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AN ELECTRON DIFFRACTION DETERMINATION OF THE MOLECULAR STRUCTURE OF TRIFLUOROSILYLMANGANESE PENTACARBONYL IN THE GAS PHASE

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Summary

The molecular structure of trifluorosilylmanganese pentacarbonyl, SiF_3-$Mn(CO)_5$, in the gas phase has been determined by electron diffraction. The principle parameters are: r_a (C—O) 113.1(3); r(Mn—C)$_{av}$ 186.0(6); r(Mn—Si) 236.0(7); r(Si—F) 158.3(4) pm: $\angle$ (F—Si—F) 112.5(4); $\angle$ (C_{ax}—Mn—C_{eq}) 92.9(4)°.

Introduction

In compounds containing elements such as silicon or germanium bonded to a transition metal, there is the possibility of $(d \rightarrow d)\pi$ interactions involving vacant $3d$ or $4d$ orbitals of the Main Group atoms, and filled d levels of the transition metal atoms. If this type of interaction does occur, then the reduction, in both size and energy, of the silicon $3d$ orbitals on replacement of a silyl group by a trifluorosilyl group, should lead to an increase in the extent of the π-bonding.

We have therefore determined the gas phase molecular structure of trifluorosilylmanganese pentacarbonyl by electron diffraction and have compared it with the gas phase structures of silylmanganese pentacarbonyl [1] and silylcobalt tetracarbonyl [2], and with the solid phase structure of trifluorosilylcobalt tetracarbonyl [3]. In silyl- and trifluorosilyl-cobalt tetracarbonyl there is a large difference (15 pm) between the two silicon—cobalt bond lengths, and this has been explained in terms of more extensive $(d \rightarrow d)\pi$ bonding in the trifluorosilyl compound. It is interesting to determine whether a similar difference exists for the silicon—manganese bonds in silyl- and trifluorosilyl-manganese pentacarbonyl.

The He(I) photoelectron spectra of silylmanganese pentacarbonyl [4] and trifluorosilylmanganese pentacarbonyl [5] indicate that the main effect of changing the silyl substituents from protons to fluorine atoms is to strengthen the manganese—silicon σ bond: π interaction seems to be unimportant. This would again lead to a shortening of the manganese—silicon bond.

Experimental

A sample of trifluorosilylmanganese pentacarbonyl was prepared by treating trifluorosilane with dimanganese decacarbonyl at 450 K and three atmospheres pressure [6]. The products were collected at 77 K and purified by fractional condensation. The purity was checked spectroscopically.

Scattering intensities were collected photographically on Agfa—Gevaert Replica 23 plates using a Balzer's KD.G2 Eidigraph in Oslo [7, 8]. Two nozzle-to-plate distances were used, 580 mm (5 plates) and 190 mm (4 plates), giving data over a range of the scattering variable, s, of about 10 to 360 nm^{-1}. The compound sample was maintained at 334 K and the nozzle at 343 K for the 580 mm exposures: temperatures of 338 and 348 K were used for the 190 mm exposures.

Apart from data reduction as far as uphill curves, all data reduction and refinements were carried out on an ICL 4-75 computer at the Edinburgh Regional Computing Centre using established programmes [9,10]. The complex scattering factors of Cox and Bonham [11] were used.

Table 1 shows weighting points (used in setting up the off-diagonal weight matrix for least-squares refinements), correlation parameters and scale factors. The electron wavelength, determined from the diffraction pattern of powdered zinc oxide, was 5.846(3) pm.*

Molecular model

Local C_{4v} symmetry was assumed for the manganese pentacarbonyl group, and local C_{3v} symmetry for the trifluorosilyl group. Free rotation about the silicon—manganese bond was also assumed, as the 12-fold barrier is almost certainly very low. All carbon—oxygen bonds were assumed to be of equal length.

The molecular structure was therefore described in terms of silicon—fluorine, silicon—manganese, carbon—oxygen and average manganese—carbon

TABLE 1

WEIGHTING FUNCTIONS, SCALE FACTORS AND CORRELATION PARAMETERS

Camera height (mm)	s (nm^{-1})	s_{min} (nm^{-1})	sw_1 (nm^{-1})	sw_2 (nm^{-1})	s_{max} (nm^{-1})	p/h	Scale factor
190	4	48	76	300	340	0.4549	0.979 ± 0.021
580	2	24	36	120	130	0.4902	0.836 ± 0.021

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* Studies of benzene and CO_2 show that the wavelength determined in this way gives distances about 0.1% too small. Allowance for this has been made in calculating distances quoted in this paper.

bond lengths, the difference between axial and equatorial manganese—carbon bond lengths, and the three angles F—Si—F, Mn—C_{eq}—O_{eq} and C_{ax}—Mn—C_{eq}.

