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A Fluoroalicyclic-Bridged Ditertiary Phosphine Derivative of Iron. The Crystal Structure of $(\pi\text{-}C_5H_5)Fe(CO)(f_6fos)SnMe_3$ [1]

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Received March 1, 1971

The crystal structure of $(\pi\text{–}C_5H_5)Fe(CO)(f_6fos)SnMe_3$ where the ligand, fe_6fos, is $(PPh_2)\overline{C=C(PPh_2)(CF_2)_2C}F_2$ has been determined from three-dimensional X-ray data collected by counter methods. The structure has been refined by full-matrix least-squares techniques (tin, iron and three fluorine atoms with anisotropic thermal parameters) to a conventional R factor of 8.0 per cent for the 1703 observed reflections. The compound crystallizes in the triclinic space group A1 with four formula units in a cell of dimensions a = *10.381 (1), b = 22.382(4),* c = *15.459(2) Å, $\alpha = 101.48(1)$, $\beta = 92.13(2)$, and $\gamma = 83.26(2)$°. The hexacoordinate iron atom is bonded to a carbonyl group, a cyclopentadienyl group, a trimethyltin group and one phosphorus atom of the f_6fos group. The iron-tin bond length of 2.562(41 Å is slightly longer than the bonded distance in cyclopentadienyldicarbonyliron triphenyltin (average value of 2.536(3) Å for the Fe–Sn length). The conformation and structural properties of the five-membered fluorocarbon ring are compared to that found for the chelating f_6fos ligand as found in the anion* $\{cis\text{–}Rh(CO)_2Cl_2\}^-$.

Introduction

The reactions of metal carbonyls with fluoroalicyclic compounds have resulted in a variety of organometallic compounds with unusual structural features.[2] The fluoroalicyclic ring may be σ-bonded to a metal atom such as in $(ffos)Fe(CO_3$[3] where ffos is the ligand $(PPh_2)\overline{C=C(PPh_2)CF_2C}F_2$, or have a tridentate linkage as in the dimethylarsino complex (ffars) $\{Fe(CO)_3\}_2$.[4]

Controversy has arisen as to whether the tin-iron bonds[5] include any multiple bond character. The varied physical techniques available have allowed different structural aspects to be investigated separately for a range of substituted Sn–Fe species. Infrared spectra for the series of complexes $(\pi\text{–}C_5H_5)$-$Fe(CO)_2SnX_3$ (X = Cl, Ph, and Me),[6] far-infrared spectra of the compounds $(\pi\text{–}C_5H_5)Fe(CO)_2SnX_3$ (X = Ph and Me),[7] Mössbauer studies of $Fe(CO)_4(Cl)SnX_3$ (X = Cl and Br)[8] and related compounds,[9] and X-ray crystal structures for the series of complexes $(\pi\text{–}C_5H_5)$-$Fe(Co)_2SnX_3$ (X = Cl, Br, Ph, and Me)[10,11] have been reported. Cullen and co-workers[5] have extended this work by preparing a number of new substitution compounds by replacement of one carbonyl group by phosphine, arsine, and stibine derivatives from the parent compound $(\pi\text{–}C_5H_5)Fe(CO)_2SnX_3$ (X = Cl, Ph, and Me). Using Mössbauer, n.m.r. and i.r. data, they have been able to formulate an alternate bonding scheme for the iron-tin bond.

This paper will examine, in detail, the crystal structure of the compound of composition $(\pi\text{–}C_5H_5)Fe(CO)$-$(f_6fos)SnMe_3$, where f_6fos is the ditertiary phosphine compound, 1,2-bis (diphenylphosphino)hexafluorocyclopentene, which is capable of acting as monodentate, bidentate or tridentate ligand. This structure was undertaken in order to gain information about the bonding between the iron and tin atoms, the iron to f_6fos ligand linkage, as well as the conformation of the f_6fos ligand.

Experimental Section

A sample of the compound $(\pi\text{–}C_5H_5)Fe(CO)(f_6fos)$-$SnMe_3$, whose preparation has been described elsewhere,[5] was kindly supplied by Dr. W.R. Cullen. A red crystal was cleaved to give a roughly cubic fragment whose maximum dimensions in the directions *a*, *b*, and *c* respectively are $0.22 \times 0.18 \times 0.16$ mm^3 and was mounted with the longest dimension along the rotation axis. This single crystal yielded the complete diffraction data (obtained over a period of four weeks).

Weissenberg photographs of the *hk0–hk5* nets using CrKα radiation, together with MoKα precession photographs of the *h0ℓ and 0kℓ* zones, showed absences for hkℓ and k + ℓ = 2n + 1. This information combined with the Laue group indicated the space group A1 or A$\bar{1}$. It was found to be more convenient to work in the *A* centered cell which was used throughout our work.

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[1] Presented in part at the American Crystallographic Association Meeting, Ottawa, Canada, August, 1970.

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[5] W.R. Cullen, J.R. Sams, and J.A.J. Thomson, *Inorg. Chem.*, *10*, 843 (1971) (and references therein).

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[7] N.A.D. Carey and H.C. Clark, *Inorg. Chem.*, *1*, 94 (1968).

[8] R. Kummer and W.A.G. Graham, *Inorg. Chem.*, *1*, 1208 (1968).

[9] C.H.W. Jones and E. Wood, private communication.

[10] R.F. Bryan, *J. Chem. Soc.* (A), 192 (1967).

[11] R.F. Bryan, P.T. Greene, G.A. Melson, and P.F. Stokely, *Chem. Comm.*, 722 (1966).

Crystal Data. Cell dimensions were determined by least-squares refinement of twenty-four high-angle reflections whose 2θ values were accurately measured at 22°C on the diffractometer. An A - centered triclinic cell of dimensions: $a=10.831(1)$, $b=22.382(4)$, $c=15.459(2)$ Å, $\alpha=101.48(1)$, $\beta=92.13(2)$, and $\gamma=83.26(2)°$ was obtained with $\lambda=0.70926$ Å for $MoK\alpha_1$ radiation.

All results reported here are for the A-centered cell with general (fourfold) positions x,y,z; –x,–y,–z; x,½+y,½+z; –x,½–y,½–z, which were used for the the structure determination. $V=3646.9$ Å^3, $Dm=1.64(4)$ g cm^{-3} in ethanol (Berman density balance determination), $Z=4$, $Dx=1.57$ g cm^{-3}, $F(000)=1740$, and $\mu(MoK\alpha=12.5$ cm^{-1}.

Data Collection. The crystal was mounted on a manual Picker four-circle diffractometer equipped with our own semi-automation so that the weak (0,5,3) plane was perpendicular to the Φ circle. Reflection intensities for the unique set of data were measured using niobium filtered MoKα radiation and a scintillation detector with pulse-height analysis. Measurements for the inner set of data with $2\theta \leqslant 31°$ were made at a rate of 4° min. using a 1.4° take-off angle with a symmetrical θ-2θ scan of 1.5° width. Stationary background counts were measured at both ends of the scan (each for half the scan period). The detector was positioned 24 cm from the crystal and the symmetrically variable aperture device was arranged so that the detector was approximately 4.0 mm high and 4.0 mm wide. An outer set of data for the range $31° < 2\theta < 36°$ was measured using the stationary crystal-stationary counter method with 22.5 second counts. Background for these outer reflections was estimated in four different directions in reciprocal space and a curve as a function of θ only satisfactorily described the results obtained. Accordingly each reflection was corrected for background and those reflections which were at least 2.0σ above background were considered observed. The two sets of data were initially combined using two scale factors determined by measurement of a number of reflections by both techniques. Of the 2515 reflections measured, 1703 were observed. Three standard reflections were measured every 4 hours and retained a consistency within ±7% over the entire data collection. Lorentz and polarization factors were applied and the structure factors were calculated in the usual manner. Since the linear absorption coefficient with molybdenum radiation is 12.5 cm^{-1} and the maximum difference in the transmission coefficients between extreme cases is of the order of 3% (0.82-0.80), no absorption correction was applied to the data.

Structure Determination. The combination of vector peaks obtained in the unsharpened three-dimensional Patterson map[12] computed with the inner set of data indicated that the space group is $A\bar{1}$. This choice was confirmed by the successful structure analysis. From this Patterson function, it was possible to assign approximate positions to the tin and iron atoms. Full-matrix least-squares refinement[13] of these atomic positions and of individual isotropic temperature factors (assuming an initial value of 3.0 Å^3) were carried out yielding an unweighted R_1 value[14] of 0.363. A series of electron-density difference maps[12] based on these atomic positions and other atomic positions as they were revealed in successive maps produced positional parameters for all the atoms of the molecule in the asymmetric unit.

