cdot}889(6)$, $b = 11{\cdot}737(8)$, $c = 12{\cdot}195(9)$ Å, $\alpha = 91{\cdot}45(10)$, $\beta = 69{\cdot}71(10)$, $\gamma = 81{\cdot}55(9)°$, $U = 1044{\cdot}1$ Å^3, $Z = 2$, $D_c = 2{\cdot}11$, $F(000) = 640$. $\mu(\text{Mo-}K_\alpha) = 9{\cdot}5$ cm^{-1}. Space group $P\bar{1}$ (C_i^1, No. 2).

Crystals are orange-yellow with irregular shapes. The crystal used for intensity measurements had dimensions *ca.* $0{\cdot}3 \times 0{\cdot}3 \times 0{\cdot}3$ mm. Four-circle diffractometer data (Zr filter): 4517 independent reflections in the range $\theta < 27°$ measured; analysis based on the 3229 intensities having $I > 3\sigma(I)$. The final least-squares weighting scheme was $w^{-1} = 1 + 0{\cdot}0025(F_o - 9)^2$. The final discrepancy index was 4·5%.

Structure Analysis.—Space-group information and approximate cell parameters were obtained from Weissenberg and precession photographs. Intensity data were obtained by use of a Hilger and Watts Y 290 computer-controlled diffractometer. The crystal axes were misaligned with respect to the instrument axes in order to minimize the effects of multiple reflections. Least-squares best cell parameters and crystal orientation matrices were calculated from the positions (as determined by a peak-finder programme) of at least 12 reflections and their Friedel pairs measured at both positive and negative ω—2θ offsets. The intensities were recorded by the ω—2θ step-scan procedure, with background counts at each end of the scan range. The periodic monitoring of standard reflections established that crystal decomposition was not significant and ensured that all the intensities were on the same relative scale. Intensities were corrected for Lorentz and polarization effects but not for absorption.

Metal atom co-ordinates were derived initially from three-dimensional Patterson syntheses and the remaining atoms (apart from hydrogen) were located in successive F_o Fourier syntheses. For (1), a detailed interpretation of the electron-density maps was achieved only after allowance had been made for the anisotropic thermal motion of the cobalt and phosphorus atoms.

When all non-hydrogen atoms had been located the atomic co-ordinates and thermal parameters were adjusted by full-matrix least-squares calculations, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$. Initially isotropic thermal parameters were retained for the carbon, oxygen, and fluorine atoms and convergence was reached at *ca.* R 12%. Subsequently these atoms were assigned anisotropic parameters, and because of computer storage limitations only half the atoms were adjusted in any one cycle, the others being held fixed. The cyclopentadienyl hydrogen atoms were introduced in the model for (1) at calculated positions, assuming r(C–H) 1·00 Å, with fixed isotropic temperature factors, B 5 Å^2; the parameters of these hydrogen atoms were not refined in the least-squares procedure, although the co-ordinates were periodically recalculated. However, an attempt was made to refine the position of the hydroxy-hydrogen atom H(2) but this was unsuccessful. Thereafter this atom was placed in a fixed position midway between O(2) and O(1′) and with a fixed temperature factor, B 5 Å^2.

During the last few rounds of calculations analytical weighting schemes were introduced whereby reflections were assigned weights such that $\langle w\Delta^2\rangle$ was approximately constant for various groups of $|F_o|$ values over the whole range of $|F_o|$. In the case of complex (2) allowance was also made ($\Delta f'$, $\Delta f''$) for the real and imaginary components of the anomalous dispersion corrections[6] for manganese and sulphur. For the final stages of the refinements certain of the most intense reflections which were believed to be affected by extinction or dead-time losses and which were consistently calculated with $|F_c| > |F_o|$ were removed from the least-squares adjustment procedure, these being for (1): 012, 024, 102, and 110, and for (2): 002, 040, 1$\bar{3}$0, 1$\bar{3}$1, 203, and 212.

Difference-Fourier syntheses computed just before completion of the least-squares refinements were generally featureless except for some residual electron-density peaks *ca.* 0·6 eÅ^{-3} and some troughs *ca.* −0·3 eÅ^{-3} about the fluorine-atom positions in (1). The initial F_o Fourier syntheses for this complex had indicated either disorder, or very large thermal motion, of many of the fluorine atoms. However, because of the large number of small subsidiary peaks about the atoms affected, allowance was made only for anisotropic vibration of atoms placed at the positions of highest electron density. The situation is reflected in the high final R (6·3%) and because of this we did not deem it worth while to consider anomalous-dispersion corrections and consequent enantiomer specification; however, neglect of this effect in a non-polar space group should have little effect on the atomic co-ordinates.

Throughout the structure-factor calculations atomic

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[4] M. J. Barrow, J. L. Davidson, W. Harrison, D. W. A. Sharp, G. A. Sim, and F. B. Wilson, *J.C.S. Chem. Comm.*, 1973, 583.

