Inorganic Compounds Containing the Trifluoroacetate Group. Part I. Pentacarbonyl(trifluoroacetato)manganese and Substituted Derivatives

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Physical properties of pentacarbonyl(trifluoroacetato)manganese have been investigated. Discrepancies in i.r. spectra reported in earlier studies have been resolved and new data, including Raman, ^{19}F n.m.r., *X*-ray photoelectron, and mass spectra, and molecular-weight measurements, have been obtained. A convenient route to substituted derivatives of this compound has been developed and the new compounds $[Mn(CO)_3L_2(O_2CCF_3)]$ [L = pyridine (py) or PPh_3; L_2 = 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen), $RSCH_2CH_2SR$ (R = Et or Ph)] isolated and characterised.

PREPARATION of pentacarbonyl(trifluoroacetato)manganese $[Mn(CO)_5(O_2CCF_3)]$ has been reported in two recent studies. Green *et al.*[1] prepared the compound by reacting σ-allylpentacarbonylmanganese with anhydrous trifluoroacetic acid and characterised it by elemental analysis (Found: C, 27·0; Mn, 17·7. Calc.: C, 27·3; Mn, 17·8%). The melting point of the compound (76·5—78 °C), its i.r. spectrum, thermal decomposition, and solubility in various solvents were also given. King and Kapoor[2] isolated the compound $[Mn(CO)_5(O_2CCF_3)]$ following metathesis between $[Mn(CO)_5Br]$ and $Ag(O_2CCF_3)$: elemental analyses (Found: C, 27·0; F, 19·4. Calc.: F, 18·5%), m.p. (70 °C), and i.r. spectrum were reported; however, attempts to record the ^{19}F n.m.r. spectrum were unsuccessful. In addition to the discrepancies in the m.p.s reported in these two studies, the i.r. spectra differed significantly, particularly in the $\nu(C{\equiv}O)$ region. As part of a general study of the preparation, properties, and reactions of trifluoroacetato-complexes we have examined the physical properties of the compound $[Mn(CO)_5(O_2CCF_3)]$ in some detail.

In a separate study King and Kapoor[3] showed that substituted derivatives of $[Mn(CO)_5(O_2CCF_3)]$ could be obtained by u.v. irradiation for 1—44 h at room temperature of a benzene–hexane solution of the compound in the presence of a tricovalent phosphorus-donor ligand. The compounds $[Mn(CO)_3L_2(O_2CCF_3)]$ [L = $P(OPh)_3$; L_2 = $Ph_2PCH_2CH_2PPh_2$ or *cis*-$Ph_2PCH{=}CHPPh_2$], $[Mn(CO)_2\{P(OMe)_3\}_3(O_2CCF_3)]$, and $[Mn(CO)(Me_2PCH_2CH_2PMe_2)_2(O_2CCF_3)]$ were prepared in this manner. The present study has shown that the $[Mn(CO)_3L_2(O_2CCF_3)]$ compounds are readily prepared by heating $[Mn(CO)_5(O_2CCF_3)]$ under reflux with the ligand in chloroform for *ca.* 30 min and several new such derivatives have been obtained in this manner.

EXPERIMENTAL

All manipulations were carried out under an atmosphere of pure dry nitrogen. Solvents were stored over calcium hydride or degassed molecular sieves and distilled in an atmosphere of purified nitrogen immediately prior to use. The compound $[Mn(CO)_5(O_2CCF_3)]$ was prepared as described by King and Kapoor;[2] $[(mcp)Mn(CO)_3]$ (mcp = η-methylcyclopentadienyl) (Strem Chemicals) was converted into $Mn_2(CO)_{10}$,[4] which was treated with bromine in carbon tetrachloride solution to afford $[Mn(CO)_5Br]$,[5] which in turn was stirred with a 5% excess of $Ag(O_2CCF_3)$ for 4 h at room temperature in dichloromethane. Recrystallisation from dichloromethane–hexane afforded yellow cubic crystals, m.p. 71 ± 1 °C (Found: C, 27·1; Mn, 17·3. Calc. for $C_7F_3MnO_7$: C, 27·3; Mn, 17·8%).