The molecular structure was refined in sections making use of fixed atom contributions. With all the non-hydrogen atoms allowed appropriate coordinates and isotropic thermal parameters, the structure was refined to an unweighted R_1 of 0.081 for the 1124 observed reflections of the inner set.

Using the full set of collected data, a difference map was computed at this stage and prominent features were interpreted as suggesting that the tin, iron and three of the fluorine atoms were vibrating anisotropically. The R_1 and R_2 values for the 1703 observed reflections of the full set after two cycles of least-squares including anisotropic thermal parameters for these atoms were respectively 0.080 and 0.095. All reflections received a constant weight ($w=0.040$) such that the standard deviation of an observation of unit weight was 1.01. The final parameter shifts were all less than 0.20 standard deviations. Thoroughout the refinement, the structure factor agreement was examined as a function of both $|F_o|$ and sinθ. At no time were significant trends in $\Sigma w(|F_o|-|F_c|)^2$ found. A final electron density difference map did not show any residual peaks larger than 0.23 e/Å^3.

Scattering factors used were those calculated on the Relativistic Dirac-Slater model[15] for the tin atom and self-consistent-field values[16] for the remainder. Full allowance was made for anomalous scattering[17] by the tin and iron atoms.

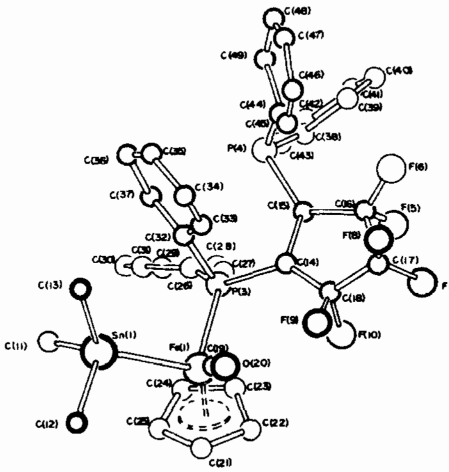

Figure 1. The molecular structure of (π-C_5H_5)Fe(CO)($f_6$fos)-$SnMe_3$.

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[12] Program used for computation was « FORDAP, Crystallographic Fourier Summation with optional numeric or alphanumeric plotting and peak searching. » This program was obtained from the University of Canterbury (N.Z.) and originated from Dr. A. Zalkin, University of California, Berkeley.

[13] Program « BUCILS, Crystallographic Structure Factor and Full-Matrix Least-Squares. » This version is essentially the same as CUCILS 360/44 version from the University of Canterbury (N.Z.).

[14] R_1 is defined as $\Sigma|Fo|-|Fe|/\Sigma|Fo|$ and R_2 is defined as equal to $[\Sigma w(|Fo|-|Fc|)^2/\Sigma wFo^2]^{1/2}$.

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

[16] International Tables for X-ray Crystallography, Vol. III, The Kynoch Press, Birmingham, England, 1962.

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

Table I. Final Positional and Thermal Parameters for $(\pi\text{—}C_5H_5)Fe(CO)(f_6fos)SnMe_3$.

Atom	x	y	z	B,Å^2
Sn(1)	0.1889(2)[a]	−0.0757(1)	0.1840(2)	
Fe(2)	0.2302(3)	0.0265(2)	0.1462(3)	
P(3)	0.3181(6)	0.0633(3)	0.2711(5)	3.4(2)
F(4)	0.4688(7)	0.1492(3)	0.4590(5)	4.3(2)
F(5)	0.4401(15)	0.2688(7)	0.3375(11)	6.5(4)
F(6)	0.3270(15)	0.2859(8)	0.4536(12)	6.9(4)
F(7)	0.2247(20)	0.3007(7)	0.2720(13)	
F(8)	0.1304(17)	0.2626(9)	0.3649(13)	
F(9)	0.1213(16)	0.1766(7)	0.2341(13)	
F(10)	0.2891(15)	0.1933(7)	0.1823(12)	6.8(4)
C(11)	0.3506(28)	−0.1422(14)	0.1728(20)	6.5(8)
C(12)	0.0589(28)	−0.1183(14)	0.0940(20)	6.4(8)
C(13)	0.1079(30)	−0.0833(15)	0.3057(22)	7.5(8)
C(14)	0.3108(23)	0.1479(11)	0.3034(17)	4.0(6)
C(15)	0.3693(22)	0.1806(11)	0.3757(16)	3.7(6)
C(16)	0.3418(27)	0.2493(13)	0.3731(20)	5.6(7)
C(17)	0.2312(28)	0.2561(14)	0.3156(20)	5.1(7)
C(18)	0.2351(31)	0.1924(14)	0.2577(22)	6.2(8)
C(19)	0.0878(26)	0.0482(12)	0.1785(17)	4.6(6)
C(20)	−0.0197(20)	0.0654(10)	0.1970(14)	7.2(5)
C(21)	0.1883(30)	0.0121(15)	0.0097(21)	6.9(8)
C(22)	0.2296(28)	0.0688(14)	0.0361(20)	6.0(7)
C(23)	0.3516(26)	0.0625(13)	0.0748(19)	5.4(7)
C(24)	0.3883(25)	−0.0002(12)	0.0727(18)	5.0(7)
C(25)	0.2869(26)	−0.0350(13)	0.0254(19)	5.5(7)
C(26)	0.4901(20)	0.0390(10)	0.2619(14)	2.6(5)
C(27)	0.5660(24)	0.0800(11)	0.2435(17)	4.2(6)
C(28)	0.6890(26)	0.0578(13)	0.2247(18)	5.1(7)
C(29	0.7362(23)	−0.0022(12)	0.2298(17)	4.4(6)
C(30)	0.6592(25)	−0.0413(12)	0.2490(18)	4.9(7)
C(31)	0.5305(27)	−0.0214(13)	0.2673(19)	5.6(7)
C(32)	0.2625(24)	0.0451(11)	0.3734(17)	4.2(6)
C(33)	0.1398(25)	0.0714(12)	0.3996(18)	4.8(7)
C(34)	0.0902(29)	0.0587(14)	0.4740(22)	6.8(8)
C(35)	0.1629(29)	0.0326(14)	0.5333(20)	6.1(7)
C(36)	0.2888(25)	0.0039(12)	0.5075(19)	5.2(7)
C(37)	0.3368(25)	0.0186(12)	0.4316(19)	5.0(7)
C(38)	0.6001(24)	0.1976(12)	0.4765(18)	4.7(6)
C(39)	0.5920(26)	0.2550(13)	0.5283(19)	5.4(7)
C(40)	0.7059(30)	0.2847(14)	0.5360(21)	6.5(8)
C(41)	0.8133(30)	0.2563(15)	0.4986(21)	6.7(8)
C(42)	0.8166(30)	0.1972(15)	0.4505(22)	7.0(8)
C(43)	0.7097(31)	0.1649(15)	0.4376(22)	7.1(8)
C(44)	0.3710(24)	0.1790(11)	0.5558(17)	4.1(6)
C(45)	0.2437(27)	0.1902(13)	0.5529(19)	5.6(7)
C(46)	0.1754(27)	0.2051(13)	0.6302(20)	5.6(8)
C(47)	0.2348(29)	0.2111(4)	0.7117(21)	5.8(8)
C(48)	0.3609(28)	0.1990(13)	0.7165(20)	5.3(7)
C(49)	0.4338(26)	0.1810(13)	0.6381(20)	5.3(7)

Anisotropic thermal parameters. The form of the anisotropic ellipsoid is

$$\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\ \beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)$$

	β_{13}	β_{22}	β_{33}	β_{12}	β_{13}	β_{13}
Sn(1)	0.0107(3)	0.0020(1)	0.0067(2)	−0.0011(1)	0.0001(1)	0.0003(1)
Fe(2)	0.0074(5)	0.0024(1)	0.0055(3)	−0.0009	−0.0001(3)	0.0007(1)
F(7)	0.0343(37)	0.0018(5)	0.0095(14)	−0.0012(10)	−0.0066(18)	0.0020(6)
F(8)	0.0151(24)	0.0047(7)	0.0094(14)	0.0030(10)	−0.0008(15)	−0.0000(8)
F(9)	0.0134(21)	0.0029(5)	0.0136(16)	−0.0006(8)	−0.0063(15)	0.0020(7)

[a] Standard deviations of the least significant figures are given in parentheses here and in subsequent tables.

The final atomic positions and their standard deviations are given in Table I, and the observed and calculated structure factors are given in Table II; F_{calc} is given the sign of the real component and the magnitude of the structure amplitude.