[5] C. W. Bird, *J. Organometallic Chem.*, 1973, **47**, 281.

[6] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

scattering factors of ref. 7 were used for non-hydrogen atoms and of ref. 8 for hydrogen atoms. Observed and calculated

TABLE 1

Atomic parameters, with estimated standard deviations in parentheses, for (I)

Atom	x	y	z
Co	0·19289(10)	0·02600(12)	0·12311(5)
P	0·22459(17)	0·21994(22)	0·01603(11)
O(1)	0·0757(5)	0·2527(8)	−0·0078(4)
O(2)	0·3312(5)	0·3055(7)	−0·0299(4)
C(1)	0·2717(8)	0·0469(8)	0·0176(4)
C(2)	0·3796(8)	0·0245(9)	0·0731(4)
C(3)	0·3737(7)	0·1258(8)	0·1290(4)
C(4)	0·2615(7)	0·2204(8)	0·1126(4)
C(5)	0·0865(15)	0·0082(16)	0·2211(5)
C(6)	−0·0111(10)	0·0294(16)	0·1651(6)
C(7)	0·0014(12)	−0·0703(15)	0·1141(6)
C(8)	0·1083(17)	−0·1591(14)	0·1394(10)
C(9)	0·1610(13)	−0·1105(20)	0·2067(8)
C(11)	0·2391(13)	−0·0435(12)	−0·0476(6)
C(12)	0·4883(12)	−0·0867(11)	0·0709(6)
C(13)	0·4769(13)	0·1370(14)	0·1921(6)
C(14)	0·2213(13)	0·3362(11)	0·1628(7)
F(11)	0·3428(12)	−0·0466(11)	−0·0959(4)
F(12)	0·1242(14)	−0·0024(17)	−0·0812(7)
F(13)	0·2110(15)	−0·1682(9)	−0·0332(5)
F(21)	0·4945(14)	−0·1601(14)	0·1267(9)
F(22)	0·6068(11)	−0·0591(10)	0·0549(13)
F(23)	0·4531(25)	−0·1748(23)	0·0269(13)
F(31)	0·5079(18)	0·2616(16)	0·2053(8)
F(32)	0·4538(14)	0·0783(21)	0·2465(6)
F(33)	0·6098(10)	0·1182(22)	0·1721(7)
F(41)	0·2043(16)	0·3069(12)	0·2316(5)
F(42)	0·0911(10)	0·3822(13)	0·1412(8)
F(43)	0·3033(13)	0·4401(8)	0·1566(6)
H(2)	0·4535	0·2764	−0·0110
H(5)	0·1015	0·0685	0·2652
H(6)	−0·0803	0·1063	0·1624
H(7)	−0·0551	−0·0794	0·0670
H(8)	0·1409	−0·2430	0·1133
H(9)	0·2372	−0·1524	0·2383

Anisotropic temperature coefficients in the form: $t = \exp[-2\pi^2 10^{-3}(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$:

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	30·8(4)	53·3(5)	34·7(4)	−4·6(5)	3·8(4)	8·3(5)
P	16·4(6)	53·5(11)	45·3(10)	−1·3(7)	−1·6(7)	14·6(9)
O(1)	19(2)	105(5)	78(4)	4(3)	−7(2)	37(4)
O(2)	21(2)	74(4)	80(4)	−1(2)	2(3)	33(3)
C(1)	36(3)	51(4)	36(3)	−13(3)	2(3)	−3(3)
C(2)	38(3)	44(4)	48(4)	−1(4)	4(3)	11(4)
C(3)	33(3)	50(4)	41(3)	−1(3)	−7(3)	−1(4)
C(4)	32(3)	50(4)	39(3)	2(3)	5(3)	−4(3)
C(5)	90(9)	122(11)	44(5)	−28(9)	15(5)	25(6)
C(6)	40(4)	118(10)	71(6)	−13(6)	18(5)	21(8)
C(7)	60(6)	111(10)	61(6)	−43(7)	2(5)	17(7)
C(8)	98(10)	84(8)	117(12)	−29(8)	48(10)	35(9)
C(9)	57(7)	165(15)	94(8)	−0(8)	8(6)	89(10)
C(11)	86(8)	90(8)	53(5)	−29(7)	0(5)	−16(5)
C(12)	60(6)	63(6)	78(7)	21(5)	10(5)	−7(6)
C(13)	67(6)	103(9)	65(6)	−7(6)	−31(5)	−16(6)
C(14)	69(7)	67(6)	94(8)	18(6)	13(6)	−22(6)
F(11)	179(9)	162(9)	74(4)	−81(8)	64(5)	68(5)
F(12)	168(10)	234(15)	164(9)	32(10)	−110(9)	−115(10)
F(13)	233(12)	87(5)	113(6)	−77(8)	30(8)	−45(5)
F(21)	191(12)	171(10)	238(14)	132(10)	103(11)	148(11)
F(22)	78(6)	99(7)	528(20)	55(5)	113(12)	118(13)
F(23)	322(25)	308(23)	350(26)	255(22)	−204(22)	−247(23)
F(31)	195(15)	207(15)	176(12)	−48(12)	−112(12)	−41(12)
F(32)	190(12)	513(29)	91(6)	−227(16)	−100(7)	160(11)
F(33)	64(5)	352(22)	136(8)	−29(9)	−39(6)	57(12)
F(41)	252(14)	162(9)	75(5)	31(11)	41(7)	−63(6)
F(42)	102(6)	167(10)	223(12)	87(7)	−20(8)	−97(10)
F(43)	142(8)	76(5)	171(9)	−4(6)	17(8)	−63(5)

