Metal Complexes of Novel Sulphur- and Phosphorus-containing Heterocycles. Preparation and Structure of Tricarbonyl-η^4-(1-pentafluorophenyl-2,3,4,5,-tetrakistrifluoromethylthiophen)manganese and π-Cyclopentadienyl-(1-hydroxy-2,3,4,5,-tetrakistrifluoromethylphosphole 1-oxide)cobalt†

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Summary Heterocyclic derivatives $Mn(CO)_3(C_4F_6)_2SR$ and $C_5H_5Co(C_4F_6)_2PF_3$ are formed by reaction between hexafluorobut-2-yne and $[Mn(CO)_4SR]_2$, (R = CF_3, C_6F_5), and (π-C_5H_5)$Co(PF_3)_2$; these derivatives contain non-planar heterocyclic rings with non-bonding metal heteroatom separations.

Few metal complexes of heterocyclic analogues of the cyclopentadienyl ligand have been characterised by *X*-ray diffraction. Previously studied compounds, tricarbonylthiophenchromium,[2] and tricarbonyltetraphenylarsolemanganese[3] have planar rings with metal–heteroatom bonds. We now describe complexes formed by interaction of hexafluorobut-2-yne with metal complexes.

Our results, together with previous studies of related reactions[4] indicate that heterocyclic derivatives are readily formed by reaction between electrophilic acetylenes and appropriate transition metal derivatives.

Table. *Key crystallographic dimensions*

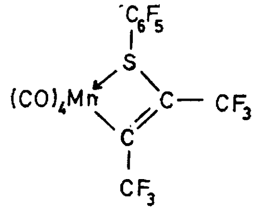
Complex	(IIb)	(V)
M–C(2)	2·109 Å	2·040 Å
M–C(3)	2·062	1·962
M–C(4)	2·068	1·961
M–C(5)	2·103	2·036
M–heteroatom	2·793	2·730
X–C(2)	1·78(1)	1·77(1)
X–C(5)	1·77(1)	1·76(1)
C(2)–C(3)	1·43(1)	1·43(1)
C(3)–C(4)	1·46(1)	1·42(1)
C(4)–C(5)	1·44(1)	1·44(1)
∠C(2)–X–C(5)	85·7(3)°	86·5(4)°

Hexafluorobut-2-yne reacts with $[Mn(CO)_4SC_6F_5]_2$ at 20° to give insoluble $Mn(CO)_4(C_4F_6)SC_6F_5$ (I) which reacts with excess of acetylene at 80° to give $Mn(CO)_3(C_4F_6)_2SC_6F_5$ (IIb). $[Mn(CO)_4SCF_3]_2$ reacts directly with hexafluorobut-2-yne to give $Mn(CO)_3(C_4F_6)_2SCF_3$ (IIa). On the basis of analysis, i.r. and n.m.r. spectroscopy (I) is formulated as shown with

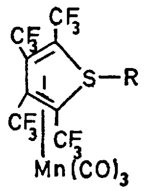
† No reprints available.

the $C(CF_3)C(CF_3)SR$ fragment acting as a 3-electron donor to the manganese. 3-Electron donors containing sulphur have been reported previously.[5] Compound (IIb) has been characterised by spectroscopy and *X*-ray diffraction and contains a heterocyclic C_4S ring (see below).

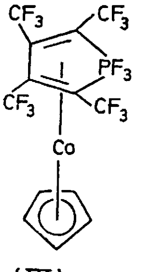
Trifluorophosphine complexes of transition metals have been reacted previously[6] with acetylenes but the formation of heterocyclic derivatives by oxidative addition to phosphorus(III) fluoride in the presence of a transition metal does not appear to have been described although heterocyclic derivatives are formed by oxidative addition of hexafluorobut-2-yne and dimethyl acetylenedicarboxylate to triphenylphosphine.[7] $(\pi\text{-}C_5H_5)Co(PF_3)_2$ reacts with hexafluorobut-2-yne to give $C_5H_5Co(C_4F_6)_2PF_3$(III) which undergoes hydrolysis to (IV) and (V). Compounds (III) and (IV) have been characterised by spectroscopy, (V) by spectroscopy and *X*-ray diffraction.



