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BASICITY OF TRANSITION METAL CARBONYL COMPLEXES

XVI *. REACTIONS OF η-CYCLOPENTADIENYLMANGANESE COMPLEXES WITH MERCURY TRIFLUOROACETATE

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Summary

Cyclopentadienyl manganese tricarbonyl, $CpMn(CO)_3$, reacts with excess mercury trifluoroacetate in methylene chloride or in ether at 20°C, giving exhaustive mercuration of all five hydrogen atoms of the Cp ligand to give $(CO)_3MnC_5(HgOCOCF_3)_5$. Conversely, the complex $CpMn(CO)_2PPh_3$ in which the basicity of the metal is considerably higher due to the presence of the donor phosphine ligand, forms an adduct. The structure of the dimeric compound $[CpMn(CO)_2PPh_3 \cdot Hg(OCOCF_3)_2]_2$ has been established by an X-ray study. The crystals are triclinic, cell parameters (at $-120°C$): $a = 9.472(5)$, $b = 9.369(7)$, $c = 16.813(9)$ Å, $\alpha = 92.06(5)$, $\beta = 103.01(4)$, $\gamma = 91.59(5)°$, $V = 1452(1)$ Å^3, $Z = 2$, space group $P\bar{1}$.

Introduction

The concept of transition metal basicity has been widely recognized during the last decade or so. It is common knowledge that η-complexes display prominent basic properties towards aprotic acids, i.e. compounds consisting of elements of Groups IIA–IVA of the Periodic Table. One can cite many examples of the interaction of η-complexes containing a cyclopentadienyl or benzene ligand of the type η^n-$C_nH_nM(CO)_x(L)_y$ ($n = 5$ or 6) with aprotic acids, i.e. mercury(II) salts, with compounds of Group III elements (halides, alkyl and aryl derivatives of B, Al and Ga), with tin and titanium halides (cf. ref. 2). Mercury chloride forms adducts with the transition metal atom in the η-complexes $CpCo(CO)_2$ [3,4], $(Arene)M(CO)_3$ (M = Cr, Mo, W [5,6]), $CpM(CO)_2PPh_3$ (M = Mn, Re [7]), $CpM(CO)(NO)(PPh_3)$

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* For part XV see ref. 1.

(M = Mo, W [8]), etc. Reactions of η-complexes with the other mercury(II) salts have received less attention. In particular, the mercuration of the cyclic ligands C_5H_5 and C_6H_6 in manganese and chromium η-complexes has been reported [9–11]. The interaction of η-complexes with mercury trifluoroacetate, $Hg(OCOCF_3)_2$ (MTFA) has not been studied, except for its reactions with ferrocene and alkyl ferrocenes [12,13]. In these cases one can observe a complete replacement of all ten or nine hydrogens of the Cp rings by the $HgOCOCF_3$ residues, i.e. towards ferrocene and alkyl ferrocenes MTFA acts as a strong mercuration reagent.

Results and discussion

A study of the reaction of MTFA with η-cyclopentadienyl manganese complexes revealed that the reaction path and the structure of the resulting products depend heavily on the basicity of manganese and its ligand environment. First, in the reaction of 1 mol MTFA with $CpMn(CO)_3$ (Ia) in CH_2Cl_2, attack of the mercury atom on the manganese atom takes place, and the IR spectra of the reaction mixture first shows ν(CO) modes of the product of coordination with the Mn atom at about 2010 cm^{-1} (mode E, broad) and at 2070 cm^{-1} (mode A, narrow), shifted by 60–80 cm^{-1} to higher frequencies as compared with those of the starting Ia, ν(CO) 2025, 1940 cm^{-1} [1]. The intensity of the modes at 2010 and 2070 cm^{-1} decreases rapidly, and after no more than in 10–15 min they practically disappear.