All hydrogen atoms have B 5·0 Å^2.

TABLE 2

Molecular geometry for (I)

(*a*) Intramolecular distances (Å), with estimated standard deviations in parentheses

Co · · · P	2·730(2)	C(2)–C(12)	1·50(1)
Co · · · O(1)	3·425(8)	C(3)–C(13)	1·49(1)
Co–C(1)	2·040(7)	C(4)–C(14)	1·51(1)
Co–C(2)	1·962(7)	C(5)–C(6)	1·37(2)
Co–C(3)	1·961(7)	C(5)–C(9)	1·39(2)
Co–C(4)	2·036(8)	C(6)–C(7)	1·35(2)
Co–C(5)	2·026(11)	C(7)–C(8)	1·41(2)
Co–C(6)	2·051(10)	C(8)–C(9)	1·39(2)
Co–C(7)	2·035(12)	C(11)–F(11)	1·30(2)
Co–C(8)	2·016(15)	C(11)–F(12)	1·30(2)
Co–C(9)	2·039(17)	C(11)–F(13)	1·29(2)
P–O(1)	1·492(6)	C(12)–F(21)	1·24(2)
P–O(2)	1·545(6)	C(12)–F(22)	1·18(2)
P–C(1)	1·768(8)	C(12)–F(23)	1·22(3)
P–C(4)	1·764(7)	C(13)–F(31)	1·29(2)
C(1)–C(2)	1·434(10)	C(13)–F(32)	1·16(2)
C(1) · · · C(4)	2·419(11)	C(13)–F(33)	1·31(2)
C(2)–C(3)	1·418(11)	C(14)–F(41)	1·28(2)
C(3)–C(4)	1·436(11)	C(14)–F(42)	1·36(2)
C(1)–C(11)	1·50(1)	C(14)–F(43)	1·29(2)

(*b*) Intramolecular angles (°), with estimated standard deviations in parentheses

C(1)–Co–C(4)	72·8(3)	C(1)–C(2)–C(3)	110·7(7)
C(2)–Co–C(3)	42·4(3)	C(2)–C(3)–C(4)	110·1(6)
O(1)–P–O(2)	109·3(4)	C(11)–C(1)–C(2)	126·2(8)
O(1)–P–C(1)	116·6(4)	C(1)–C(2)–C(12)	124·9(8)
O(1)–P–C(4)	117·5(4)	C(12)–C(2)–C(3)	124·4(7)
O(2)–P–C(1)	112·2(3)	C(2)–C(3)–C(13)	124·3(8)
O(2)–P–C(4)	113·2(3)	C(13)–C(3)–C(4)	125·5(8)
C(1)–P–C(4)	86·5(4)	C(3)–C(4)–C(14)	123·8(7)
P–C(1)–C(2)	109·6(6)	C(9)–C(5)–C(6)	109·1(12)
P–C(4)–C(3)	110·0(5)	C(5)–C(6)–C(7)	109·0(12)
P–C(1)–C(11)	120·9(6)	C(6)–C(7)–C(8)	107·5(11)
P–C(4)–C(14)	122·7(7)	C(7)–C(8)–C(9)	108·4(13)
		C(8)–C(9)–C(5)	106·0(12)

(*c*) Equations of least-squares planes, in which X, Y, Z refer to orthogonal co-ordinates in Å. Distances (Å) of relevant atoms from the plane are shown in square brackets

Plane (1): C(1)—(4)

$$0{\cdot}6426X + 0{\cdot}5576Y - 0{\cdot}5255Z - 1{\cdot}7265 = 0$$

[Co −1·583, P 0·686, C(1) −0·001, C(2) 0·002, C(3) −0·002, C(4) 0·001, C(11) −0·081, C(12) 0·063, C(13) 0·087, C(14) −0·075]

Plane (2): C(5)—(9)

$$0{\cdot}6871X + 0{\cdot}5294Y - 0{\cdot}4976Z + 1{\cdot}3816 = 0$$

[C(5) 0·008, C(6) −0·008, C(7) 0·004, C(8) 0·001, C(9) −0·006, Co 1·659]