Discussion

Description of Structure. The compound, $(\pi\text{—}C_5H_5)Fe(CO)(f_6fos)SnMe_3$, whose configuration is shown in Figure 1 consists of discrete molecules arranged in the *A*-centered triclinic unit cell (Figure 2) such that one molecule comprises the asymmetric unit. The iron atom is bonded to a carbonyl group, a cyclopentadienyl group, a trimethyltin group and one phosphorus atom of the $f_6$fos gorup. It appears that the molecule may be derived by direct substitution of the $f_6$fos ligand for one carbonyl group in the parent compound, $(\pi\text{—}C_5H_5)Fe(CO)_2SnMe_3$.

Table II. Measured and calculated structure factors for (π—C_5H_5)Fe(CO)($f_6$fos)$SnMe_3$. The unobserved reflections which were not significantly above background have been indicated by a *negative* F_{obs}. (Scale = $0.2F_{absolute}$)

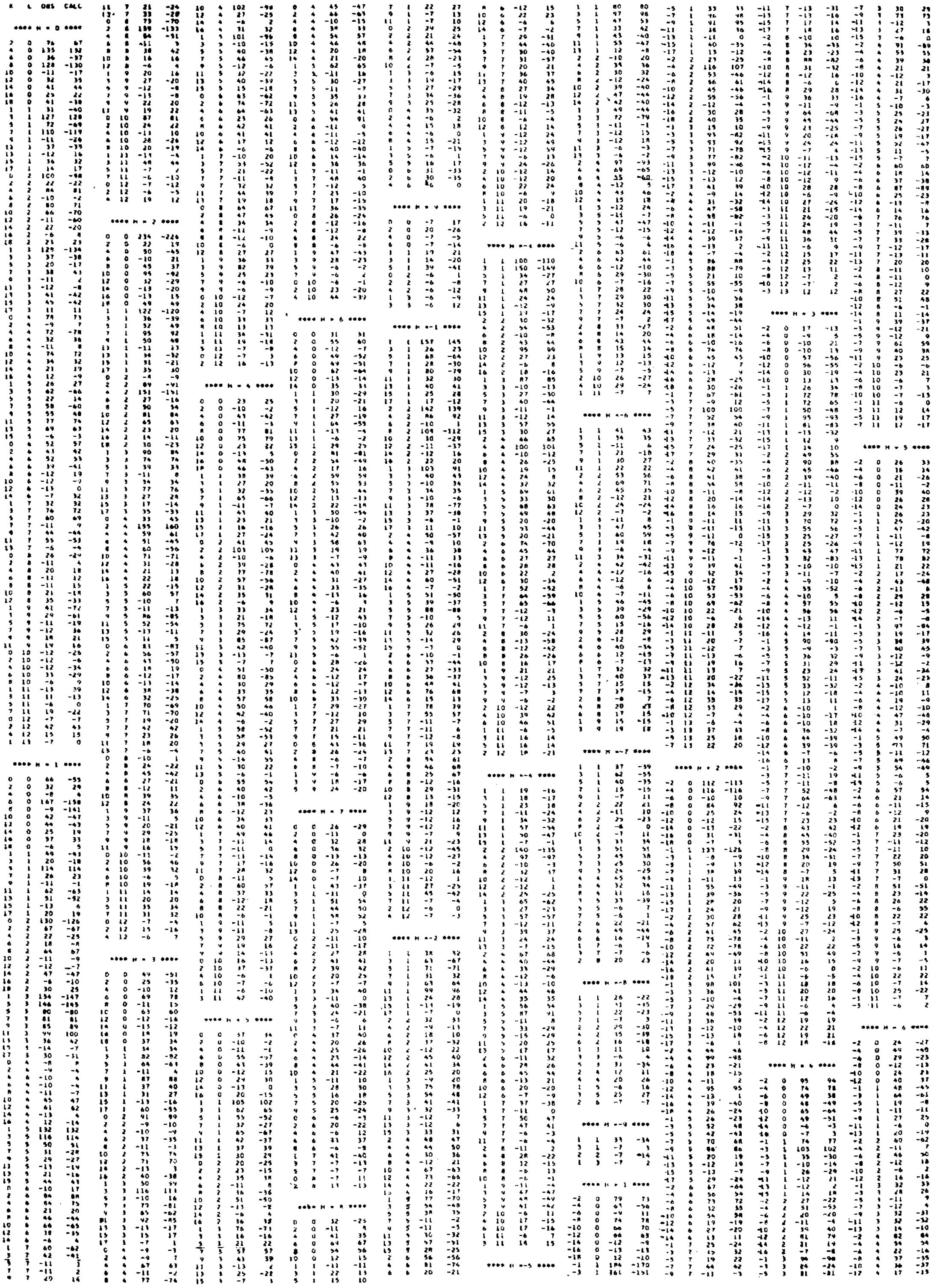

Table III. (Continued)