^{19}F N.m.r. spectra were determined in acetone solutions on a Varian HA-100 instrument at 100 MHz with α,α,α-trifluorotoluene as internal standard. Perkin-Elmer 225 and 457 spectrometers calibrated with polystyrene film were used to record i.r. spectra and an A.E.I. MS12 spectrometer was employed for mass-spectral measurements with a 70 eV beam. Raman spectra were obtained on a Cary 81A spectrometer using a neon-laser excitation at 6 328 Å and carbonyl carbon and oxygen 1*s*-binding energies were measured on an A.E.I. ES200 spectrometer using Al-$K_{\alpha1,\alpha2}$ radiation. Molecular-weight data for 0·01-, 0·05-, and 0·1M-acetone and 0·02-, 0·05-, and 0·08M-dichloromethane solutions were achieved by vapour-phase osmometry using a Mechrolab 301A osmometer.

Preparations.— *Pentacarbonylbis(pyridine)(trifluoroacetato)manganese.* The compound $[Mn(CO)_5(O_2CCF_3)]$ (0·20 g, 0·65 mmol) was dissolved in chloroform (10 cm³) and pyridine (py) (0·13 g, 1·30 mmol) added. The solution was then heated under reflux at 60 °C for 30 min after which time an i.r. spectrum of the carbonyl stretching-frequency region showed the absence of peaks due to $[Mn(CO)_5(O_2CCF_3)]$ and the presence of three new intense bands at 2 040, 1 952, and 1 914 cm^{-1}. The solvent was evaporated

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[1] M. L. H. Green, A. G. Massey, J. T. Moelwyn-Hughes, and P. L. I. Nagy, *J. Organometallic Chem.*, 1967, **8**, 511.

[2] R. B. King and R. N. Kapoor, *J. Organometallic Chem.*, 1968, **15**, 457.

[3] R. B. King and R. N. Kapoor, *J. Inorg. Nuclear Chem.*, 1969, **31**, 2173.

[4] R. B. King, J. C. Stokes, and T. F. Korenowski, *J. Organometallic Chem.*, 1968, **11**, 641.

[5] E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1959, 501.

until crystallisation commenced and the solution set aside at −10 °C whence bright yellow *crystals* of $[Mn(CO)_3(py)_2(O_2CCF_3)]$ were obtained (0·25 g, 94%). This reaction was also studied with pyridine in large excess; however, further substitution was not achieved. A 1 : 1 mixture of the compound $[Mn(CO)_5(O_2CCF_3)]$ and pyridine afforded a 1 : 1 mixture of $[Mn(CO)_3(py)_2(O_2CCF_3)]$ and unchanged $[Mn(CO)_5(O_2CCF_3)]$.

Pentacarbonyl(trifluoroacetato)bis(triphenylphosphine)manganese. This compound was prepared in an analogous manner to the pyridine complex from a 1 : 2 mixture of $[Mn(CO)_5(O_2CCF_3)]$ and PPh_3.

$[Mn(CO)_3(L_2)(O_2CCF_3)]$ [L_2 = *2,2′-bipyridyl, 1,10-phenanthroline, 1,2-bis(ethylthio)ethane, or 1,2-bis(phenylthio)ethane*] *and* $[Mn(CO)_3(Ph_2PCH_2CH_2PPh_2)(O_2CCF_3)],CHCl_3$. These preparations were carried out as described for the pyridine complex using a 1 : 1 mixture of the compound $[Mn(CO)_5(O_2CCF_3)]$ and ligand (L_2). The reaction between the compound $[Mn(CO)_5(O_2CCF_3)]$ and $Ph_2PCH_2CH_2PPh_2$ in chloroform yielded a bright yellow, microcrystalline, *product* which analysed for $[Mn(CO)_3(Ph_2PCH_2CH_2PPh_2)(O_2CCF_3)],CHCl_3$; however, when the reaction was carried out in diethyl ether or tetrahydrofuran the pale yellow compound [3] $[Mn(CO)_3(Ph_2PCH_2CH_2PPh_2)(O_2CCF_3)]$ was obtained. The chloroform molecule is quite firmly attached in this adduct; thus, on heating, it is retained until *ca.* 140 °C and the molecular weight of the adduct in acetone was found to be 760 ± 35 (calc. 770). {The molecular weight of the compound $[Mn(CO)_3(Ph_2PCH_2CH_2PPh_2)(O_2CCF_3)]$ in acetone was determined at 636 ± 30 (calc. 650)}.