Plane (3): P, C(1), C(4)

$$0{\cdot}9515X + 0{\cdot}2417Y - 0{\cdot}1904Z - 2{\cdot}4698 = 0$$

[O(1) −1·166, O(2) 1·310, C(2) 0·717, C(3) 0·716]

Angles (°) between planes:

(1)–(2) 3·4 (1)–(3) 32·2

TABLE 3

Intermolecular approaches (<3·0 Å) and intermolecular angles for (I)

O(1) · · · O(2$^{\mathrm{I}}$)	2·453(7)	F(13) · · · F(22$^{\mathrm{V}}$)	2·89
		F(33) · · · H(6$^{\mathrm{VI}}$)	2·91
F(11) · · · H(5$^{\mathrm{II}}$)	2·55	F(11) · · · F(42$^{\mathrm{III}}$)	2·95
O(2) · · · H(6$^{\mathrm{III}}$)	2·66	F(23) · · · H(7$^{\mathrm{VII}}$)	2·96
F(31) · · · H(9$^{\mathrm{IV}}$)	2·73	H(2) · · · H(6$^{\mathrm{III}}$)	2·97
F(13) · · · F(23$^{\mathrm{V}}$)	2·87	O(2) · · · H(7$^{\mathrm{III}}$)	2·99
P–O(2)–O(1$^{\mathrm{III}}$)	109·1(4)	P–O(1)–O(2$^{\mathrm{I}}$)	137·8(5)

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

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

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

[8] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

structure factors are listed in Supplementary Publication No. SUP 21154 (23 pp., 1 microfiche).[*]

RESULTS AND DISCUSSION

Final atomic co-ordinates and thermal parameters for complex (1) are in Table 1, details of the molecular geometry derived from these in Table 2, and intermolecular contacts in Table 3. Figures 1 and 2 show the molecule projected, respectively, on and perpendicular to the least-squares plane defined by atoms C(1)—(4); Figure 2 also illustrates the hydrogen-bonding pattern.

Table 4 lists the final positional and thermal parameters for complex (2) and details of the molecular geometry are in Table 5. The molecules are separated by normal van der Waals distances, the shorter of which are listed in Table 6. Figures 3 and 4 show the molecule projected, respectively, on and perpendicular to the least-squares plane defined by atoms C(1)—(4).

TABLE 4

Atomic parameters, with estimated standard deviations in parentheses, for (II)

Atom	*x*	*y*	*z*
Mn	0·01599(8)	0·24122(5)	0·14671(4)
S	−0·25494(12)	0·24662(7)	0·36739(7)
C(1)	−0·0641(5)	0·1408(3)	0·2905(3)
C(2)	0·1061(5)	0·1805(3)	0·2768(3)
C(3)	0·0778(5)	0·3403(3)	0·2850(3)
C(4)	−0·1125(5)	0·3469(3)	0·3028(3)
C(5)	−0·3107(5)	0·2491(3)	0·5251(3)
C(6)	−0·1938(5)	0·2667(3)	0·5851(3)
C(7)	−0·2496(6)	0·2695(3)	0·7041(3)
C(8)	−0·4254(6)	0·2532(3)	0·7675(3)
C(9)	−0·5456(5)	0·2350(3)	0·7119(3)
C(10)	−0·4858(5)	0·2329(3)	0·5910(3)
C(11)	−0·1027(6)	0·0188(3)	0·2987(4)
C(12)	0·2816(6)	0·1027(4)	0·2658(4)
C(13)	0·2161(6)	0·3780(4)	0·2931(4)
C(14)	−0·2074(6)	0·4696(3)	0·3194(4)
C(15)	0·1627(7)	0·1275(4)	0·0358(4)
O(15)	0·2559(6)	0·0565(3)	−0·0323(3)
C(16)	0·1131(6)	0·3482(4)	0·0501(3)
O(16)	0·1749(5)	0·4159(3)	−0·0104(3)
C(17)	−0·1687(7)	0·2446(5)	0·0872(4)
O(17)	−0·2801(6)	0·2486(5)	0·0493(4)
F(6)	−0·0217(3)	0·2810(2)	0·5256(2)
F(7)	−0·1356(4)	0·2861(2)	0·7596(2)
F(8)	−0·4783(4)	0·2535(3)	0·8833(2)
F(9)	−0·7144(3)	0·2201(2)	0·7731(2)
F(10)	−0·6035(3)	0·2151(2)	0·5384(2)
F(11)	−0·0190(4)	−0·0474(2)	0·1999(2)
F(12)	−0·2813(4)	0·0183(2)	0·3285(3)
F(13)	−0·0527(5)	−0·0335(2)	0·3812(3)
F(21)	0·2933(4)	0·0853(3)	0·3698(3)
F(22)	0·4279(4)	0·1430(3)	0·2015(3)
F(23)	0·2912(4)	−0·0009(2)	0·2139(3)
F(31)	0·3164(4)	0·3307(3)	0·3516(3)
F(32)	0·3265(5)	0·3997(4)	0·1923(3)
F(33)	0·1298(5)	0·4774(2)	0·3543(4)
F(41)	−0·2518(5)	0·5178(2)	0·4274(2)
F(42)	−0·3659(4)	0·4751(2)	0·3006(3)
F(43)	−0·1102(4)	0·5358(2)	0·2469(2)