-1	5	57	54
-3	5	-11	-2
-5	5	-11	5
-7	5	-12	-4
-9	5	20	24
-11	5	15	18
-2	6	44	-37
-4	6	-12	-11
-6	6	-12	9
-8	6	39	43
-10	6	54	57
-1	7	-11	-8
-3	7	53	-50
-5	7	-6	0
-7	7	41	42
-9	7	16	14
-2	8	-6	7
-4	8	16	20
-6	8	-6	0
-8	8	-7	-7
-1	9	-6	2
-3	9	-7	13
-5	9	-7	8
-7	9	-7	-8
-2	10	-7	12
**** H = 7 ****			
-2	0	56	-51
-4	0	37	-28
-6	0	28	-21
-8	0	21	24
-10	0	27	20
-1	1	42	-39
-3	1	-12	-22
-5	1	28	30
-7	1	-6	6
-9	1	-7	-13
-11	1	19	-20
-2	2	35	37
-4	2	22	21
-6	2	-12	15
-8	2	-7	-3
-10	2	31	-26
-1	3	51	48
-3	3	61	62
-5	3	-12	11
-7	3	22	-22
-9	3	26	-24
-11	3	-7	-11
-2	4	-12	18
-4	4	-12	10
-6	4	-6	0
-8	4	26	28
-10	4	34	38
-1	5	33	-33
-3	5	42	-41
-5	5	22	-26
-7	5	-6	-3
-9	5	30	27
-2	6	45	-48
-4	6	19	-19
-6	6	-6	9
-8	6	-7	8
-1	7	23	-21
-3	7	-7	18
-5	7	-6	-7
-7	7	-7	-9
-2	8	11	15
-4	8	-7	6
**** H = 8 ****			
-2	0	34	-31
-4	0	-7	4
-6	0	19	22
-8	0	-6	-4
-1	1	44	43
-3	1	17	26
-5	1	-6	8
-7	1	-7	14
-2	2	55	55
-4	2	28	27
-6	2	-7	-7
-8	2	25	-28
-1	3	24	27
-3	3	-6	11
-5	3	-6	-1
-7	3	-6	-6
-2	4	53	-59
-4	4	34	-36
-6	4	-6	-12
-1	5	21	-22
-3	5	35	-39
-5	5	17	-18
-2	6	18	17
-4	6	-7	2
**** H = 9 ****			
-2	0	29	33
-1	1	27	26
-3	1	31	33
-2	2	13	12
-1	3	38	-38
**** H = 0 ****			
1	-1	117	111
3	-1	43	38
5	-1	17	16
7	-1	20	19
9	-1	101	106
11	-1	-12	4
13	-1	24	27
15	-1	40	-39
17	-1	19	-15
19	-1	27	-24
2	-2	120	-105
4	-2	31	-36
6	-2	168	160
8	-2	103	111
10	-2	71	73
12	-2	40	33
14	-2	20	-22
16	-2	41	-40
18	-2	12	8
1	-3	123	-125
3	-3	-9	2
5	-3	46	46
7	-3	-11	27
9	-3	59	60
11	-3	-12	-20
13	-3	21	-25
15	-3	29	28
17	-3	23	23
19	-3	35	34
2	-4	-10	19
4	-4	100	93
6	-4	20	-17
8	-4	82	-87
10	-4	62	-67
12	-4	46	-41
14	-4	28	31
16	-4	37	43
18	-4	33	35
1	-5	86	91
3	-5	67	67
5	-5	58	-59
7	-5	73	-76
9	-5	117	-123
11	-5	34	-32
13	-5	-12	-17
15	-5	31	36
17	-5	19	17
2	-6	27	-29
4	-6	-11	-16
6	-6	47	-42
8	-6	-11	-10
10	-6	-11	-16
12	-6	57	53
14	-6	-13	-17
16	-6	32	-36
18	-6	35	-31
1	-7	-10	6
3	-7	39	-45
5	-7	28	-25
7	-7	32	30
9	-7	63	64
11	-7	-12	14
13	-7	-13	-12
15	-7	31	-33
17	-7	40	-45
2	-8	-11	-5
4	-8	81	80
6	-8	60	59
8	-8	67	48
10	-8	20	24
12	-8	-13	-16
14	-8	36	-35
16	-8	15	-11
1	-9	-12	-6
3	-9	21	21
5	-9	39	39
7	-9	64	55
9	-9	-12	-11
11	-9	-13	-4
13	-9	13	-12
15	-9	13	12
2	-10	22	17
4	-10	-12	-7
6	-10	43	-40
8	-10	-13	-20
10	-10	-13	-2
12	-10	31	31
14	-10	40	39
1	-11	30	29
3	-11	[illegible]	-21
5	-11	66	-43
7	-11	41	-34
9	-11	39	-35
11	-11	-6	-7
13	-11	13	9
2	-12	-6	-3
4	-12	-7	-5
6	-12	27	-25
8	-12	-6	11
10	-12	-7	9
1	-13	-7	-6
3	-13	26	-24
5	-13	-7	6
7	-13	13	32
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3	-1	13	-5
5	-1	94	-86
7	-1	43	21
9	-1	100	-97
11	-1	32	32
13	-1	22	39
15	-1	-13	5
17	-1	-6	-14
19	-1	38	-39
0	-2	74	65
2	-2	91	87
4	-2	94	-85
6	-2	29	24
8	-2	37	37
10	-2	77	84
12	-2	-11	14
14	-2	25	-23
16	-2	31	-35
18	-2	60	-54
1	-3	135	-141
3	-3	63	56
5	-3	-9	13
7	-3	128	142
9	-3	95	98
11	-3	49	47
13	-3	-12	11
15	-3	29	-31
17	-3	42	-41
19	-3	-7	13
0	-4	79	-90
2	-4	53	-59
4	-4	-9	-1
6	-4	78	79
8	-4	54	50
10	-4	17	16
12	-4	29	26
16	-4	48	50
18	-4	22	23
1	-5	-10	-7
3	-5	63	62
5	-5	-10	2
7	-5	-10	-12
9	-5	81	-83
11	-5	37	-37
13	-5	27	25
15	-5	44	44
17	-5	54	57
19	-5	33	32
0	-6	72	66
2	-6	118	116
4	-6	35	36
6	-6	60	-60
8	-6	75	-76
10	-6	55	-59
12	-6	23	-15
14	-6	-13	17
16	-6	30	26
18	-6	-7	2
1	-7	-10	2
3	-7	-10	2
5	-7	61	-61
7	-7	42	-44
9	-7	-11	-4
11	-7	20	16
13	-7	-13	25
15	-7	25	-26
17	-7	44	-42
0	-8	36	38
2	-8	-11	-9
4	-8	35	-41
6	-8	-10	1
8	-8	30	32
10	-8	39	37
12	-8	-13	7
14	-8	25	-15
16	-8	14	-12
1	-9	-11	-10
3	-9	-11	26
5	-9	47	62
7	-9	27	53
9	-9	-12	7
11	-9	-12	-4
13	-9	43	-41
15	-9	41	-39
0	-10	-11	-10
2	-10	-12	33
4	-10	-12	43
6	-10	26	52
8	-10	-12	38
10	-10	-12	-15
12	-10	12	-10
14	-10	-6	-3
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3	-11	-12	31
5	-11	-12	-7
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4	-12	34	-14
6	-12	27	-22
8	-12	28	-22
10	-12	-6	-2
12	-12	15	14
1	-13	-7	-7
3	-13	22	-17
5	-13	-7	-7
7	-13	29	-22
**** H = 2 ****			
1	-1	-7	-2
3	-1	77	80
5	-1	20	21
7	-1	120	-122
9	-1	81	-80
11	-1	35	-38
13	-1	25	-28
15	-1	28	24
17	-1	33	28
19	-1	-7	-1
0	-2	109	112
2	-2	22	-13
4	-2	54	-52
6	-2	105	-109
8	-2	48	-56
10	-2	50	-49
12	-2	-11	-4
14	-2	54	53
16	-2	22	-15
18	-2	20	-20
1	-3	19	20
3	-3	32	-37
5	-3	61	-68
7	-3	27	20
9	-3	37	42
11	-3	48	53
13	-3	-12	-15
15	-3	28	-27
17	-3	29	-29
19	-3	43	-41
0	-4	50	-52
2	-4	101	-105
4	-4	38	-44
6	-4	70	69
8	-4	95	100
10	-4	63	66
12	-4	18	5
14	-4	54	-56
16	-4	57	-58
18	-4	43	-44
1	-5	90	-90
3	-5	52	-38
5	-5	51	49
7	-5	76	72
9	-5	43	51
11	-5	-11	11
13	-5	-12	3
15	-5	20	-7
17	-5	24	19
19	-5	-7	4
0	-6	-10	-12
2	-6	-10	-10
4	-6	46	35
6	-6	38	-26
8	-6	53	-54
10	-6	73	-75
12	-6	-12	-4
14	-6	53	57
16	-6	-7	46
18	-6	57	54
1	-7	46	42
3	-7	36	40
5	-7	19	-13
7	-7	61	-60
9	-7	23	-27
11	-7	-12	-15
13	-7	-13	13
15	-7	43	44
17	-7	26	25
0	-8	19	29
2	-8	60	-63
4	-8	55	-53
6	-8	56	-52
8	-8	40	-38
10	-8	41	40
12	-8	21	22
14	-8	-14	-5
16	-8	47	-46
1	-9	-11	10
3	-9	31	-51
5	-9	45	-46
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9	-9	29	33
11	-9	-13	17
13	-9	-6	-5
15	-9	-6	-4
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2	-10	-11	-2
4	-10	-12	22
6	-10	26	28
8	-10	-12	-3
10	-10	-12	2
12	-10	18	-16
14	-10	37	-29
1	-11	-12	29
3	-11	-12	50
5	-11	-13	39
7	-11	-13	58
9	-11	-6	-4
11	-11	15	-19
13	-11	-7	-6
0	-12	-6	3
2	-12	-7	4
4	-12	37	36
6	-12	-6	5
8	-12	-6	-3
10	-12	-7	10
1	-13	-7	15
3	-13	-7	-7
5	-13	26	-26
7	-13	23	-20
**** H = 3 ****			
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3	-1	17	28
5	-1	58	65
7	-1	44	43
9	-1	26	-26
11	-1	74	-80
13	-1	43	-34
15	-1	35	37
17	-1	33	36
0	-2	38	-39
2	-2	15	12
4	-2	36	40
6	-2	-11	2
8	-2	61	-68
10	-2	37	-39
12	-2	-12	-12
14	-2	-12	-10
16	-2	43	39
18	-2	26	28
1	-3	59	64
3	-3	30	-30
5	-3	74	-74
7	-3	67	-73
9	-3	59	-60
11	-3	-11	-8
13	-3	37	43
15	-3	24	17
17	-3	32	-30
19	-3	31	-31
0	-4	48	44
2	-4	-10	13