Refinements

All bonded distances and their amplitudes of vibration, except u(C—O), refined satisfactorily, as did the C_{eq}—Mn—C_{ax} and F—Si—F angles. Owing to the overlap of many peaks in the radial distribution curve (Fig. 1) certain amplitudes of vibration had to be refined in groups. Even then, not all groups of amplitudes could be refined simultaneously, and so several amplitudes were fixed at typical values, as shown in Table 2.

The difference between axial and equatorial manganese—carbon bond lengths and the Mn—C_{eq}—O_{eq} angle were both determined by doing series of

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TABLE 2

MOLECULAR PARAMETERS FOR $SiF_3Mn(CO)_5$[a]

(a). Independent distances and amplitudes[b]				
r1	(C—O)	113.1(3)	3.5 (fixed)	
r2	(Mn—C)$_{av}$	186.0(6)	5.4(5)	
r3	(Mn—Si)	236.0(7)	7.6(7)	
r4	(Si—F)	158.3(4)	4.7(5)	
(b). Dependent distances, amplitudes and shrinkage corrections applied[c]				
d5	(Mn—C_{eq})	185.6(8)	5.4	0.00
d6	(Mn—C_{ax})	187.6(8)	5.4	0.00
d7	(Mn · · · O_{eq})	298.1(13)	6.8(5)	0.59
d8	(Mn · · · O_{ax})	300.1(13)		0.59
d9	(C_{eq} · · · C_{eq})	369.4(20)	11.4(14)	1.33
d10	(C_{eq} · · · O_{eq})	481.5(24)		2.27
d11	(O_{eq} · · · O_{eq})	593.4(28)		3.42
d12	(C_{eq} · · · C_{eq})	270.5(12)	14.6(fixed)[d]	0.25
d13	(C_{eq} · · · C_{ax})	261.9(15)		0.25
d14	(O_{eq} · · · O_{eq})	430.5(16)	25.0(fixed)[d]	1.40
d15	(O_{eq} · · · O_{ax})	420.5(19)		1.40
d16	(C_{eq} · · · O_{eq})	360.4(15)	15.9(9)	0.82
d17	(C_{ax} · · · O_{eq})	358.0(13)		0.82
d18	(C_{eq} · · · O_{ax})	350.5(18)		0.82
d19	(Si · · · C_{ax})	422.2(15)	11.9 (28)	1.43
d20	(Si · · · O_{ax})	534.3(20)	13.2	2.38
d21	(Si · · · C_{eq})	292.5(16)	15.3 (14)	0.28
d22	(Si · · · O_{eq})	372.5(20)	18.5	0.90
d23	(Mn · · · F)	330.1(8)	10.5(7)	0.59
d24	(F · · · C_{ax})	503.5(14)	16.7(fixed)	2.27
d25	(F · · · O_{ax})	611.5(18)	16.7(fixed)	3.42
d26	(F · · · F)	253.2(12)	9.9(fixed)	0.07
	(F · · · C_{eq})	Between 295 and 439		
	(F · · · O_{eq})	Between 329 and 528		
(c). Angles				
< 1	(F—Si—F)	112.5(4)		
< 2	(C_{ax}—Mn—C_{eq})	92.9(4)		
< 3	(Mn—C_{eq}—O_{eq})	178.3(fixed)		

[a] All distances and amplitudes are given in pm; angles in degrees. [b] Independent distances are r_a. [c] Shrinkages applied were the same as those used for $SiH_3Mn(CO)_5$ [1]. [d] Derived from calculated amplitudes of vibration for $Mn_2(CO)_{10}$ [13].