Elemental analyses, m.p.s, and yields of all the substituted products are given in Table 3.

RESULTS AND DISCUSSION

The observed m.p. of the compound $[Mn(CO)_5(O_2CCF_3)]$ (71 ± 1 °C) is in good agreement with that obtained by King and Kapoor.[2] The mass spectrum of this compound is presented in Table 1. Three modes of decomposition of $[Mn(CO)_5(O_2CCF_3)]^+$ may be suggested. The moderately intense peak at *m/e* 195 implies that loss of the trifluoroacetato-group [equation (1)] is possible. A weak metastable peak at *m/e* 124 suggests

$$[Mn(CO)_5(O_2CCF_3)]^+ \longrightarrow Mn(CO)_5{}^+ + CF_3CO_2 \tag{1}$$

that this fragmentation occurs at least to some extent. No peak corresponding to the ion $CF_3CO_2{}^+$ was observed, and it seems probable that, if formed, this species would rapidly fragment into the more stable entities $CF_3{}^+$ and CO_2. An alternative scheme leading to formation of the ion $Mn(CO)_5{}^+$ is *via* loss of CF_3 and CO_2 in successive steps [equations (2) and (3)]. Weak metastable peaks

$$[Mn(CO)_5(O_2CCF_3)]^+ \longrightarrow [Mn(CO)_5(O_2C)]^+ + CF_3 \tag{2}$$

$$[Mn(CO)_5(O_2C)]^+ \longrightarrow Mn(CO)_5{}^+ + CO_2 \tag{3}$$

corresponding to these fragmentations were observed at *m/e* 185 and 159, respectively. The other mode of fragmentation for the ion $[Mn(CO)_5(O_2CCF_3)]^+$ appears to involve loss of CO groups. Peaks of significant intensity were observed for all the ions $[Mn(CO)_n(O_2CCF_3)]^+$ (n = 0—5), as were metastable peaks at *m/e* 254, 205, 163, 124, and 91 corresponding to loss of 1—5 CO groups, respectively, from the parent ion. In addition, metastable peaks consistent with loss of a CO group from the ions $[Mn(CO)_n(O_2CCF_3)]^+$ (n = 4, 3, and 2) were obtained. The relative intensities of the peaks for fragmentation of the ion $[Mn(CO)_5(O_2CCF_3)]^+$ by loss of trifluoroacetato- or carbonyl groups suggest that these processes occur concurrently, with no route being particularly favoured. Peaks observed at *m/e* higher than 308 can be accounted for by the formation, and subsequent fragmentation, of the compound $Mn_2(CO)_{10}$. It is believed that dimanganese species arise from combination of monomanganese fragments in the mass spectrometer, either by molecular combination or by ion–molecule reactions, since: (*i*) recording the mass spectrum at a higher pressure resulted in appreciable increase in intensity of the ion $Mn_2(CO)_{10}{}^+$ and its daughter peaks relative to $[Mn(CO)_5(O_2CCF_3)]^+$ and its daughter peaks {a behaviour paralleled in the mass spectrum of the compound $[Mn(CO)_5Br]$,[6]}; (*ii*) i.r. and Raman spectra of the compound $[Mn(CO)_5(O_2CCF_3)]$, *vide infra*, showed no evidence for any $Mn_2(CO)_{10}$ impurity; and (*iii*) dimanganese species have been identified as thermal-decomposition products of the compound $[Mn(CO)_5(O_2CCF_3)]$.[1] Subsequent decomposition of $Mn_2(CO)_{10}$ agreed with that reported for the pure compound.[7]