The complex $(CO)_3MnC_5(HgOCOCF_3)_5$ is the final interaction product of Ia with 5 mol MTFA as a result the exhaustive mercuration of all five hydrogens of the Cp ligand. The IR spectra of this complex contains ν(CO) modes of the $Mn(CO)_3$ fragment at 1950 cm^{-1} (mode E, broad) and at 2030 cm^{-1} (mode A, narrow), as well as a strong ν(C=O) mode of the $HgOCOCF_3$ residues at 1680–1690 cm^{-1} (Fig. 1).

In the presence of $CpMn(CO)_2PPh_3$ (Ib) in methylene chloride or in dichloroethane, MTFA undergoes rapid dissolution, although in the absence of the manganese complex it is practically insoluble in these solvents. In the IR spectrum of the solution one can observe the following distinctive changes which are indicative of coordination of mercury to the manganese atom (Fig. 1c):

1) a shift of the asymmetric and symmetric ν(CO) modes of the $Mn(CO)_2PPh_3$ fragment from 1865 and 1935 cm^{-1} in the starting Ib to 1958 and 1995 cm^{-1};
2) a sharp change in the intensity ratio of the ν(CO) modes.

In the starting pseudooctahedral complex Ib the structural data show the OC–Mn–CO angle to be 90° [14], and the two ν(CO) modes in the IR spectrum to have the same intensity. In the spectrum of the product resulting from the interaction of Ib with MTFA the asymmetric ν(CO) mode at 1958 cm^{-1} is far stronger than that of the symmetric ν(CO) mode at 1995 cm^{-1}. According to the expression [15,16]

$$A_{asym}/A_{sym} = tg^2(\alpha/2),$$

where A are the intensities of the ν(CO) modes and α is the angle between the carbonyl groups, such a change in intensities occurs if the OC–Mn–CO angle in the reaction product is ≫ 90°.

The general pattern of the IR spectra is time-independent, i.e., as distinct from the reaction with $CpMn(CO)_3$, the product resulting from the interaction of MTFA

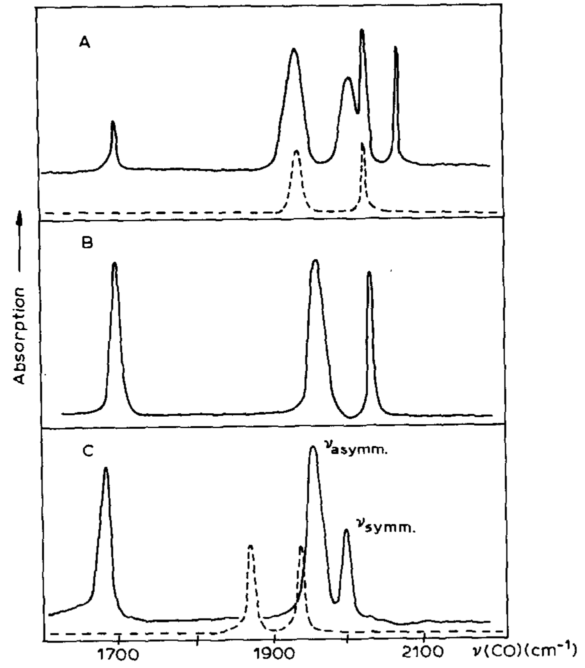
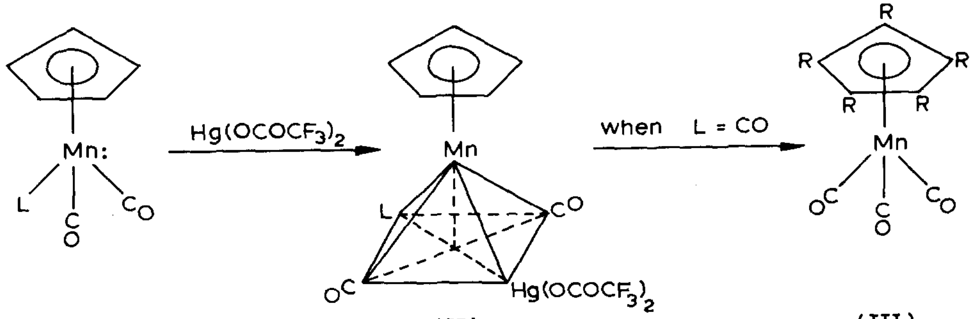