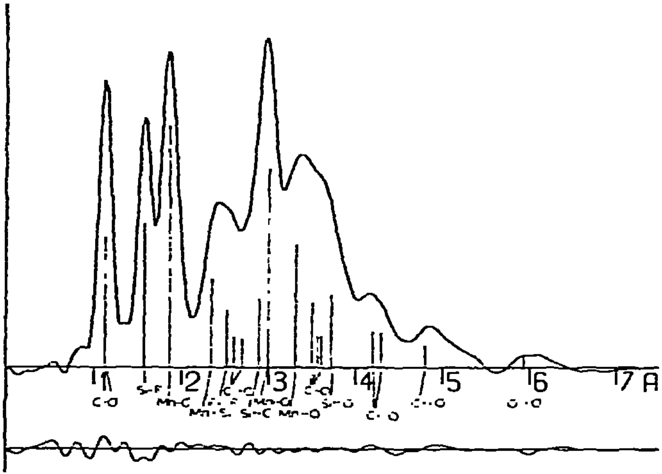

Fig. 1. Radial distribution curve, $P(r)/r$, for $SiF_3Mn(CO)_5$, showing principal interatomic distances. Before Fourier inversion the data were multiplied by $s \exp[-0.0015s^2/(Z_{Mn}-f_{Mn})(Z_O-f_O)]$.

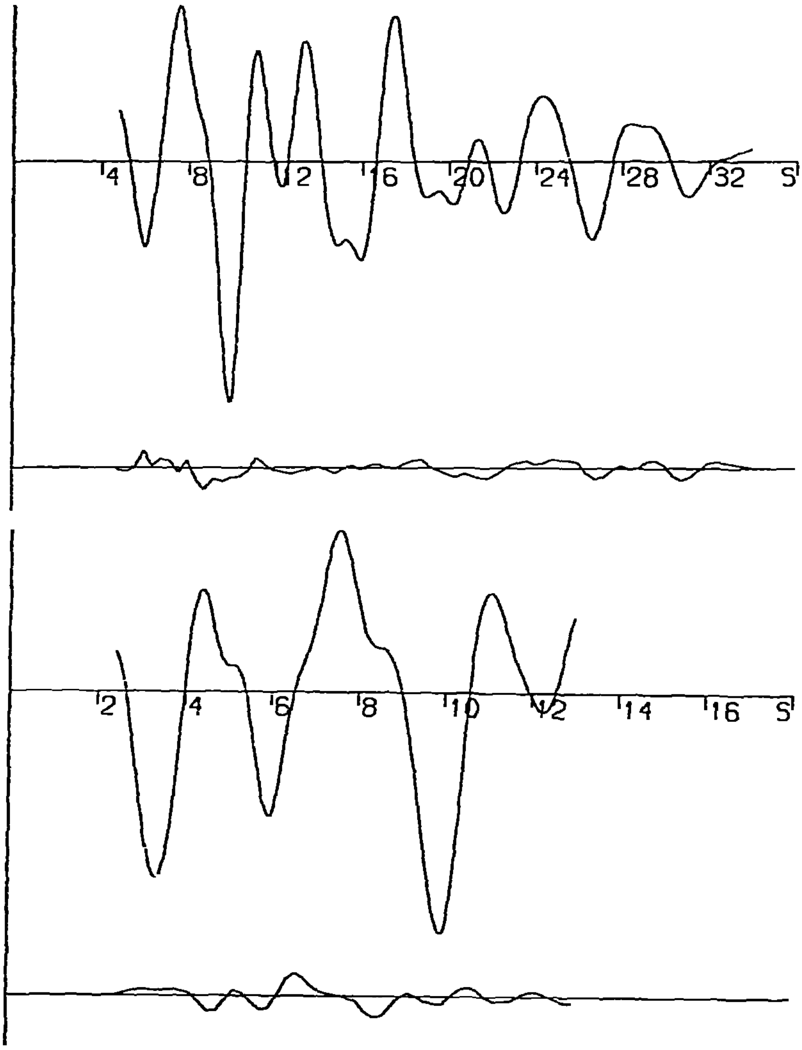

Fig. 2. Observed and final weighted difference molecular scattering intensities for $SiF_3Mn(CO)_5$.

TABLE 3

LEAST SQUARES CORELATION MATRIX MULTIPLIED BY 100

*r*1	*r*2	*r*3	*r*4	< 1	< 2	*u*3	*u*4	*u*5	*u*7	*u*9	*u*16	*u*10	*u*21	*u*23	*k*1	*k*2
100	16	12	13	−25	−17	9	−4	4	6	12	−32	0	−24	−25	3	−8
	100	24	44	−43	−57	6	3	−11	2	5	−40	1	−9	−11	−8	−8
		100	1	−62	28	−10	−11	−5	−10	1	2	−11	12	7	−22	−13
			100	−5	−38	−10	−2	−18	−1	−11	2	3	−16	4	−15	−16
				100	−39	10	5	0	29	−30	37	13	−39	4	8	13
					100	−30	−4	8	−30	19	2	−13	48	−2	2	1
						100	9	7	19	−3	5	6	−20	1	20	12
							100	11	15	2	−1	5	3	−3	34	7
								100	21	8	3	6	11	−1	53	25
									100	−3	11	8	−42	1	41	18
										100	−17	−32	5	−9	11	6
											100	−8	−1	58	3	6
												100	1	−2	12	5
													100	33	12	8
														100	−4	−7
															100	26
																100

refinements with different fixed values of these parameters and comparing R factors. Once determined in this way, these parameters were fixed at their optimum values in subsequent refinements.