4	-4	61	-62
6	-4	107	-100
8	-4	41	-35
10	-4	25	30
12	-4	21	-15
14	-4	-12	9
16	-4	26	-21
18	-4	21	-17
1	-5	54	-50
3	-5	29	-30
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7	-5	57	57
9	-5	72	71
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13	-5	41	-44
15	-5	42	-47
17	-5	44	-37
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2	-6	-10	-1
4	-6	-10	-2
6	-6	122	118
8	-6	50	49
10	-6	40	35
12	-6	30	-27
14	-6	24	-24
16	-6	-6	2
18	-6	-7	3
1	-7	17	12
3	-7	24	24
5	-7	50	48
7	-7	20	18
9	-7	62	-59
11	-7	19	-9
13	-7	-13	10
15	-7	34	29
17	-7	-7	25
0	-8	38	-35
2	-8	26	32
4	-8	26	-19
6	-8	65	-57
8	-8	35	-36
10	-8	22	-18
12	-8	-12	4
14	-8	35	37
16	-8	30	30
1	-9	44	-40
3	-9	43	-33
5	-9	55	-53
7	-9	35	-40
9	-9	-12	-13
11	-9	21	28
13	-9	24	24
15	-9	19	-16
0	-10	-12	4
2	-10	52	-36
4	-10	67	-58
6	-10	29	-25
8	-10	-13	12
10	-10	33	31
12	-10	-6	-3
14	-10	12	-6
1	-11	15	-11
3	-11	13	-7
5	-11	-6	6
7	-11	-6	4
9	-11	-6	-7
11	-11	-6	1
13	-11	33	-30
0	-12	11	-9
2	-12	19	22
4	-12	21	19
6	-12	23	32
8	-12	-7	15
10	-12	27	-25
**** H = 4 ****			
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3	-1	20	-17
5	-1	89	89
7	-1	36	40
9	-1	65	65
11	-1	39	43
13	-1	36	-38
15	-1	-14	-23
17	-1	13	10
0	-2	100	-97
2	-2	-9	13
4	-2	-10	2
6	-2	77	81
8	-2	41	41
10	-2	48	-50
12	-2	21	-28
14	-2	-13	-1
16	-2	26	28
18	-2	50	49
1	-3	-9	13
3	-3	32	30
5	-3	-9	12
7	-3	45	-37
9	-3	48	-51
11	-3	37	-14
13	-3	-13	0
15	-3	26	28
17	-3	-7	40
0	-4	71	69
2	-4	-10	10
4	-4	63	-53
6	-4	76	-74
8	-4	54	-56
10	-4	26	-30
12	-4	56	54
14	-4	63	62
16	-4	-6	7
18	-4	12	-1
1	-5	34	33
3	-5	-10	8
5	-5	97	-82
7	-5	61	-57
9	-5	-12	4
11	-5	-13	3
13	-5	-13	-10
15	-5	-7	-9
17	-5	26	-27
0	-6	-11	-10
2	-6	46	-46
4	-6	-11	14
6	-6	59	56
8	-6	40	39
10	-6	-11	14
12	-6	-13	0
14	-6	66	-64
16	-6	32	-31
1	-7	-11	-6
3	-7	29	23
5	-7	67	62
7	-7	46	48
9	-7	33	45
11	-7	43	-40
13	-7	30	-25
15	-7	22	-21
17	-7	-7	11
0	-8	-11	2
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4	-8	46	44
6	-8	58	48
8	-8	-12	10
10	-8	[illegible]	-27
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14	-8	19	19
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1	-9	33	33
3	-9	39	35
5	-9	-13	1
7	-9	24	-27
9	-9	-12	-7
11	-9	-6	-2
13	-9	23	24
15	-9	36	40
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2	-10	25	-22
4	-10	23	-16
6	-10	28	-24
8	-10	15	-13
10	-10	-7	9
12	-10	28	40
1	-11	22	-22
3	-11	42	-41
5	-11	39	-43
7	-11	-6	-9
9	-11	15	16
11	-11	-7	2
2	-12	18	-14
4	-12	-7	6
6	-12	-7	5
8	-12	-6	1
**** H = 5 ****			
1	-1	-9	-16
3	-1	-11	-2
5	-1	62	-59
7	-1	24	24
9	-1	43	47
11	-1	30	28
13	-1	-13	8
15	-1	33	-33
17	-1	48	-45
0	-2	-10	0
2	-2	21	-20
4	-2	40	49
6	-2	56	55
8	-2	74	75
10	-2	44	53
12	-2	-13	7
14	-2	52	-43
16	-2	-7	-4
1	-3	-10	-2
3	-3	45	42
5	-3	70	68
7	-3	87	86
9	-3	-12	13
11	-3	24	-25
13	-3	-13	-15
15	-3	-7	9
17	-3	35	36
0	-4	31	-27
2	-4	-10	5
4	-4	66	60
6	-4	19	-19
8	-4	-12	10
10	-4	23	-19
12	-4	-13	13
14	-4	27	26
16	-4	41	39
1	-5	38	34
3	-5	63	-61
5	-5	50	-53
7	-5	74	-69
9	-5	49	-49
11	-5	-13	11
13	-5	70	63
15	-5	36	30
17	-5	15	11
0	-6	20	14
2	-6	23	-12
4	-6	57	-49
6	-6	73	-75
8	-6	19	-17
10	-6	13	15
12	-6	24	-8
14	-6	11	9
16	-6	23	-23
1	-7	30	-27
3	-7	-12	-20
5	-7	-12	24
7	-7	25	25
9	-7	-12	15
11	-7	-12	5
13	-7	31	-27
15	-7	39	-38
0	-8	29	-24
2	-8	-13	-7
4	-8	-13	22
6	-8	49	47
8	-8	26	26
10	-8	-12	15
12	-8	34	-31
14	-8	32	-27
1	-9	33	28
3	-9	50	47
5	-9	34	35
7	-9	-13	15
9	-9	17	-19
11	-9	-6	-2
13	-9	-7	4
0	-10	22	22
2	-10	33	38
4	-10	23	24
6	-10	-7	-11
8	-10	12	-6
10	-10	17	-17
12	-10	-7	11
1	-11	-7	2
3	-11	14	-17
5	-11	-7	-1
7	-11	15	-15
9	-11	11	11
**** H = 6 ****			
1	-1	16	10
3	-1	-12	-3
5	-1	63	-65
7	-1	55	-58
9	-1	30	-29
11	-1	-13	9
13	-1	15	19
15	-1	12	-10
0	-2	50	50
2	-2	54	-49
4	-2	33	-31
6	-2	27	-26
8	-2	23	25
10	-2	52	50
12	-2	-13	6
14	-2	-7	-10
16	-2	53	-46
1	-3	18	-10
3	-3	35	-28
5	-3	44	49
7	-3	25	20
9	-3	50	53
11	-3	-13	9
13	-3	24	-22
15	-3	28	-27
0	-4	-11	2
2	-4	50	44
4	-4	48	46
6	-4	86	88
8	-4	-13	19
10	-4	-13	-11
12	-4	41	-43
14	-4	-7	-8
16	-4	11	10
1	-5	19	21
3	-5	56	50
5	-5	33	35
7	-5	-11	-3
9	-5	-13	-4
11	-5	-14	7
13	-5	-7	5
15	-5	46	44
0	-6	24	18
4	-6	-13	-56
6	-6	20	-19
8	-6	37	-30
10	-6	-13	4
12	-6	51	48
14	-6	47	51
1	-7	-12	-9
3	-7	-13	-13
5	-7	68	-65
7	-7	32	-32
9	-7	-13	0
11	-7	17	16
13	-7	12	10
0	-8	-6	-6
2	-8	39	-44
4	-8	-13	-2
6	-8	13	9
8	-8	17	15
10	-8	-6	-5
12	-8	12	-11
1	-9	14	-10
3	-9	-6	-8
5	-9	-7	18
7	-9	-6	11
9	-9	20	19
11	-9	20	-17
0	-10	-7	10
2	-10	24	21
4	-10	28	27
6	-10	22	23
8	-10	-7	-11
**** H = 7 ****			
1	-1	32	32
3	-1	-13	11
5	-1	25	-17
7	-1	40	-41
9	-1	37	-36
11	-1	29	-24
13	-1	16	16
0	-2	13	15
2	-2	-11	0
4	-2	27	-26
6	-2	47	-51
8	-2	45	-44
10	-2	-13	-1
12	-2	-7	6
14	-2	-6	-4
1	-3	-12	-17
3	-3	64	-59
5	-3	66	-65
7	-3	-13	4
9	-3	20	11
11	-3	22	16
13	-3	-7	-9
0	-4	19	-16
2	-4	-12	-17
4	-4	-11	-5
6	-4	-11	6
8	-4	32	22
10	-4	-7	9
12	-4	-7	-8
14	-4	40	-37
1	-5	22	22
3	-5	54	43
5	-5	52	46
7	-5	-13	43
9	-5	21	-17
11	-5	49	-40
13	-5	17	-18
0	-6	17	-13
2	-6	33	27
4	-6	84	85
6	-6	19	17
8	-6	20	20
10	-6	-6	4
12	-6	13	-9
1	-7	-6	6
3	-7	46	-42
5	-7	41	-41
7	-7	13	-11
9	-7	18	-23
11	-7	25	27
0	-8	12	8
2	-8	-6	-5
4	-8	36	-16
6	-8	-6	-54
8	-8	17	-10
10	-8	11	9
1	-9	26	-27
3	-9	20	-18
5	-9	-7	-10
7	-9	-7	3
**** H = 8 ****			
1	-1	31	-32
3	-1	34	30
5	-1	43	46
7	-1	32	30
9	-1	-6	2
11	-1	-7	1
0	-2	-6	9
2	-2	27	25
4	-2	-14	-9
6	-2	41	-36
8	-2	31	-29
10	-2	29	-27
12	-2	12	14
1	-3	-6	2
3	-3	-6	3
5	-3	32	-35
7	-3	59	-52
9	-3	17	-17
11	-3	-7	12
0	-4	-6	6
2	-4	17	-17
4	-4	45	-46
6	-4	15	10
8	-4	17	17
10	-4	18	16
1	-5	34	-38
3	-5	-6	-4
5	-5	-6	-3
7	-5	12	11
9	-5	24	24
0	-6	-6	0
2	-6	29	10
4	-6	18	17
6	-6	35	35
8	-6	-6	5
1	-7	-6	1
3	-7	32	33
5	-7	33	37
7	-7	-7	0
**** H = 9 ****			
1	-1	-6	10
3	-1	-7	-3
5	-1	40	35
7	-1	33	33
0	-2	-7	-32
2	-2	-7	10
4	-2	30	32
6	-2	40	40
1	-3	31	33
3	-3	-7	9
5	-3	-7	2
7	-3	17	-17
2	-4	-6	-1
4	-4	14	-15