Fig. 1. IR-Spectra (in CH_2Cl_2 solution):
A. $CpMn(CO)_3 + Hg(OCOCF_3)_2$, after 3 min;
B. $CpMn(CO)_3 + Hg(OCOCF_3)_2$, after 1 hour;
C. $CpMn(CO)_2PPh_3 + Hg(OCOCF_3)_2$.
ν(CO) modes of the starting compounds (Ia,b) are shown by dotted lines.

with Ib is stable. An air-stable crystalline 1 : 1 complex $CpMn(CO)_2PPh_3 \cdot Hg(OCOCF_3)_2$ (IIb) was isolated from the solution, and its structure established by X-ray analysis (see below).

Reactions of the manganese η-complexes with MTFA can be described as follows:



(I)
L = CO(Ia)
L = PPh3(Ib)

(II)
L = CO(IIa)(unstable)
L = PPh3(IIb)(stable)

(III)
R = HgOCOCF3

Reactions of the complexes $CpMn(CO)_2(L)$ ($L = CO$ or PPh_3) with MTFA are typical examples of donor-acceptor interactions involving transition metal complexes which are strong organometallic Lewis bases. The attack of the acceptor $Hg(OCOCF_3)_2$ is directed towards the metal atom to give adducts IIa and IIb whose molecules are square pyramidal. The adduct IIa ($L = CO$), whose formation was confirmed by IR spectra seems to be a kinetically controlled product, although it is unstable. Because of the low basicity of the manganese atom in $CpMn(CO)_3$, adduct IIa following its formation, undergoes rapid decomposition, and in the presence of excess of MTFA there is exhaustive mercuration of the Cp ligand, as in the case with ferrocene and alkyl ferrocenes. With the phosphine complex Ib, in which the manganese basicity is much higher due to the addition of the donor ligand PPh_3, the adduct on the manganese atom (IIb) is stable and does not convert into mercuration products of the Cp ligand. Products similar to IIb, in which mercury is coordinated to the manganese and rhenium atoms, is also formed in the interaction of MTFA with the complex $CpM(CO)_2(L)$, where $M = Mn$ and $L = P(C_6H_{11})_3$, $P(C_3H_7)_3$, $AsPh_3$, $SbPh_3$ or $M = Re$ and $L = PPh_3$ [1].

The structure of IIb is shown in Fig. 2, the bond lengths are listed in Table 1 and the bond angles in Table 2. In the crystal, complex IIb is a centrosymmetric dimer formed by a pair of asymmetric trifluoroacetate bridges which combine two $CpMn(CO)_2(PPh_3)(HgOC(O)CF_3$ fragments. The bridging trifluoroacetate groups turn out to be monodentate as each of them has only one oxygen atom, O(1) and O(1′), coordinated by two mercury atoms, Hg and Hg′, of the dimer, whereas the second oxygens, O(2) and O(2′), do not interact with the mercury atoms. The Hg atoms in the dimer form a pair of stronger ("covalent") bonds with the Mn and O(3)