TABLE 1

Mass spectrum of the compound $[Mn(CO)_5(OCOCF_3)]$

	m/e	Intensity *	Assignment
(A)	390	20	$Mn_2(CO)_{10}{}^+$
(B)	362	5	$Mn_2(CO)_9{}^+$
(C)	334	1	$Mn_2(CO)_8{}^+$
(D)	308	40	$[Mn(CO)_5(OCOCF_3)]^+$
(E)	280	10	$[Mn(CO)_4(OCOCF_3)]^+$
(F)	252	40	$[Mn(CO)_3(OCOCF_3)]^+$
(G)	250	10	$Mn_2(CO)_5{}^+$
(H)	239	20	$[Mn(CO)_5(OCO)]^+$
(I)	224	70	$[Mn(CO)_2(OCOCF_3)]^+$
(J)	222	20	$Mn_2(CO)_4{}^+$
(K)	196	100	$[Mn(CO)(OCOF_3)]^+$
(L)	195	60	$Mn(CO)_5{}^+$
(M)	194	10	$Mn_2(CO)_3{}^+$
(N)	168	90	$Mn(OCOCF_3)^+$
(O)	167	20	$Mn(CO)_4{}^+$
(P)	139	60	$Mn(CO)_3{}^+$
(Q)	111	80	$Mn(CO)_2{}^+$
(R)	110	30	$Mn_2{}^+$
(S)	102	40	$Mn(COF)^+$
(T)	99	40	$Mn(OCO)^+$
(U)	83	100	$Mn(CO)^+$
(V)	74	90	MnF^+
(W)	69	90	$CF_3{}^+$
(X)	55	100	Mn^+
(Y)	44	90	$CO_2{}^+$

* Relative to the parent-ion peak = 100.

Metastable peaks.

m/e	Transition	*m/e*	Transition
254	(D) → (E)	144	(K) → (N)
227	(E) → (F)	126	(I) → (N)
205	(D) → (F)	124	(D) → (J)
185	(D) → (H)		and/or
171	(I) → (K)		(D) → (L)
163	(D) → (I)	91	(D) → (N)
159	(H) → (L)		

A value of 300 ± 15 was obtained for the molecular weight of the compound $[Mn(CO)_5(O_2CCF_3)]$ (calc. 308)

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[6] C. D. Garner and B. Hughes, unpublished work.

[7] J. Lewis, A. R. Manning, J. R. Miller, and J. M. Wilson, *J. Chem. Soc.* (*A*), 1966, 1663.

dissolved in acetone. However, in dichloromethane a value of 440 ± 20 was obtained. The ^{19}F n.m.r. spectrum of the compound [$Mn(CO)_5(O_2CCF_3)$] consisted of a single peak at 76·2 p.p.m. upfield of $CFCl_3$, in the range 69·1 ± 78·5 p.p.m. upfield of $CFCl_3$ reported for other trifluoroacetate derivatives.[8] The failure of earlier workers [2] to observe any signal for ^{19}F resonances of the compounds [$Mn(CO)_5(O_2CR_f)$] ($R_f = CF_3$, C_2F_5, or n-C_3F_7) was attributed to coupling of the fluorine atoms with the ^{55}Mn nucleus ($I = 5/2$). This does not seem to be the explanation in view of the results obtained here.

1*s*-Electron binding energies of the carbonyl carbon and oxygen atoms were determined as 293·2 and 534·8 ± 0·2 eV, respectively, using *X*-ray photoelectron spectroscopy.[9] In view of the decomposition of the compound when an *X*-ray diffraction study was attempted (*vide infra*), it is possible that some decomposition may have occurred in these studies, however no complications were observed in this respect. These values are the highest of the binding energies reported [10] for the series of compounds [$Mn(CO)_5X$] [X = $Mn(CO)_5$, Me, Br, I, CF_3, or CF_3CO_2] and thus trifluoroacetate appears to be the most electrophilic of these substituents.

