

Organometalloidal derivatives of the transition metals

XVII *. The crystal structure of bis(dicarbonyl- η^5 -cyclopentadienyliron)diphenyltin

László Párkányi

*Central Research Institute of Chemistry of the Hungarian Academy of Sciences, H-1525-Budapest,
P.O. Box 17 (Hungary)*

Keith H. Pannell * and Carlos Hernandez

Department of Chemistry, The University of Texas at El Paso, El Paso, TX 79968-0513 (U.S.A.)

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Abstract

The crystal structure of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2\text{SnPh}_2$ is reported for the first time. It has less tetrahedral distortion than previously erroneously reported and the new data provides a superior "fit" to Mössbauer data relating to the nature of the bonding in tetrahedral compounds and complexes of tin.

Introduction

The crystal structures of symmetric complexes of the general type $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2\text{SnR}_2$ (R = Cl (I), C₅H₅ (II), ONO (III), Me (IV) have been investigated by O'Connor and Corey [2] and Biryukov and Struchkov [3,4]. The results of these studies indicated a relationship between the Sn–Fe bond length and the electron-withdrawing ability of the R-groups. Thus, the bond length varies from 2.602(4) Å for R = Me to 2.492(8) Å for R = Cl.

In a related study, Bancroft et al. studied the Mössbauer spectra of a series of tin compounds of the general type A_2SnB_2 , and correlated these data with available structural data [5]. The results of such an analysis indicated that the various Mössbauer parameters related directly to the extent of s-character in the Sn–A and Sn–B bonds. In the tabulations they presented structural data for the complex

* For Part XVI see ref. 1.

$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2\text{SnPh}_2$, however, the data reported was inadvertently that from the related complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2\text{Sn}(\text{C}_5\text{H}_5)_2$ (II) i.e. the dicyclopentadienylnit as opposed to the diphenyltin complex. It appears that the structure of the diphenyltin complex has not been published, hence in this article we report this structure for the first time.

Experimental

The title compound was synthesized by a published method [6]. A transparent crystal of the approx. size of $0.1 \times 0.1 \times 0.2$ mm was used for the determination of the unit cell and the collection of the intensity data.

Crystal data. $\text{C}_{26}\text{H}_{20}\text{O}_4\text{SnFe}_2$, Fwt.: 626.8 a.m.u., a 34.580(3), b 9.730(4), c 16.031(2) Å, β 111.91(1)°, V 4819(3) Å³ (from single crystal diffractometry),

Table 1. Atomic coordinates and B_{eq}^a values (Å²) for the non-hydrogen atoms with their e.s.d.'s