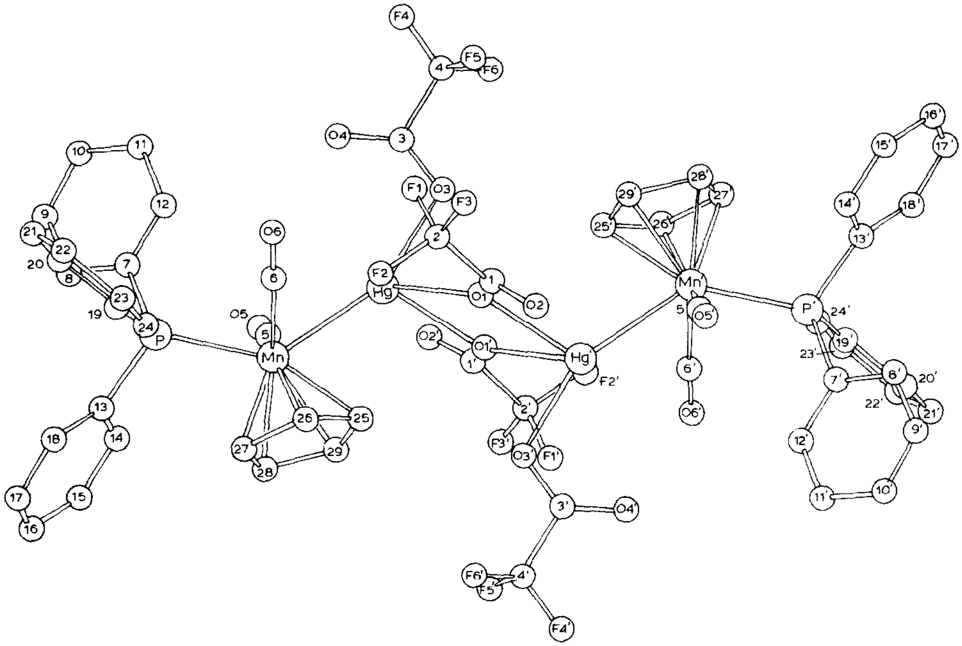


Fig. 2. The structure of IIb and atom numbering scheme.

TABLE 1

BOND DISTANCES, *d*

Bond	*d*(Å)	Bond	*d*(Å)	Bond	*d*(Å)	Bond	*d*(Å)
Hg-Mn	2.602(2)	P-C(13)	1.82(1)	F(6)-C(14)	1.34(2)	C(17)-C(18)	1.39(2)
Hg-O(3)	2.19(1)	P-C(19)	1.83(1)	C(1)-C(2)	1.52(2)	C(18)-C(13)	1.39(2)
Hg-O(1)	2.39(1)	O(1)-C(1)	1.27(2)	C(3)-C(4)	1.56(2)	C(19)-C(20)	1.39(2)
Hg-O(1')	2.67(1)	O(2)-C(1)	1.20(2)	C(7)-C(8)	1.35(2)	C(20)-C(21)	1.40(2)
Mn-P	2.306(4)	O(3)-C(3)	1.26(2)	C(8)-C(9)	1.41(2)	C(21)-C(22)	1.42(2)
Mn-C(5)	1.83(2)	O(4)-C(3)	1.23(2)	C(9)-C(10)	1.36(2)	C(22)-C(23)	1.39(2)
Mn-C(6)	1.83(1)	O(5)-C(5)	1.12(2)	C(10)-C(11)	1.44(2)	C(23)-C(24)	1.36(2)
Mn-C(25)	2.19(2)	O(6)-C(6)	1.15(2)	C(11)-C(12)	1.39(2)	C(24)-C(19)	1.42(2)
Mn-C(26)	2.16(2)	F(1)-C(2)	1.33(2)	C(12)-C(7)	1.35(2)	C(25)-C(26)	1.38(2)
Mn-C(27)	2.16(1)	F(2)-C(2)	1.38(2)	C(13)-C(14)	1.42(2)	C(26)-C(27)	1.44(2)
Mn-C(28)	2.15(1)	F(3)-C(2)	1.31(2)	C(14)-C(15)	1.40(2)	C(27)-C(28)	1.48(2)
Mn-C(29)	2.17(2)	F(4)-C(4)	1.31(2)	C(15)-C(16)	1.40(2)	C(28)-C(29)	1.43(2)
P-C(7)	1.89(1)	F(5)-C(4)	1.32(2)	C(16)-C(17)	1.41(2)	C(29)-C(25)	1.46(2)

atoms of the terminal trifluoroacetate groups and a pair a weaker ("coordination") bonds with the O(1) and O(1') bridges. As usual, the two strongest bonds formed by the Hg atom tend to be colinear: the MnHgO(3) angle is 154.9(3)°, being the largest in the coordination polyhedron of the Hg atom (the remaining five angles are within 68.1–115.5°).