I.r. and Raman spectra of the compound [$Mn(CO)_5$-(O_2CCF_3)] were recorded for the crystalline solid and for solutions in dichloromethane, chloroform, and hexane. A summary of these results and those obtained in earlier studies [1,2] are presented in Table 2 and the carbonyl stretching-frequency region of the Raman spectrum of crystalline [$Mn(CO)_5(O_2CCF_3)$] is shown in the Figure. The Raman spectra of the various solutions, however, were poorly resolved because of fluorescence of the hexane solution in the laser beam and limited solubility of the compound [$Mn(CO)_5(O_2CCF_3)$] in the chlorinated solvents. Also, a slight amount of photodecomposition occurred on continued exposure to even a low-powered laser beam. Assignments of the wavenumbers presented in Table 2 are based on previous studies of [$Mn(CO)_5X$] complexes [11-15] and trifluoroacetate groups.[16,17]

The carbonyl stretching frequencies are in reasonable agreement with those reported by King and Kapoor,[2] except that the positions are some 10 cm^{-1} to higher

TABLE 2

Vibrational spectra (cm^{-1}) of the compound [$Mn(CO)_5(O_2CCF_3)$]

	Raman		I.r.			
Assignment [a]	Solid [b]	Hexane soln.[b]	Nujol mull [b]	Hexane soln.[b]	Nujol and C_4Cl_6 mull [c]	Cyclohexane soln.[d]
A_1 (eq.) C≡O str.	2 153vs	2 145vs (pol.)	2 154w	2 148w	2 170sh	2 136w
A_1 (eq.) ^{13}C≡O str.	2 144sh					
B_1 (eq.) C≡O str.	2 097vs	2 094s (depol.)		2 098wv		2 088w
B_1 (eq.) ^{13}C≡O str.	2 088sh					
E (eq.) C≡O str.	2 067wv		2 063sh	2 068vs	2 070s	
	2 051vw	2 056vw	2 052s			2 054vs
A_1 (ax.) C≡O str.	2 026s				2 025s	
	2 004m	2 004m (depol.)	2 002s,b	2 009s		1 997s
					1 711sh	
CO_2 asym. str.	1 695w		1 680s	1 689m	1 687s	1 686m
					1 645sh	
			1 582vw	1 587vw	1 589w	1 587w
				1 455vw		
CO_2 sym. str.	1 416m		1 410m	1 420w	1 410m	1 411m
			1 205sh	1 205sh		
CF_3 str.	1 192w		1 187s	1 191s	1 190vs	1 189s
			1 148s	1 150s	1 150vs	1 154s
					883vw	
			848w	850w	844m	852m
C–C str.			840sh	842w	836w	
OCO def.			790w	795m	785m	794m
CF_3 bend			728m	731m	722m	732m
CF_3 bend			625s,b	630s,b		
MnCO bend			607s	611w		
MnCO bend			538m	540w		
CF_3 bend			525sh	530w		
CCO γ bend			500w	508w		

I.r. bands were also observed at 461w, 392s, 298w, and 276w cm^{-1} for the compound mulled in Nujol. s = Strong, m = medium, w = weak, vw = very weak, sh = shoulder, b = broad, pol. = polarised, and depol. = depolarised.

[a] ν(C≡O) assigned assuming C_{4v} symmetry for the molecule; str. = stretch, asym. = asymmetric, sym. = symmetric, and def. = deformation. [b] This work. [c] Ref. 1., [d] Ref. 2.

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[8] C. D. Garner and B. Hughes, *Adv. Inorg. Chem. Radiochem.*, to be published.

[9] C. Nordling and K. Siegbahn, *Rev. Roumaine Phys.*, 1966, **11**, 797.

[10] J. A. Connor, M. B. Hall, I. H. Hillier, W. N. E. Meredith, M. Barber, and Q. Herd, *J.C.S. Faraday II*, 1973, 1677; M. Barber, J. A. Connor, I. H. Hiller, and W. N. E. Meredith, to be published.

[11] D. M. Adams, *J. Chem. Soc.*, 1964, 1771.

[12] J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, 1965, **4**, 389.

[13] H. D. Kaesz, R. Bau, D. Hendrickson, and J. M. Smith, *J. Amer. Chem. Soc.*, 1967, **89**, 2844.

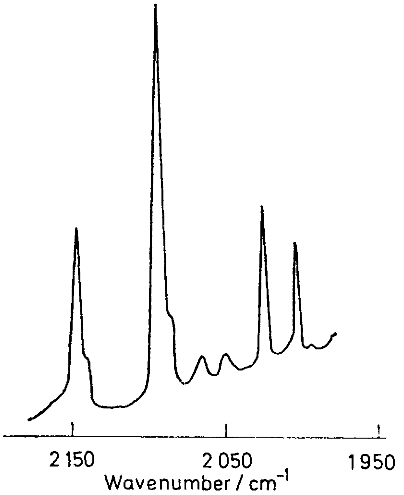
[14] I. J. Hyams and E. R. Lippincott, *Spectrochim. Acta*, 1969, **25A**, 1848.