Under these conditions refinement converged to give the parameters of Table 2, with an R factor (R_G) of 0.129. The estimated standard deviations quoted include random errors determined in the least squares analysis, and allowances for systematic errors and any constraints applied during refinement [12]. The final least-squares correlation matrix is given in Table 3. Molecular intensity data, shown diagrammatically in Fig. 2, is available from the authors on request.

Discussion

In silylmanganese pentacarbonyl the silicon—manganese bond length is 240.7 ± 0.5 pm [1], whereas in the trifluoro derivative the length is 236.0 ± 0.7 pm. This shortening is consistent both with $(d \rightarrow d)\pi$ bonding, as suggested for the cobalt carbonyl compounds [2], and with the purely σ effects that have been proposed, based on evidence from photoelectron spectra. It is unfortunate that the molecular structures provide no evidence that enables us to say that the observed shortening is due mainly to one of the two effects.

Despite this, there are features of interest in the structure of trifluorosilylmanganese pentacarbonyl. In particular, it should be noted that the difference in silicon—manganese distances in the compounds under consideration is only about 5 pm, whereas the difference for the cobalt tetracarbonyls is more than 15 pm. This difference cannot entirely be due to phase effects (the trifluorosilylcobalt tetracarbonyl structure is for a crystal) or to the rather poor data used for silylcobalt tetracarbonyl. Steric crowding should be considered, since at least one fluorine—carbon distance must be shorter in trifluorosilylmanganese pentacarbonyl (292 pm) with C_{3v} and C_{4v} groups, than in trifluorosilylcobalt tetracarbonyl (ca. 316 pm) where all the fluorines are staggered with respect to the equatorial carbonyl groups. However, the C_{eq}—M—C_{ax} angles in the trifluorosilyl compounds are the same as in other manganese and cobalt carbonyl derivatives, and the F—Si—F angle is smaller in the cobalt compound than in the manganese one. One would expect crowding of the fluorine atoms to show itself in changes of valence angles, before bond lengths were affected significantly.

We therefore suggest that the differences may be due to the larger number of d electrons in cobalt than in manganese, making the silicon—cobalt bond length more susceptible to changes of substituent at silicon. More data is required if this is to be confirmed: we intend to carry out further studies of structures of carbonyl derivatives, so that the nature of silicon—metal bonds may be better understood.

References

1 D.W.H. Rankin and A. Robertson, J. Organometal. Chem., 85 (1975) 225.
2 A.G. Robiette, G.M. Sheldrick, R.N.F. Simpson, B.J. Aylett and J.A. Campbell, J. Organometal. Chem., 14 (1968) 279.
3 K. Emerson, P.R. Ireland and W.T. Robinson, Inorg. Chem., 9 (1970) 436.

4 S. Cradock, E.A.V. Ebsworth and A. Robertson, J. Chem. Soc. Dalton Trans., (1973) 22.
5 S. Cradock and A. Robertson, unpublished results.
6 M.E. Redwood, B.E. Reichert, R.R. Schrieke and B.O. West, Aust. J. Chem., 26 (1973) 247.
7 O. Bastiansen, R. Graber and L. Wegmann, Balzer's High Vacuum Report, 25 (1969) 1.
8 W. Zeil, J. Haase and L. Wegmann, Z. Instrumentenk., 74 (1966) 84.
9 G.C. Holywell, D.W.H. Rankin, B. Beagley and J.M. Freeman, J. Chem. Soc. A, (1971) 785.
10 D.M. Bridges, G.C. Holywell, D.W.H. Rankin and J.M. Freeman, J. Organometal. Chem., 32 (1971) 87.
11 H.L. Cox and R.A. Bonham, J. Chem. Phys., 47 (1967) 605.
12 M.A. MacGregor and R.K. Bohn, Chem. Phys. Lett., 11 (1971) 29.
13 J. Brunvoll and S.J. Cyvin, Acta Chem. Scand., 22 (1968) 2709.