TABLE 2

BOND ANGLES, *ω*

Angle	*ω*(°)	Angle	*ω*(°)	Angle	*ω*(°)
Mn-Hg-O(3)	154.9(3)	O(1)-C(1)-O(2)	127(1)	C(10)-C(11)-C(12)	117(1)
Mn-Hg-O(1)	115.5(3)	O(1)-C(1)-C(2)	115(1)	C(11)-C(12)-C(7)	121(1)
Mn-Hg-O(1')	111.2(2)	O(2)-C(1)-C(2)	118(1)	P-C(13)-C(14)	118(1)
O(1)-Hg-O(3)	81.3(3)	C(1)-C(2)-F(1)	113(1)	P-C(13)-C(18)	122(1)
O(1)-Hg-O(1')	68.1(3)	C(1)-C(2)-F(2)	109(1)	C(18)-C(13)-C(14)	120(1)
O(3)-Hg-O(1')	81.3(4)	C(1)-C(2)-F(3)	113(1)	C(13)-C(14)-C(15)	119(1)
Hg-Mn-P	133.2(1)	F(1)-C(2)-F(2)	107(1)	C(14)-C(15)-C(16)	121(1)
Hg-Mn-C(5)	73.4(4)	F(1)-C(2)-F(3)	108(1)	C(15)-C(16)-C(17)	120(1)
Hg-Mn-C(6)	69.7(4)	F(2)-C(2)-F(3)	107(1)	C(16)-C(17)-C(18)	120(1)
P-Mn-C(5)	82.6(5)	O(3)-C(3)-O(4)	130(1)	C(17)-C(18)-C(13)	121(1)
P-Mn-C(6)	81.7(4)	O(3)-C(3)-C(4)	113(1)	P-C(19)-C(20)	121(1)
C(5)-Mn-C(6)	109.3(6)	O(4)-C(3)-C(4)	117(2)	P-C(19)-C(24)	121(1)
Mn-P-C(7)	115.6(4)	C(3)-C(4)-F(4)	114(2)	C(24)-C(19)-C(20)	118(1)
Mn-P-C(13)	112.9(5)	C(3)-C(4)-F(5)	109(1)	C(19)-C(20)-C(21)	121(1)
Mn-P-C(19)	115.9(5)	C(3)-C(4)-F(6)	110(1)	C(20)-C(21)-C(22)	119(1)
Mn-C(5)-O(5)	175(1)	F(4)-C(4)-F(5)	107(1)	C(21)-C(22)-C(23)	120(1)
Mn-C(6)-O(6)	173(1)	F(4)-C(4)-F(6)	107(2)	C(22)-C(23)-C(24)	121(1)
C(7)-P-C(13)	104.1(6)	F(5)-C(4)-F(6)	110(2)	C(23)-C(24)-C(19)	122(1)
C(7)-P-C(19)	100.9(6)	P-C(7)-C(8)	120(1)	C(19)-C(25)-C(26)	108(1)
C(13)-P-C(19)	105.9(6)	P-C(7)-C(12)	117(1)	C(25)-C(26)-C(27)	111(1)
Hg-O(1)-Hg'	111.9(4)	C(12)-C(7)-C(8)	123(1)	C(26)-C(27)-C(28)	105(1)
Hg-O(1)-C(1)	141.3(9)	C(7)-C(8)-C(9)	118(1)	C(27)-C(28)-C(29)	108(1)
Hg'-O(1)-C(1)	106.2(9)	C(8)-C(9)-C(10)	121(1)	C(28)-C(29)-C(25)	108(2)
Hg-O(3)-C(3)	11.9(9)	C(9)-C(10)-C(11)	120(1)		

The Mn–Hg bond length, 2.602(2) Å, coincides with the length of the covalent bond in $Hg[Mn(CO)_5]_2$, 2.610 Å [17] or 2.608 Å [18], but it is somewhat shorter than that in the tetrameric complex $[(\eta^5\text{-}MeC_5H_4)Mn(CO)_2Hg]_4$, containing an 8-membered Mn_4Hg_4 ring in which this bond length is 2.640(7) Å [19]. However, even this latter length is still far shorter than the sum of the covalent radii, 2.76 Å, if half the Mn–Mn bond length in the complex $Mn_2(CO)_{10}$, 1.46 Å [20], is taken as a covalent Mn radius and the covalent Hg radius is equal to 1.30 Å [21]. If 1.38 Å is accepted as a covalent Mn radius [22], then the Mn–Hg bond length found by us is still shorter than the sum of the covalent radii (2.68 Å).