Anisotropic temperature coefficients in the form: $t = \exp[-2\pi^2 10^{-4}(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn	407(3)	369(3)	300(3)	−38(2)	−127(2)	32(2)
S	352(4)	364(4)	307(4)	−50(3)	−136(3)	29(3)
C(1)	417(19)	302(16)	341(16)	−45(14)	−149(14)	24(13)
C(2)	378(18)	316(16)	349(17)	−8(13)	−126(14)	31(13)
C(3)	414(19)	328(17)	338(16)	−58(14)	−149(14)	59(13)
C(4)	418(18)	288(16)	323(16)	−37(13)	−142(14)	27(13)
C(5)	413(19)	325(17)	325(16)	−51(14)	−137(14)	40(13)
C(6)	393(18)	364(18)	383(18)	−52(14)	−124(15)	25(14)
C(7)	505(22)	402(19)	422(19)	−53(16)	−226(17)	41(15)
C(8)	534(22)	384(19)	324(17)	−22(16)	−128(16)	25(14)
C(9)	457(20)	376(19)	399(19)	−78(15)	−98(16)	48(15)
C(10)	416(19)	345(17)	433(19)	−47(14)	−170(16)	26(14)
C(11)	600(25)	351(19)	529(23)	−151(17)	−185(19)	37(17)
C(12)	428(21)	439(21)	563(23)	21(16)	−157(18)	88(18)
C(13)	517(23)	449(21)	558(23)	−165(18)	−227(19)	93(18)
C(14)	517(23)	347(19)	522(22)	12(16)	−190(18)	26(16)
C(15)	703(28)	483(23)	394(20)	−78(21)	−174(20)	43(18)
O(15)	1155(32)	638(22)	509(19)	170(21)	−85(10)	−137(17)
C(16)	513(23)	527(23)	378(19)	2(18)	−126(17)	42(17)
O(16)	782(23)	661(20)	635(20)	−135(18)	−123(17)	303(17)
C(17)	594(27)	794(32)	405(21)	−192(23)	−187(20)	89(21)
O(17)	729(25)	1860(50)	729(24)	−405(29)	−490(21)	317(28)
F(6)	457(12)	820(17)	453(12)	−192(12)	−187(10)	86(11)
F(7)	667(15)	738(16)	480(12)	−160(12)	−334(12)	51(11)
F(8)	728(17)	840(18)	325(11)	−120(14)	−134(11)	44(11)
F(9)	516(14)	761(16)	476(13)	−199(12)	−59(10)	94(11)
F(10)	471(13)	742(16)	492(12)	−198(11)	−216(10)	85(11)
F(11)	957(20)	391(12)	691(16)	−135(12)	−218(14)	−130(11)
F(12)	613(16)	503(14)	1227(25)	−238(12)	−262(16)	21(15)
F(13)	1089(23)	463(14)	722(17)	−146(14)	−349(16)	250(12)
F(21)	768(18)	891(20)	710(17)	169(15)	−425(15)	134(15)
F(22)	390(13)	716(17)	1093(23)	−3(12)	−101(14)	150(16)
F(23)	687(17)	425(13)	964(20)	128(12)	−302(15)	−63(13)
F(31)	763(19)	758(18)	1104(23)	−279(15)	−646(18)	219(16)
F(32)	1141(27)	1643(35)	710(19)	−1015(27)	−353(19)	413(21)
F(33)	861(21)	484(15)	1495(30)	−121(14)	−600(21)	−216(17)
F(41)	1113(23)	472(14)	613(16)	148(14)	−226(15)	−173(12)
F(42)	629(16)	506(14)	1311(26)	90(12)	−520(17)	38(15)
F(43)	867(19)	375(12)	773(17)	−78(12)	−266(15)	194(12)

The molecules of complex (1) are associated in the

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

TABLE 5

Molecular geometry for (II)

(*a*) Intramolecular distances (Å), with estimated standard deviations in parentheses