Interatomic bond lengths and angles are given as Table III. The R.M.S. amplitudes of vibration of those atoms refined anisotropically are listed in Table IV. The angles between the principal axis of vibration of the tin atom and the vector formed between the tin and iron atoms is 30°. This would indicate that the direction of least motion is approximately parallel to the tin-iron bond. This not the case for the iron atom where the corresponding angle is 62° However, the iron atom has significantly smaller amplitudes of vibration than the tin atom and its vibration is nearly isotropic. This would suggest that the most appropriate correction for thermal motion would assume the tin atom to « ride »[18] on the iron atom giving a corrected bond distance of 2.568 Å. However, since this correction is small and not important to our arguments, the uncorrected Sn–Fe length of 2.562(4) Å will be used throughout this discussion.

The Trimethyltin Group. The mean Sn–CH_3 bond distance of 2.14(3) Å is slightly shorter than the average 2.18 Å observed for tetramethyltin and trimethyltin halides,[19] but falls within the range of lengths found in other tin compounds as summarised by Schempler.[20]

The tin-carbon bond distance in the compound under study is longer than the mean values 2.07(6) Å (cation) and 2.11(5) Å anion found for the Sn–C bonds in $\{Me_2SnCl,terpyridyl\}^+$ $\{Me_2SnCl_3\}^-$.[21] In the latter compound it was argued from second-order hybridisation considerations,[22] that there is maximum s–character in the Sn–C bonds. By an analogous interpretation of ^{119}Sn and ^{57}Fe Mössbauer spectra as well as proton n.m.r. spectra, Cullen and co-workers[5] report a decrease in s–character in the Sn–C bonds in $(\pi\text{–}C_5H_5)Fe(CO)(f_6fos)SnMe_3$ and related compounds.

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(18) W.R. Busing and H.A. Levy, *Acta Cryst.*, *17*, 142 (1964).

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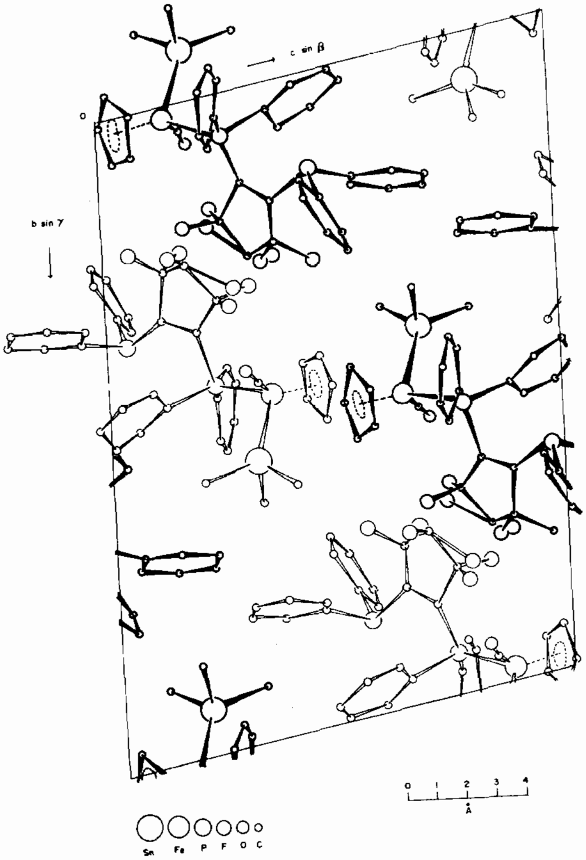

Figure 2. The crystal structure of (π-C_5H_5)Fe(CO)($_6$fos)$SnMe_3$ viewed down the a* axis.

The tin atom has an approximate tetrahedral environment consisting of three methyl groups and a fourth position occupied by the iron atom. The inter tin-carbon bond angles average to 102.3(12)° which is reduced below the regular tetrahedral value. The average Fe–Sn–C angle is correspondingly increased to 115.9(9)°. These angles are similar to values reported for compounds of the type (π–C_5H_5)Fe(CO)-SnX_3[10,11] where X = Cl, Br, or Ph as shown in Table V. Cullen and co-workers[5] have suggested that an imbalance in the p-orbital charge density at the tin atom would result in a distortion from tetrahedral environment (this would imply[22] that the s–character has increased at the tin atom). However, this distortion may also be partly due to the different substituents attached to the tin atom. As seen from Table V, the Fe–Sn–X (and X–Sn–X) angles for the compound (π–C_5H_5)Fe$(CO)_2$$SnCl_3$ of 119.2(1)° (and 98.31 (1)°) are slightly larger (and smaller) than the corresponding angles of 115.9(9)° (and 102.3(12°) for the compound (π–C_5H_5)Fe(CO)($f_6$fos)$SnMe_3$. This would indicate that there is more s-character in the Sn–Fe bond in the former compound where a shorter bond has been observed. Certainly, the strongest tendency for a π–inductive effect would occur with the –$SnCl_3$ derivative where the more electronegative groups would make the d–orbitals of the tin atom more accessible to π–bonding[23] and would present an alternative argument for a shorter bond for the –$SnCl_3$ derivative.

The Geometry Around the Iron Atom. The configuration about the iron atom may be described as distorted octahedral (or tetrahedral) depending on the description of the π–bonding linkage to the cyclopentadienyl ring. The angles subtended at the iron atom by the covalently bonded atoms average 92.2 (10)° which would suggest a pseudo-octahedral geometry about the iron atom. Attainment of an inert gas configuration is still possible if, as is customary, the π–cyclopentadienyl ligand is considered tridentate, and then the complex may be regarded as a d^7 Fe^I derivative. If a "single bond" is drawn from the iron atom to the centroid of the ring, an approximate tetrahedral ararngement results. However, the average angle subtended at the iron atom by the centroid position is 123.1(10)° indicating considerable distortion.

The Iron-Tin Interaction. As noted by Graham and co-workers,[23] it has been customary to interpret bond shortening relative to single bond radii as indicative of multiple bond character. An appropriate covalent radius of tin may be taken as 1.39Å, which is half the Sn-Sn distance in $\{Sn(Ph)_2\}_6$.[24] No similar distance could be found for iron. The unbridged Fe-Fe linkage of mean 2.67Å reported in $Fe_3(CO)_{12}$[25] appears to be a long bond. While the single bond radii for low oxidation transition metals are in considerable doubt, using Pauling's single bond metallic radius of 1.17Å for iron,[26] and the above mentioned value for tin, then the Fe–Sn bond length of 2.562(4)Å in π(–C_5H_5)Fe(CO) ($f_6$fos)$SnMe_3$ is not significantly different from the sum of the covalent radii (2.57 Å) suggesting a single covalent bond.

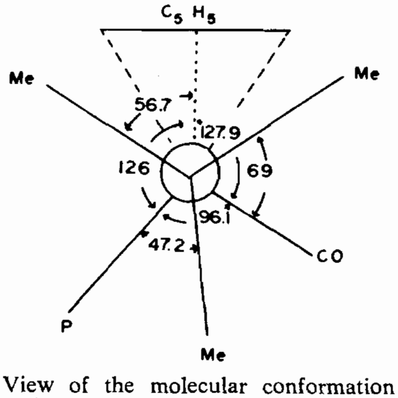

Figure 3. View of the molecular conformation down the Sn-Fe axis. The dotted line represents the projection of a vector from the iron atom to the centroid of the cyclo-pentadienyl ring.

The Fe–Sn bond distance in (π–C_5H_5)Fe(CO)($f_6$fos) $SnMe_3$ is significantly longer ($p<0.01$)[27] than the mean value of 2.536(3)Å found in the compound (π–C_5H_5)

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Table III. Bond Distances and Angles with Standard Deviations.