Such a shortening in the mercury–transition metal distance is a general feature, which has been also studied by us previously [23]. As suggested elsewhere [17], one possible reason for this fact may be a d_π–p_π interaction of the occupied d_{xy} and d_{yz} orbitals of the Mn atom with the vacant p_x and p_y orbitals of the *sp*-hybridized Hg atom. The possibility of such an interaction is suggested by IR and Mössbauer data for the compounds $M[Fe(\eta^5\text{-}Cp)(CO)_2]_2$ (M = Zn, Cd, Hg) as well as by mass spectrometry of the compounds $M[Co(CO)_4]_2$ and $M[Cr(\eta\text{-}Cp)(CO)_3]_2$ with the same metals [24]. However this explanation of the shortened Mn–Hg bond length in IIb is not entirely applicable as the hybridization of the Hg atom here is closer to sp^3 (which is suggested by the bond angles, see Table 2), all the hybridized Hg orbitals being involved in the bonding. As an alternative explanation, Katches and Simon [17] recognize the possibility of the intramolecular interaction between the Hg atoms and the Mn-bonded CO groups. This is confirmed by the regularly diminishing Hg–Mn–C(CO) bond angles, average 84.3(2)° compared to an ideal value of 90°. In the structure studied by us the similar bond angles, Hg–Mn–C(5) and Hg–Mn–C(6), are 73.4(4) and 69.7(4)°, respectively, i.e. their decrease is even greater. However, it is not clear if the distortion of these angles reflects the interaction of the CO groups with the adjacent Hg atom or the steric repulsion of these groups by the bulky PPh_3 ligand.

The Hg–O(3) bond, 2.19(1) Å, in a terminal trifluoroacetate group, is somewhat longer than the similar bond in $C(HgOCOCF_3)_4$, 2.07(1) Å [25] to approximate the sum of the covalent mercury and oxygen (0.74 Å) [26] radii. At the same time, the length of the Hg–O(3) bond is close to that in crystals of the mercury acetate pyridine complex, $C_5H_5N \cdot Hg(CH_3COO)_2$, 2.17(2) Å [27]. In this complex the mercury atom is strongly bonded to the pyridine nitrogen atom and to one of the oxygen atoms of the first acetate group, it being also coordinated by the two oxygen atoms of the second bidentate acetate group (Hg ··· O, 2.433 and 2.511 Å). Thus a certain weakening of the covalent Hg–O bond in this compound is caused by the mercury atom participating in coordination with the oxygen atom of the second acetate group. In a like manner, in compound IIb the weakening of the Hg–O(3) bond can be apparently attributed to the mercury atom participating in the interaction with O(1) and O(1′), the Hg–O(1) and Hg–O(1′) distances being 2.39(1) and 2.67(1) Å, respectively. In other mercury(II) complexes containing a Hg-coordinated trifluoroacetate group the latter is, as a rule, bidentate, and the distances at which a Hg ··· O coordination interaction takes place, are in a fairly wide range from 2.43 to 2.96 Å [27–31].