Mn · · · S	2·789(1)	C(6)–F(6)	1·338(4)
Mn–C(1)	2·102(3)	C(7)–F(7)	1·331(6)
Mn–C(2)	2·055(4)	C(8)–F(8)	1·327(4)
Mn–C(3)	2·060(4)	C(9)–F(9)	1·322(5)
Mn–C(4)	2·089(3)	C(10)–F(10)	1·335(6)
Mn–C(15)	1·822(4)	C(11)–F(11)	1·320(5)
Mn–C(16)	1·812(4)	C(11)–F(12)	1·329(6)
Mn–C(17)	1·836(6)	C(11)–F(13)	1·334(6)
S–C(1)	1·761(3)	C(12)–F(21)	1·322(6)
S–C(4)	1·758(4)	C(12)–F(22)	1·312(5)
S–C(5)	1·816(4)	C(12)–F(23)	1·336(5)
C(1)–C(2)	1·442(6)	C(13)–F(31)	1·314(6)
C(1)–C(11)	1·506(5)	C(13)–F(32)	1·293(5)
C(2)–C(3)	1·433(5)	C(13)–F(33)	1·324(5)
C(2)–C(12)	1·504(5)	C(14)–F(41)	1·327(5)
C(3)–C(4)	1·449(5)	C(14)–F(42)	1·340(6)
C(3)–C(13)	1·515(6)	C(14)–F(43)	1·310(5)
C(4)–C(14)	1·496(5)	C(15)–O(15)	1·134(5)
C(5)–C(6)	1·395(6)	C(16)–O(16)	1·144(6)
C(5)–C(10)	1·380(5)	C(17)–O(17)	1·122(8)
C(6)–C(7)	1·361(5)	Mn · · · O(15)	2·956(3)
C(7)–C(8)	1·379(6)	Mn · · · O(16)	2·956(4)
C(8)–C(9)	1·379(7)	Mn · · · O(17)	2·957(5)
C(9)–C(10)	1·381(5)	S · · · C(17)	2·243(5)
		C(1) · · · C(4)	2·386(5)

(*b*) Intramolecular angles (°), with estimated standard deviations in parentheses

C(15)–Mn–C(16)	89·3(2)	C(2)–C(3)–C(4)	108·8(3)
C(15)–Mn–C(17)	91·6(2)	C(2)–C(3)–C(13)	125·2(3)
C(16)–Mn–C(17)	90·9(2)	C(13)–C(3)–C(4)	125·3(3)
Mn–C(15)–O(15)	178·9(7)	C(3)–C(4)–S	111·9(2)
Mn–C(16)–O(16)	179·6(6)	C(3)–C(4)–C(14)	128·3(4)
Mn–C(17)–O(17)	178·4(5)	C(14)–C(4)–S	114·9(2)
C(1)–S–C(4)	85·4(2)	S–C(5)–C(6)	126·0(3)
C(1)–S–C(5)	112·2(2)	S–C(5)–C(10)	116·6(3)
C(4)–S–C(5)	112·7(2)	C(6)–C(5)–C(10)	117·4(3)
S–C(1)–C(2)	111·7(2)	C(5)–C(6)–C(7)	121·8(3)
S–C(1)–C(11)	114·2(3)	C(6)–C(7)–C(8)	119·4(4)
C(11)–C(1)–C(2)	128·1(3)	C(7)–C(8)–C(9)	120·9(3)
C(1)–C(2)–C(3)	109·7(3)	C(8)–C(9)–C(10)	118·6(4)
C(1)–C(2)–C(12)	124·4(3)	C(9)–C(10)–C(5)	122·0(4)
C(12)–C(2)–C(3)	125·7(4)		

(*c*) Equations of least-squares planes in which X, Y, Z refer to orthogonal (Å) co-ordinates obtained by the transformation:

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} 1/a^*, & 0, & 0 \\ -a \sin\beta\cos\gamma^*, & b \sin\alpha, & 0 \\ a \cos\beta, & b \cos\alpha, & c \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

Distances (Å) of relevant atoms from the planes are shown in square brackets

Plane (1): C(1)—(4)

$$-0{\cdot}2211X - 0{\cdot}0170Y + 0{\cdot}9751Z - 3{\cdot}3168 = 0$$

[Mn −1·674, S 0·668, C(1) 0·002, C(2) −0·004, C(3) 0·004, C(4) −0·002, C(11) 0·120, C(12) 0·085, C(13) 0·207, C(14) 0·038]

Plane (2): S, C(1), C(4)

$$0{\cdot}3081X + 0{\cdot}0636Y + 0{\cdot}9492Z - 3{\cdot}1124 = 0$$

[C(2) 0·698, C(3) 0·711, C(5) 1·552]

Plane (3): C(15)—(17)

$$-0{\cdot}1320X - 0{\cdot}0084Y + 0{\cdot}9912Z - 0{\cdot}6650 = 0$$

[Mn 1·041]