A. Intramolecular Distances (Å)

Sn-Fe distance	
Sn(1)-Fe(2)	2.562(4)
corrected [a]	2.568(4)
Sn-C(methyl distance	
Sn(1)-C(11)	2.11(3)
Sn(1)-C(12)	2.15(3)
Sn(1)-C(13)	2.15(3)
Fe-P($f_6$fos) distance	
Fe(2)-P(3)	2.175(8)
Fe-(CO) distance	
Fe(2)-C(19)	1.63(3)
C-O distance	
C(19)-O(20)	1.29(3)
Fe-C(π-C_5H_5) distances	
Fe(2)-CT(centroid)	1.71(3)
Fe(2)-C(21)	2.11(3)
Fe(2)-C(22)	2.11(3)
Fe(2)-C(23)	2.08(3)
Fe(2)-C(24)	2.05(3)
Fe(2)-C(25)	2.15(3)
P-C distances	
P(3)-C(14)	1.85(3)
P(4)-C(15)	1.84(3)
C-F($f_6$fos) distances	
C(16)-F(5)	1.37(3)
C(16)-F(6)	1.36(3)
C(17)-F(7)	1.31(3)
C(17)-F(8)	1.33(3)
C(18)-F(9)	1.34(3)
C(18)-F(10)	1.33(3)

C=C($f_6$fos) distance	
C(14)-C(15)	1.38(3)
C-C($f_6$fos) distance	
C(14)-C(18)	1.49(4)
C(15)-C(16)	1.54(4)
C(16)-C(17)	1.48(4)
C(17)-C(18)	1.52(4)
C-C(π-C_5H_5) distances	
C(21)-C(25)	1.46(4)
C(21)-C(22)	1.38(4)
C(22)-C(23)	1.43(4)
C(23)-C(24)	1.41(3)
C(24)-C(25)	1.50(4)
C-C(phenyl) distances	
C(26)-C(31)	1.39(3)
C(26)-C(27)	1.38(3)
C(27)-C(28)	1.39(3)
C(28)-C(29)	1.40(3)
C(29)-C(30)	1.36(3)
C(30)-C(31)	1.36(3)
C(32)-C(37)	1.36(3)
C(32)-C(33)	1.43(3)
C(33)-C(34)	1.38(4)
C(34)-C(35)	1.36(4)
C(35)-C(36)	1.47(4)
C(36)-C(37)	1.41(4)
C(38)-C(43)	1.41(4)
C(38)-C(39)	1.37(3)
C(39)-C(40)	1.46(4)
C(40)-C(41)	1.35(4)
C(41)-C(42)	1.38(4)
C(42)-C(43)	1.42(4)
C(44)-C(49)	1.42(3)
C(44)-C(45)	1.37(3)
C(45)-C(46)	1.37(3)
C(46)-C(47)	1.38(4)
C(47)-C(48)	1.36(4)
C(48)-C(49)	1.43(4)

B. Bond Angles, Deg

Trimethyltin angles	
C(11)-Sn(1)-C(12)	104.3(12)
C(11)-Sn(1)-C(13)	103.4(12)
C(12)-Sn(1)-C(13)	99.2(12)
C(11)-Sn(1)-Fe(2)	113.3(8)
C(12)-Sn(1)-Fe(2)	110.6(8)
C(13)-Sn(1)Fe(2)	123.7(9)
Angles centered on Fe(2)	
Sn(1)-Fe(2)-C(19)	83.5(9)
Sn(1)-Fe(2)-P(3)	97.1(2)
P(3)-Fe(2)-C(19)	96.1(10)
Sn(1)-Fe(2)-CT	115.4(10)
P(3)-Fe(2)-CT	126.0(10)
C(19)-Fe(2)-CT	127.9(10)
C(21)-Fe(2)-C(22)	38.1(10)
C(21)-Fe(2)-C(25)	40.1(10)
C(22)-Fe(2)-C(23)	40.1(10)
C(23)-Fe(2)-C(24)	39.8(10)
C(24)-Fe(2)-C(25)	41.9(10)
Cyclopentadienyl ring angles	
C(22)-C(21)-C(25)	108.9(28)
C(21)-C(22)-C(23)	110.1(27)
C(22)-C(23)-C(24)	108.5(25)
C(23)-C(24)-C(25)	107.1(23)
C(24)-C(25)-C(21)	105.1(24)

Angles for $f_6$fos group, angles centered on P(3)	
Fe(2)-P(3)-C(14)	117.1(9)
Fe(2)-P(3)-C(26)	118.2(7)
Fe(2)-P(3)-C(32)	118.6(9)
C(14)-P(3)-C(26)	102.6(10)
C(14)-P(3)-C(32)	100.2(11)
C(26)-P(3)-C(32)	109.0(11)
Angles centered on P(4)	
C(15)-P(4)-C(38)	103.8(11)
C(15)-P(4)-C(44)	98.9(12)
C(38)-P(4)-C(44)	104.0(12)
Angles for fluorocarbon ring	
C(14)-C(18)-C(17)	108.7(26)
C(14)-C(15)-C(16)	107.9(22)
C(15)-C(16)-C(17)	107.0(24)
C(16)-C(17)C(18)	102.0(26)
F(5)-C(16)-F(6)	104.9(23)
F(7)-C(17)-F(8)	109.4(27)
F(9)-C(18)-F(10)	104.9(26)
Angles for phenyl rings	
C(26)-C(31)-C(30)	116.0(24)
C(26)-C(27)-C(28)	117.0(23)
C(27)-C(28)-C(29)	121.7(25)
C(28)-C(29)-C(30)	119.8(24)

Table III. (Continued)

Carbonyl angle		C(32)-C(37)-C(36)	121.9(26)
Fe(2)-C(19)-O(20)	175.6(25)	C(32)-C(33)-C(34)	119.6(26)
		C(33)-C(34)-C(35)	121.4(30)
		C(34)-C(35)-C(36)	118.9(28)
		C(38)-C(43)-C(42)	115.4(29)
		C(38)-C(39)-C(40)	115.2(25)
		C(39)-C(40)-C(41)	122.4(29)
		C(40)C(41)-C(42)	119.5(30)
		C(44)-C(49)-C(48)	117.7(26)
		C(44)-C(45)-C(46)	120.8(27)
		C(45)-C(36)-C(47)	120.6(28)
		C(47)-C(48)-C(49)	121.0(28)

C. Intermolecular contacts less than 3.5Å.

F(5)-F(5),I	2.97(3)	I	1—x,½—y,½—z
F(5)-F(10),I	3.19(2)	II	x,½+y,½+z
F(6)-C(11),II	3.47(3)	III	—x,½—y,½—z
F(7)-C(28),I	3.40(3)	IV	x—1,y,z
F(7)-C(42),I	3.46(4)	V	1—x,—y,—z
F(7)-C(20),III	3.48(3)		
F(8)-F(9),III	3.36(2)		
F(10)-C(41),I	3.32(4)		
C(20)-C(28),IV	3.23(4)		
C(20)-C(29),IV	3.30(3)		
C(24)-C(24),V	3.36(5)		

[a] The quoted value is an interatomic distance averaged over thermal motion with the first atom assumed to ride on the second. This correction was applied according to a model used by W.R. Busing, K.O. Martin, and H.A. Levy in their program, « ORFFE, A fortran crystallographic function and error program. »

Table IV. Root-Mean-Square Amplitudes of Vibration (Å) along axes of the thermal ellipsoids.

Atom	Principal axis	Axis 1	Axis 2
Sn(1)	0.213(3)	0.254(3)	0.285(3)
Fe(2)	0.203(6)	0.240(6)	0.252(6)
F(7)	0.18(3)	0.30(2)	0.48(2)
F(8)	0.24(2)	0.32(2)	0.42(2)
F(9)	0.22(2)	0.27(2)	0.43(2)

Table V. A comparison of average molecular dimensions between the parent compound $(\pi\text{—}C_5H_5)Fe(CO)_2SnX_3$(A) and $(\pi\text{—}C_5H_5)Fe(CO)(f_6fos)SnX_3$(B).