The Mn atom is coordinated by the η^5-Cp ligand, the PPh_3 ligand, two CO groups and the Hg atom. The Mn atom coordination is tetragonal-pyramidal with a formally monodentate Cp ligand in the apical position. The carbonyl groups are in *trans* positions at the pyramid base. The Mn–C(Cp) distances lie within 2.15–2.19(1) Å, i.e. they are quite typical of η^5-cyclopentadienyl manganese complexes (cf., for example, ref. 19). The Mn–C bond lengths to the CO carbons are equal to 1.83(2) and 1.83(1) Å and coincide with those found for $Hg[Mn(CO)_5]_2$ [17,18] and for $Mn_2(CO)_{10}$ [20]. The Mn–PPh_3 bond length in IIb, 2.306(4) Å, is somewhat longer than that of the complexes $CpMn(CO)_2PPh_3$, 2.236 Å [14] and $CpMn(CO)(PPh_3)_2$, 2.234 and 2.239 Å [32], and it is shorter than that in the complex $[CpMn(CO)_2(PPh_3)(SnCl_3)]^+SnCl_5^-$,, 2.367(4) Å [33]. The differences in the bond lengths for P–C, 1.82(1), 1.83(1) and 1.89(1) Å, and for C–C in the Cp rings, 1.38(2)–1.48(2) Å (exceeding 3σ) is likely to be due to the errors caused by neglecting absorption and to partial decomposition of the crystal.

The geometry of the trifluoroacetate groups is conventional in that the distances for C(1)–O(1), 1.27(2) Å, and for C(3)–O(3), 1.26(2)Å, to the oxygen atoms involved in the coordination are somewhat longer than those for C(1)–O(2), 1.20(2) Å, and C(3)–O(4), 1.23(2) Å. The C(1)–C(2) and C(3)–C(4) bond lengths, 1.52(2) and 1.56(2) Å, respectively, coincide within experimental errors with the standard C(sp^3)–C(sp^3) bond length, 1.54 Å. The C–F bond lengths lie within 1.31(2)–1.38(2) Å, their mean value, 1.36(2) Å, being close to the standard one, 1.33 Å [34].

Experimental

$(CO)_3MnC_5(HgOCOCF_3)_5$ (III)

To a solution of $CpMn(CO)_3$ (0.204 g, 1 mmol) in CH_2Cl_2 or ether (20–25 ml) was added mercury trifluoroacetate powder (2.35 g, 5.5 mmol). Magnetic stirring for 3 h at 20°C gave a pale yellow solution. An excess of MTFA was filtered off, and after removal of the solvent and trituration of the resulting yellow-coloured oil under the hexane layer, the air-stable yellow complex $(CO)_3MnC_5(HgOCOCF_3)_5$ was isolated. The microcrystalline powder obtained was poorly soluble in most organic solvents, except for $CHCl_3$ and CH_2Cl_2. On heating it decomposed without melting at ca. 100°C. IR spectrum (in CH_2Cl_2): 1690 cm^{-1}, ν(C=O), $HgOCOCF_3$; 1950–1960 (mode *E*, broad) and 2030 (mode *A*, narrow), $Mn(CO_3)$.

Found: C, 12.44; H, 0.00; Hg, 55.98; Mn, 3.38. Calcd. for $C_{18}F_{15}O_{10}MnHg_5$: C, 12.22; H, 0.00; Hg, 56.76; Mn, 3.11%.

$[CpMn(CO)_2PPh_3 \cdot Hg(OCOCF_3)_2]_2$ (IIb)

To a solution of $CpMn(CO)_2PPh_3$ (0.44 g, 1 mmol) in CH_2Cl_2 (10–15 ml) at 20°C was added MTFA powder (0.47 g, 1.1 mmol). Under magnetic stirring MTFA rapidly dissolved to give a pale yellow solution. After 15 min the solution was filtered off and the solvent was removed to give IIb, d.p. 110°C, in practically quantitative yield. The yellow crystals obtained were air-stable, poorly soluble in methylene chloride and dichloroethane, insoluble in benzene, hexane, carbon bisulfide and light-sensitive.

Found: C, 39.50; H, 2.38; Hg, 23.63. Calcd. for $C_{29}H_{20}F_6PMnHg$: C, 40.25; H, 2.31; Hg, 23.20%.