Plane (4): C(5)—(10)

$$-0{\cdot}3140X + 0{\cdot}9470Y - 0{\cdot}0677Z - 2{\cdot}7438 = 0$$

[C(5) 0·003, C(6) −0·004, C(7) 0·003, C(8) −0·001, C(9) 0·001, C(10) −0·002, S 0·033, F(6) −0·021, F(7) −0·008, F(8) −0·023, F(9) 0·005, F(10) −0·002]

Angles (°) between planes:

(1)–(2)	31·1	(1)–(3)	5·2
(1)–(4)	90·7	(2)–(4)	95·8

TABLE 6

Intermolecular approaches ($<3{\cdot}1$ Å) for (II)

O(17) · · · F(22^{I})	2·88	F(31) · · · F(41^{V})	3·04
F(10) · · · F(31^{I})	2·89	F(7) · · · F(43^{V})	3·04
F(10) · · · F(21^{I})	2·93	F(9) · · · F(12^{VI})	3·04
O(16) · · · F(8^{II})	2·95	F(9) · · · F(43^{VII})	3·05
O(17) · · · F(8^{III})	2·95	O(15) · · · F(9^{II})	3·06
F(7) · · · F(11^{IV})	3·01	F(9) · · · F(11^{VI})	3·07
F(6) · · · F(33^{V})	3·02	O(16) · · · O(16^{VIII})	3·08
C(8) · · · F(23^{IV})	3·04		

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

I	$-1 + x, y, z$	V	$-x, 1 - y, 1 - z$
II	$1 + x, y, -1 + z$	VI	$-1 - x, -y, 1 - z$
III	$x, y, -1 + z$	VII	$-1 - x, 1 - y, 1 - z$
IV	$-x, -y, 1 - z$	VIII	$-x, 1 - y, -z$

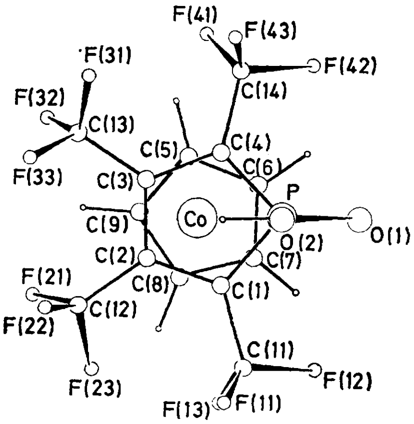


FIGURE 1 The molecule of (1), projected on the mean plane defined by atoms C(1)—(4)

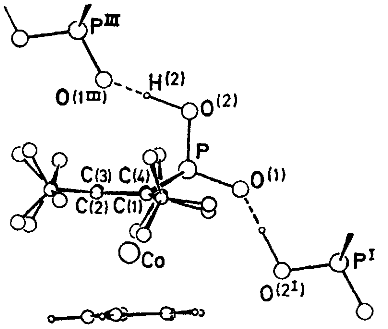


FIGURE 2 The molecular structure of (1), viewed parallel to the mean plane defined by atoms C(1)—(4), and showing the hydrogen bonding. Roman numeral superscripts are defined in Table 3

crystal by hydrogen bonds to form chains parallel to the *a* axis; the short oxygen–oxygen separation [2·453(7) Å] defines a very strong hydrogen bond which, nevertheless, is probably not truly symmetrical since the P–O(1) and P–O(2) distances are significantly different, as are also the P–O(1) · · · O(2^{I}) and P–O(2) · · · O(1^{III}) angles.

Both complexes contain five-membered heterocyclic ligands having envelope conformations characterized by four coplanar carbon atoms with the heteroatoms displaced from these planes and away from the metal atoms. The resulting metal–heteroatom distances are appreciably longer than any reasonable estimates of the sum of covalent radii.

If the differing electronic requirements of the metal atoms may be predicted from the 18-electron rule, then it is clear that in complex (1) the heterocycle should act as a four-electron donor to cobalt whereas in (2) the ligand should provide five electrons to manganese. It follows that in (1) no metal–heteroatom interaction is necessary for a closed-shell configuration of the metal whereas in (2) the absence of an Mn–S bond would superficially indicate a 35-electron structure, a description which, however, is incompatible with the diamagnetism of the complex. Moreover, mass and n.m.r. spectroscopy preclude the possibility of a hydride ligand being present. Accordingly, we must consider a large contribution from a zwitterion structure (3a) so that the complex is formally a sulphonium derivative with a manganese (—1) species. The cationic nature of the sulphur atom is reflected in the large ^{19}F chemical shift (ϕ 68·2 p.p.m.) of the CF_3 group attached to sulphur in the related complex (3)b.[4]

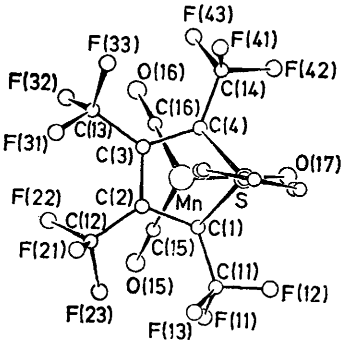


FIGURE 3 The molecule of (2) projected on the mean plane defined by atoms C(1)—(4). For the sake of clarity the fluorine atoms of the C_6F_5 group have been omitted