[15] D. K. Ottesen, H. B. Gray, L. H. Jones, and M. Goldblatt, *Inorg. Chem.*, 1973, **12**, 1051.

[16] R. L. Redington and K. C. Lin, *Spectrochim. Acta*, 1971, **27A**, 2445.

[17] P. J. Miller, R. A. Butler, and E. R. Lippincott, *J. Chem. Phys.*, 1972, **57**, 5451.

energy, but these frequencies differ markedly from those reported by Green *et al.*[1] This latter spectrum resembles those of more fully substituted pentacarbonylmanganese derivatives. The carbonyl stretching frequencies have been assigned assuming C_{4v} molecular symmetry. However, the ' inert-gas formalism ' requires that the trifluoroacetato-group donates one electron-pair to the manganese and this would imply that this ligand is co-ordinated in a unidentate manner; thus C_{4v} symmetry will only be a good approximation if there is completely free rotation of the trifluoroacetato-group about the Mn–O bond. The weak appearance of the ' i.r.-forbidden ' B_1 stretching mode (2 098 cm^{-1}) in solution is probably due to the period of rotation of this group being of the same order as the timescale for absorption of i.r. radiation.[12]



Raman spectrum of $[Mn(CO)_5(O_2CCF_3)]$ crystals

In the solid-state spectrum the bands assigned on the basis of C_{4v} molecular symmetry will be split because of intermolecular interactions and thus unit-cell rather than molecular symmetry should be considered. These intermolecular interactions are doubtless responsible for splitting of E and A_1 (axial) carbonyl-stretching modes of C_{4v} symmetry observed in the Raman spectrum of the solid (Figure) but not in the i.r. or Raman solution spectra. A crystal-structure determination has been attempted, but the compound decomposed on exposure to X rays.[18] In the absence of crystal-structure data, further analysis of the solid-state spectrum is difficult.

In chloroform solution carbonyl overtone and combination bands were observed at 4 002s, 4 076sh, 4 105sh, and 4 147s cm^{-1}, which may be assigned in terms of the fundamental frequencies in this medium [A_1(ax.) 2 021s, E 2 064vs, B_1 2 097vw, and A_1(eq.) 2 150w cm^{-1}] as $2A_1$(ax.), A_1(ax.) + E, A_1(ax.) + B_1, and A_1(ax.) + A_1(eq.) with $E + B_1$, respectively. The positions of the carbonyl i.r. stretching frequencies in hexane solution afford 16·4 and 17·6 mdyn Å^{-1} for the Cotton–Kraihanzel[19] force constants of the axial and equatorial carbonyl C–O bonds, respectively. These force constants lead to values of Graham's $\Delta\sigma$ and $\Delta\pi$ parameters[20] of 1·3 and —0·5 mdyn Å^{-1}, respectively indicating that, relative to methyl, trifluoroacetate is a strong π-donor and σ-acceptor and in these respects resembles chloride ($\Delta\sigma$ 1·3 and $\Delta\pi$ —0·6 mdyn Å^{-1}). Vibrational bands observed between 1 800 and 625 cm^{-1} were assigned to modes of the trifluoroacetato-group. The similarity of the spectra, recorded by Green *et al.*[1] on the one hand and those recorded by King and Kapoor[2] and ourselves on the other, in this region is not surprising since vibrational frequencies of this group, with the exception of carboxylato-stretches, occur at very similar positions irrespective of the mode and extent of co-ordination.