X-ray study of IIb

The crystals were obtained by slow recrystallization from a CH_2Cl_2-hexane mixture. The crystals of $[CpMn(CO)_2PPh_3 \cdot Hg(OCOCF_3)_2]_2$ were triclinic

TABLE 3

ATOMIC COORDINATES ($\times 10^4$, for Hg and Mn $\times 10^5$)

Atom	X	Y	Z	Atom	X	Y	Z
Hg	6750(10)	3030(10)	12730(0)	Mn	26830(20)	22550(20)	18620(10)
P	3540(4)	3304(4)	3148(2)	O(1)	1033(11)	−1088(11)	119(6)
O(2)	2286(15)	−2333(13)	1103(8)	O(3)	−1236(11)	−1053(11)	1282(7)
O(4)	−1096(14)	−174(12)	2564(7)	O(5)	3683(11)	−344(11)	2727(7)
O(6)	−95(11)	3248(12)	2180(7)	F(1)	2533(10)	−2202(11)	−884(6)
F(2)	1444(12)	−4065(11)	−521(7)	F(3)	3680(11)	−3499(12)	56(7)
F(4)	−3503(13)	−1665(16)	2607(8)	F(5)	−4175(12)	−954(18)	1409(10)
F(6)	−3144(14)	−3003(13)	1632(10)	C(1)	1884(15)	−2056(14)	402(9)
C(2)	2421(16)	−2945(17)	−237(10)	C(3)	−1660(16)	−875(15)	1933(10)
C(4)	−3150(18)	−1642(21)	1901(12)	C(5)	3242(14)	619(15)	2393(9)
C(6)	948(15)	2780(14)	2064(9)	C(7)	3245(13)	2219(13)	4023(8)
C(8)	4329(17)	2111(15)	4693(9)	C(9)	4006(18)	1424(18)	5366(10)
C(10)	2635(17)	925(17)	5348(10)	C(11)	1513(17)	1009(17)	4617(10)
C(12)	1899(17)	1639(15)	3959(9)	C(13)	5489(14)	3688(14)	3382(8)
C(14)	6415(15)	2533(16)	3351(10)	C(15)	7906(17)	2818(17)	3473(10)
C(16)	8485(16)	4221(17)	3623(10)	C(17)	7558(17)	5356(17)	3652(11)
C(18)	6075(15)	5077(15)	3536(10)	C(19)	2721(14)	4975(14)	3359(9)
C(20)	2580(16)	5367(15)	4145(9)	C(21)	1867(16)	6606(16)	4296(10)
C(22)	1289(17)	7473(15)	3636(11)	C(23)	1459(18)	7092(16)	2856(12)
C(24)	2150(17)	5885(16)	2721(11)	C(25)	2359(21)	2404(19)	538(11)
C(26)	2522(21)	3760(19)	903(11)	C(27)	3905(16)	3967(17)	1468(9)
C(28)	4637(18)	2600(17)	1437(9)	C(29)	3680(17)	1657(18)	861(10)

(−120°C); $a = 9.472(5)$, $b = 9.369(7)$, $c = 16.813(9)$ Å, $\alpha = 92.06(5)$, $\beta = 103.01(4)$, $\gamma = 91.59(5)°$, $V = 1452(1)$ Å^3, $D_{\text{calcd}} = 1.99$ g/cm^3, $Z = 2$, space group $P\bar{1}$.

The unit cell parameters and intensity of 4545 independent reflections were measured with a 4-circle Syntex P2$_1$ automatic diffractometer (at −120°C, λMoK_α, graphite monochromator, $\theta/2\theta$-scan, $2 < 2\theta < 50°$). No correction was made for the absorption, $\mu(\text{Mo-K}_\alpha) = 59.9$ cm^{-1}). During irradiation the crystal decomposed slowly, the total intensity drop of the standard reflections being 5–7%.

The structure was solved by the heavy-atom method and refined by a least-squares technique in a full-matrix anisotropic approximation to $R = 0.0807$ ($R_w = 0.0804$) for 3787 reflections with $F > 5\sigma$. Atomic coordinates are listed in Table 3.

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