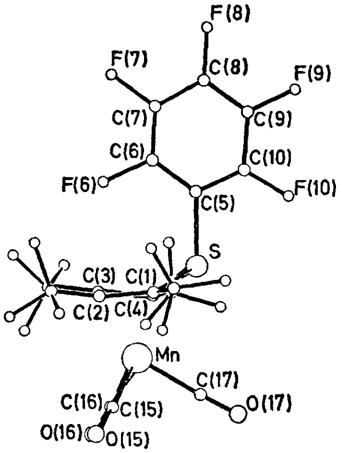
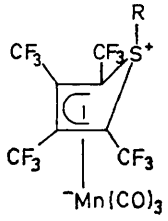


FIGURE 4 The molecular structure of (2), viewed parallel to the mean plane defined by atoms C(1)—(4)

The nonplanarity of the heterocyclic ligands and the electronic descriptions of the complexes are inconsistent with the ligands being considered as analogues of cyclopentadienyl. Furthermore, whereas the carbon–carbon bonds in the heterocycles are approximately equal which suggests delocalization of the π-electrons over the four-carbon chain, the carbon–heteroatom distances are little, if any, shorter than expected for $C(sp_2)$–X single bonds; the C–S distances (mean 1·760 Å) in (2) are not distinguishable from the mean C(Ph)–S distance (1·75 Å) in *e.g.* a number of *p*-bromobenzenesulphonyl esters,[9] and are significantly longer than the C–S separation (1·718 Å) reported for thiophen.[10] Additionally, the two longer metal–carbon bonds to C(1) and C(4) and two shorter ones to C(2) and C(3), together with the orientation of the $Mn(CO)_3$ group in (2), are features characteristic of metal–diene systems. In contrast, the metal atom is equidistant from the four carbon atoms of the planar heterocycle in tricarbonyl(tetraphenylarsole)manganese.[3]



(3) a; $R = C_6F_5$
b; $R = CF_3$

The Mn–C(diene) distances in (2) are in the range 2·055—2·102 Å and the mean distance (2·08 Å) is substantially shorter than the mean Mn–C(heterocycle) distance in tricarbonyl (tetraphenylarsole) manganese (2·19 Å),[3] and mean Mn–C(π-C_5H_5) [2·15 (ref. 11) and 2·17 Å (refs. 12 and 13)] and mean Mn–C(pentadienyl) distances in other compounds [2·18 (ref. 14), 2·19 (ref. 15), and 2·19 Å (ref. 13)]. The C–C distances in the diene in (2) are 1·433—1·449 (mean 1·441 Å), significantly longer than mean distances in complexes containing pentadienyl chains [1·40 Å (refs. 14 and 15)] and it is evident that the stronger metal–carbon bonding in (2) is correlated with weaker bonding between the carbon atoms of the complexed diene. The formal negative charge on the manganese atom, the positive charge on the sulphur, and the electron-withdrawing trifluoromethyl groups on the diene should all promote back-donation of metal d_π electrons into the antibonding orbitals of the diene.

Details of a zwitterion structure comparable to (2) but involving cyclopentadiene itself have yet to be reported; however, in the case of (1) direct analogies exist with the substituted-cyclopentadiene complexes π-cyclopentadienyl(1-phenylcyclopentadiene)cobalt[16] and π-cyclopentadienyl(1-benzoylcyclopentadiene)cobalt.[17] The envelope conformation, which is typical of the ligands in

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such complexes, has been ascribed to an inward twisting of the *p* orbitals of the C(1) and C(4) carbon atoms of the diene system in order to optimize overlap with the metal orbitals.[17,18] The resulting dihedral angle probably reflects the nature of the atom at the apex of the envelope: in (1) and (2) where the heteroatom orbitals directed towards C(1) and C(4) of the diene are between *p* and sp^3 in character the dihedral angles are 32·2 and 31·1°, respectively, not unlike the corresponding angle (36·5°) in (π-C_5H_5)(PhC_5H_5)Co, sp^3 hybridized carbon,[16] but quite different from that (21·3°) for tetrakis(trifluoromethyl)cyclopentadienone(π-cyclopentadienyl)cobalt,[19] sp^2 hybridized carbon atom. The mean Co–C(diene) distance in (1) (2·00 Å) is only very slightly shorter than the mean Co–C(π-C_5H_5) distance (2·03 Å) and these values are in good agreement with results for the other cobalt complexes, *cf.* respective distances of 2·00 and 2·05 Å in π-cyclopentadienyl(1-benzoylcyclopentadiene)cobalt.[17]

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