	A			B
	Cl	Br	Ph	Me
Bond				
Sn-Fe	2.466(2)Å	2.465(3)	2.537(3)	2.562(4)
Sn-X	2.358(6)	2.50(1)	2.13(2)	2.14(3)
Fe-(CO)	1.78(2)	1.83(3)	1.72(1)	1.63(3)
C-O	1.13(2)	1.08(3)	1.17(2)	1.29(3)
Fe-C(π-C_5H_5)	2.10(2)	2.11(3)	2.10(1)	2.10(3)
Angle				
Fe-Sn-X	119.2(1)°	117.7(2)	113.4(2)	115.9(9)
X-Sn-X	98.3(1)	100.2(2)	105.2(2)	102.3(12)
Sn-Fe-CO	90.5(3)	89.1(6)	86.5(6)	83.5(9)

$Fe(CO)_2SnPh_3$.[10] To the author's knowledge, no structural data has been reported for the Fe—Sn bond in the parent compound, $(\pi\text{—}C_5H_5)Fe(CO)_2SnMe_3$. The former comparison appears to be a valid one if one takes into account other structural information. Identical values were obtained for the Mn—Sn bond in $Mn(CO)_5SnMe_3$ and $Mn(CO)_5SnPh_3$.[28] Moreover, the M—P distance in complexes containing the $f_6$fos ligand appears to be similar to other phosphine derivatives. The Rh—P distance in $\{Rh(f_6fos)_2\}^+$ $\{cis\text{-}Rh(CO)_2Cl_2\}$ [29] of mean value 2.291(6) Å is not significantly different from the average 2.323(8) Å found in $HRh(PPh_3)_3CO$.[30]

In the series of compounds $(\pi C_5H_5)Fe(CO)_2SnX_3$,[10,11] different conformations about the Fe–Sn bond

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Table VI. Equations of Best Mean Planes with Distances (Å) of Atoms from These Planes[a].

(1) Plane of cyclopentadienyl ring $0.4331X+0.1214Y-0.8931Z-0.8193=0$		(2) Plane formed by (C(14),C(15),C(16) and C(18) of the fluorocarbon ring $0.8041X+0.0769Y-0.5896Z-0.3204=0$	
Atom	distance from plane	Atom	distance from plane
C(21)	−0.03	C(14)	0.03
C(22)	0.01	C(15)	−0.03
C(23)	0.01	C(16)	0.02
C(24)	−0.03	C(18)	−0.02
C(25)	0.03	C(17)	−0.37
Fe(2)	−1.71		
(3) Plane of phenyl ring formed by C(26)-C(31) $-0.2206X-0.0932Y-0.9709Z+5.0294=0$		Max. devn. 0.017Å	Devn. of P(3) 0.225Å
(4) Plane of phenyl ring formed by C(32)-C(37) $-0.3919X-0.7828Y-0.4834Z+3.7554=0$		Max. devn. 0.059Å	Devn. of P(3) −0.043Å
(5) Plane of phenyl ring formed by C(39)-C(43) $-0.1677X+0.5409Y-0.8242Z+5.5102=$		Max. devn. 0.025Å	Devn. of P(4) −0.052Å
(6) Plane of phenyl ring formed by C(44)-C(49) $-0.1988X-0.9788Y-0.0234Z+3.2534=0$		Max. devn. 0.025Å	Devn. of P(4) 0.169Å

[a] The orthogonal system of axes has X along the a-axis, y in the (a,b) plane and Z along the c*-axis. Unit weights were used for all atoms forming the plane. All planes were calculated by « Program Meanplane, Calculation of weighted mean planes through atom groups, also atom deviations », written by M.E. Pippy and F.R. Ahmed at the National Research Council of Canada.

axis have been found. A comparison of the conformation shown in Figure 3 with values for the parent compound $(\pi C_5H_5)Fe(CO)_2SnX_3$ reveals that the conformation of the compound under study differs quite significantly. Bryan and coworkers[10,11] have suggested that substantial free rotation about the Fe—Sn bond is indicated and that this would be consistent with σ—bond formation which we propose as an adequate description of the Fe–Sn bond in $(\pi-C_5H_5)Fe(CO)(f_6fos)SnMe_3$. However, conformital restriction of rotation about the Sn—Fe bond *may* be due to steric factors rather than π—bond character, since, for a molecule of this type, the degenerate d—orbitals involved could provide a π—bond with no significant barrier to rotation.

The Iron-Carbon System. As was found for $(\pi-C_5H_5)Fe(CO)_2SnPh_3$, the Fe—C distance in the carbonyl system for the molecule $(\pi-C_5H_5)Fe(CO)(f_6fos)SnMe_3$ is also shorter than normal. An examination of the Fe—C distances in the cyclopentadienyl rings for the compounds quoted in Table V shows that they are all longer than usual but are internally consistent (average 2.10(3) Å). However, the iron to ring carbon distances are slightly shorter than the average value, 2.12 Å, found in double-ring complexes such as $\{\pi-C_5H_5)Fe(CO)_2\}_2$.[31]

The Fe—C and C—O distances are respectively shorter and longer in $(\pi-C_5H_5)Fe(CO)(f_6fos)SnMe_3$ than the similar distances in $(\pi-C_5H_5)Fe(CO)_2SnPh_3$. This comparison should be treated with caution owing to the comparatively poor precision of the carbon coordinates for the former compound. The slightly higher carbonyl stretching frequency for $(\pi-C_5H_5)Fe(CO)(f_6fos)SnPh_3$ (1931 cm^{-1} broad in cyclohexane solution)[10] as compared with $(\pi-C_5H_5)Fe(CO)(f_6fos)SnMe_3$ (1923 cm^{-1})[15] supports a stronger C—O bond in the former compound. Although the higher carbonyl stretching frequencies[6] for the compounds $(\pi-C_5H_5)Fe(CO)_2SnX_3$ (X = Ph or Me) having been measured in different solvents ($CHCl_3$ and CS_2 respectively), weakens arguments involving direct comparisons, it might be inferred that the Fe—(CO) bond should be stronger in $(\pi-C_5H_5)Fe(CO)(f_6fos)SnMe_3$.

The f₆fos Ligand. It is interesting to compare the bonding arrangement of the $f_6$fos group in a system which could be either monodentate, bidentate or tridentate. In the compound, $(\pi-C_5H_5)Fe(CO)({}_6fos)SnMe_3$, the $f_6$fos ligand is attached to the iron atom by a monodentate linkage which appears to have occurred due to the steric restrictions imposed by the bulky phenyl groups « propeller » arrangement about the phosphorus atoms together with the hindrance provided by the fluorocarbon bridging system. In this compound, the P—P separation is 3.60(1) Å, as compared to a value of 3.08 Å found in the compound, $f_6fosFe(NO)_2$.[32] In the compound $\{Rh(F_6fos)_2\}^+$ $\{cis-Rh(CO)_2Cl_2\}^-$ [29] where the $f_6$fos group complexes with the rhodium atom to give a bidentate linkage, the P—P bite is much shorter, 3.111(8) Å. This large change (0.5 Å) or flexing of the PCCP system in going from a mono- to bi-dentate systems should encourage a more cautious attitude in discussions involving bite restrictions in chelating species.

The five-membered fluorocarbon ring is in an envelope conformation in these two compounds. The mean plane through four of the ring carbon atoms is tabulated in Table VI. The atom, C(17), is significantly puckered out of this plane (0.37(3) Å).

The mean phosphorus-carbon bond length is 1.85 (3) Å as compared with value of 1.83(2) Å in the Rh complex. The average C—F and C—C lengths of 1.34 (3)Å and 1.50(4) Å respectively compare favourably with values 1.33(4) and 1.49(3) Å in the Rh complex. The C = C, fluorocarbon double bond length of 1.38(3) Å is somewhat longer than the value of 1.30 Å found in the Rh complex.

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All the intermolecular separations in Table IIIC correspond to van der Waals interactions; most of the shorter distances involve fluorine-fluorine or fluorine-carbon contacts.

The average of the twenty-four C—C distances within the phenyl rings is 1.39(3) Å identical to the accepted value for a phenyl ring. The carbon ring angles do not differ significantly from 120°. There are no significant deviations from planarity for the phenyl rings as seen from the mean planes in Table VI.

The Cyclopentadienyl Ring. The C—C lengths in the ring average to 1.44(4) Å which is larger than the corresponding mean value of 1.396(14) Å for $(\pi\text{—}C_5H_5)Fe(CO)_2SnPH_3$. However, it compares favourably with the value 1.431(5) Å found from an electron diffraction study of ferrocene.[33] The mean carbon ring angle of 107.9(28)° is close to the regular pentagonal value of 108°. The ring is planar, the maximum displacement of an atom from the plane being 0.03 Å (Table VI).

The iron atom is 1.71 Å from the cyclopentadienyl ring similar to the value of 1.73 Å found in $(\pi\text{—}C_5H_5\text{-}Fe(CO)_2SnPh_3$.[10] The cyclopentadienyl ring is normal to the Fe–ring centroid axis. The mean Fe—C distance of 2.10(3) Å is consistent with the average value, 2.10 Å, found in $(\pi\text{—}C_5H_5)Fe(CO)_2SnPh_3$[10] but longer than in ferrocene[34] (2.045 Å).

Acknowledgment. The authors wish to thank Dr. W. R. Cullen for providing the sample and for his interest in the work. We gratefully acknowledge the financial support of the National Research Council of Canada.

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