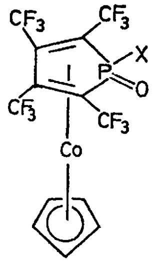
(I)



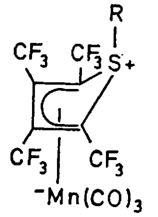
(II) a; R = CF_3
b; R = C_6F_5



(III)



(IV) X = F
(V) X = OH



(VI)

Crystal data: (IIb), $C_{17}O_3F_{17}SMn$, $M = 633{\cdot}3$. Triclinic, $a = 7{\cdot}889(6)$, $b = 11{\cdot}737(8)$, $c = 12{\cdot}195(9)$ Å, $\alpha = 91{\cdot}45(10)$ $\beta = 69{\cdot}71(10)$, $\gamma = 81{\cdot}55(9)^\circ$. Space group $P\bar{1}$, $Z = 2$, $D_c = 2{\cdot}01$. Diffractometer data (Mo-K_α radiation), current $R = 7{\cdot}1\%$ for 3229 reflections with $I > 3\sigma(I)$. (V), $C_{13}H_6O_2F_{12}PCo$, $M = 512{\cdot}1$. Orthorhombic, $a = 9{\cdot}353(7)$, $b = 9{\cdot}893(7)$, $c = 17{\cdot}923(10)$ Å. Space group $P2_12_12_1$, $Z = 4$, $D_c = 2{\cdot}05$. Diffractometer data (Mo-K_α radiation), current $R = 6{\cdot}3\%$ for 1918 reflections with $I > 3\sigma(I)$.

The structures of (IIb) and (V) confirm the spectroscopic results and show that both complexes contain 5-membered heterocyclic rings having envelope conformations. The four carbon atoms are co-planar while the heteroatoms are displaced above these planes by 0·667 Å, (IIb), and 0·686 Å, (V), giving dihedral angles of 30·8° and 32·2° respectively. The metal–C(heterocycle ring) separations have normal bonded values which vary systematically so that the M–C(3) and C(4) contacts are equal and slightly shorter than the M–C(2) and C(5) separations. However the metal to heteroatom distances are appreciably longer than any reasonable estimate of the sum of covalent radii. Whereas in (V) no metal–heteroatom bond is required for a closed shell configuration of the metal, in (IIb) the absence of this bond would superficially indicate a 35 electron structure. Such a description of the compound is not, however, in accord with the observed diamagnetism and since mass and n.m.r. spectra eliminate the possibility of the presence of a hydride ligand it is clear that we must consider a large contribution from a zwitterion structure (VI) so that the complex is formally that of a sulphonium derivative with a manganese (−1) species. The cationic nature of the sulphur atom is reflected in the large ^{19}F chemical shift ($\phi = 68{\cdot}2$ p.p.m.) of the CF_3 group attached to sulphur in (IIa).

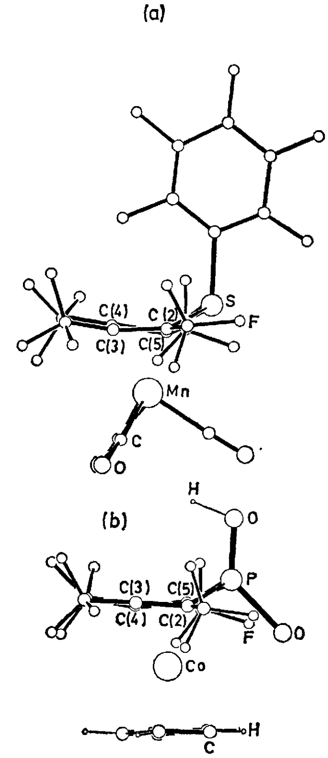


FIGURE. (a) *Molecular structure of* $Mn(CO)_3(C_4F_6)_2SC_6F_5$. (b) *Molecular structure of* $(\pi\text{-}C_5H_5)Co(C_4F_6)_2PO(OH)$.

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