TABLE 3

Yield, m.p., elemental analyses, and salient i.r.-stretching wavenumbers of $[Mn(CO)_3L_2(O_2CCF_3)]$ compounds

Compound	Yield (%)	M.p. (t/°C)		Analyses (%) C	H	Other	Carbonyl stretching wavenumbers (cm^{-1})	Symmetric carboxylato-stretching wavenumber (cm^{-1})
$[Mn(CO)_3(py)_2(O_2CCF_3)]$	94	160—161	Found	43·8	2·5	N 6·7	2 040vs, 1 952vs, 1 914vs	1 688m
			Calc.	43·9	2·5	6·8		
$[Mn(CO)_3(bipy)(O_2CCF_3)]$	89	168—169	Found	43·8	2·1	N 6·8	2 038vs, 1 949vs, 1 925vs	1 683m
			Calc.	44·0	2·2	6·6		
$[Mn(CO)_3(phen)(O_2CCF_3)]$	91	178—179	Found	46·7	1·9	N 6·7	2 039vs, 1 952vs, 1 926vs	1 690m
			Calc.	47·2	1·8	6·5		
$[Mn(CO)_3(PPh_3)_2(O_2CCF_3)]$	82	145—155	Found	63·4	4·1	Mn 7·7	2 039m, 1 952vs, 1 914s	1 681m
		(decomp.)	Calc.	63·5	3·9	8·0		
$[Mn(CO)_3(dpe)(O_2CCF_3)],CHCl_3$	89	176—178	Found	50·3	3·3	Cl 13·3	2 039m, 1 952vs, 1 914s	1 681m
			Calc.	50·3	3·2	13·4		
$[Mn(CO)_3(dpe)(O_2CCF_3)]$	88	176—178	Found	57·1	3·8	P 9·3	2 029m, 1 959vs, 1 916vs	1 680m
			Calc.	57·2	3·7	9·5		
$[Mn(CO)_3(pte)(O_2CCF_3)]$	84	122—123	Found	45·4	2·8	S 13·6	2 049vs, 1 972vs, 1 938vs	1 690m
			Calc.	45·8	2·8	12·9		
$[Mn(CO)_3(dte)(O_2CCF_3)]$	87	137—139	Found	32·2	3·7	S 15·5	2 046vs, 1 959vs, 1 922vs	1 688m
			Calc.	32·4	3·5	15·9		

py = Pyridine, bipy = 2,2′-bipyridyl, phen = 1,10-phenanthroline, dpe = 1,2-bis(diphenylphosphino)ethane, pte = 1,2-bis-(phenylthio)ethane, and dte = 1,2-bis(diethylthio)ethane; vs = very strong, s = strong, m = medium. The spectra were recorded in chloroform solution and the data are in good agreement with those already published.[3]

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[18] A. T. McPhail, personal communication.

[19] F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, 1962, **84**, 4432.

[20] W. A. G. Graham, *Inorg. Chem.*, 1968, **7**, 315.

The asymmetric carboxylato-stretching frequency at *ca.* 1 690 cm^{-1} is consistent with unidentate co-ordination of the trifluoroacetato-group.[8]

Disubstituted compounds of pentacarbonylhalogenomanganese have been prepared by the reaction between $[Mn(CO)_5X]$ (X = Cl, Br, or I) and the ligand, L, at 120 °C in the absence of solvent,[5] and also by reactions in organic solvents.[21] These latter studies showed that such reactions initially afford the *fac*-$[Mn(CO)_3L_2X]$ isomer which isomerises to the *mer*-compound in solution, the extent of this isomerisation increasing with increasing size of L. These isomers may be readily identified by the pattern of their i.r. carbonyl stretching frequencies; the former having three strong bands of approximately equal intensity and the latter a weak, very strong, strong, sequence from high to low energy. I.r. data presented in Table 3 thus indicate that the $[Mn(CO)_3L_2(O_2CCF_3)]$ compounds isolated in this study are the *fac*-isomer [L_2 = (pyridine)$_2$, 2,2′-bipyridyl, 1,10-phenanthroline, 1,2-bis(phenylthio)ethane, and 1,2-bis(diethylthio)ethane] and the *mer*-isomer [L_2 = (triphenylphosphine)$_2$ and 1,2-bis(diphenylphosphino)ethane]. The nature of the substitution reactions of $[Mn(CO)_5(O_2CCF_3)]$ thus resembles those of pentacarbonylhalogenomanganese compounds.

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[21] R. J. Angelici, F. Basolo, and A. J. Poë, *J. Amer. Chem. Soc.*, 1963, **85**, 2215.