Atom	x/a	y/b	z/c	B_{eq}
Sn	0.12420(1)	0.23227(4)	0.54677(2)	2.20(1)
Fe(1)	0.09100(2)	0.45738(9)	0.45552(5)	2.85(2)
Fe(2)	0.07644(2)	0.05096(9)	0.58348(5)	2.76(2)
O(1)	0.0630(1)	0.5316(5)	0.5984(3)	4.4(1)
O(2)	0.1721(1)	0.5901(5)	0.5370(3)	6.4(1)
O(3)	0.0117(1)	0.2632(5)	0.5458(3)	5.6(1)
O(4)	0.0474(1)	-0.0411(5)	0.3984(2)	5.5(1)
C(1)	0.1728(2)	0.03009(6)	0.6697(3)	2.5(1)
C(2)	0.2120(2)	0.2416(6)	0.6969(4)	3.9(1)
C(3)	0.2441(2)	0.2843(8)	0.7758(4)	6.0(2)
C(4)	0.2369(1)	0.3859(1)	0.8293(1)	7.1(3)
C(5)	0.1984(2)	0.4446(8)	0.8045(4)	6.1(2)
C(6)	0.1670(2)	0.4042(6)	0.7258(4)	4.4(2)
C(7)	0.1604(2)	0.1248(6)	0.4816(3)	2.4(1)
C(8)	0.1867(2)	0.2014(6)	0.4519(4)	3.8(2)
C(9)	0.2125(2)	0.1357(8)	0.4152(4)	4.8(2)
C(10)	0.2123(2)	-0.074(8)	0.4064(4)	4.9(2)
C(11)	0.1870(2)	-0.0898(6)	0.4350(4)	4.4(2)
C(12)	0.1609(2)	-0.0214(6)	0.4717(4)	3.5(2)
C(13)	0.0751(2)	0.5000(6)	0.5422(4)	3.2(1)
C(14)	0.1403(2)	0.5345(6)	0.5060(4)	4.1(2)
C(15)	0.0460(2)	0.5593(8)	0.3470(5)	7.1(2)
C(16)	0.0322(2)	0.4250(10)	0.3613(4)	7.5(3)
C(17)	0.0593(3)	0.3273(6)	0.3475(4)	7.5(2)
C(18)	0.0890(2)	0.4007(8)	0.3289(4)	5.8(2)
C(19)	0.0801(2)	0.5413(9)	0.3292(4)	6.4(2)
C(20)	0.0385(2)	0.1816(9)	0.5612(4)	3.5(2)
C(21)	0.0596(2)	-0.0042(6)	0.4726(4)	3.7(2)
C(22)	0.1055(2)	-0.1390(6)	0.6380(4)	4.4(2)
C(23)	0.0681(2)	-0.1311(6)	0.6515(4)	5.1(2)
C(24)	0.0701(2)	-0.0095(8)	0.7019(4)	5.0(2)
C(25)	0.1092(2)	0.0543(8)	0.7211(4)	6.0(2)
C(26)	0.1314(2)	-0.0273(8)	0.6817(4)	5.2(2)

^a B_{eq} is defined as $B_{\text{eq}} = 4/3 \text{ trace}(\mathbf{BG})$ where \mathbf{B} is the thermal motion tensor and \mathbf{G} is the direct metric tensor.

monoclinic space group (C_2/c (from systematic absences and structure refinement), Z 8, $F(000)$ 2480, d_x 1.728 g cm⁻³, $\mu(\text{Mo-K}\alpha, \lambda$ 0.71073 Å) 22.5 cm⁻¹).

Intensity data, structure solution and refinement. 2462 independent non-zero reflections were measured using Mo-K α radiation and θ -2 θ scan on an Enraf-Nonius CAD-4 diffractometer. The structure was solved by the heavy-atom method and Fourier techniques. The structure was refined by anisotropic full-matrix least-squares. Hydrogen atomic positions were generated from assumed geometries (C-H 0.95 Å) and were included in structure factor calculations with isotropic temperature factors [$B(\text{H}) = B(\text{C})_{\text{eq}} + 1 \text{ \AA}^2$] but they were not refined. 1736 reflections were used for refinement and the final R values were R_{obs} 0.031, R_w 0.025, R_{tot} 0.052. No absorption corrections were applied. The atomic parameters for the non-hydrogen atoms are given in Table 1.

Results and discussion

A molecular diagram of the title complex is depicted in Fig. 1, and the relevant bond distances and angles are listed in Table 2. Selected geometrical data observed in the related compounds are summarized in Table 3.

As noted, the bond length Fe-Sn changes with the electron-withdrawing capacity of R groups [2-4]. The data in Table 3 indicate the electron-withdrawing capacity of the phenyl group to be intermediate between that of the ONO and Me groups as would be expected, while that of the ($\eta^1\text{-C}_5\text{H}_5$) group lies between the Cl and ONO groups. A comparison of the structural parameters of the title compound and [$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SnPh}_3$] (VI) shows that the Fe-Sn bond is elongated in the di-iron substituted tin complex, 2.583(4) vs. 2.536(3) Å, with a corresponding increase in the Sn-C(phenyl) bond lengths, 2.156(5) vs. 2.134(15) Å. Such variations

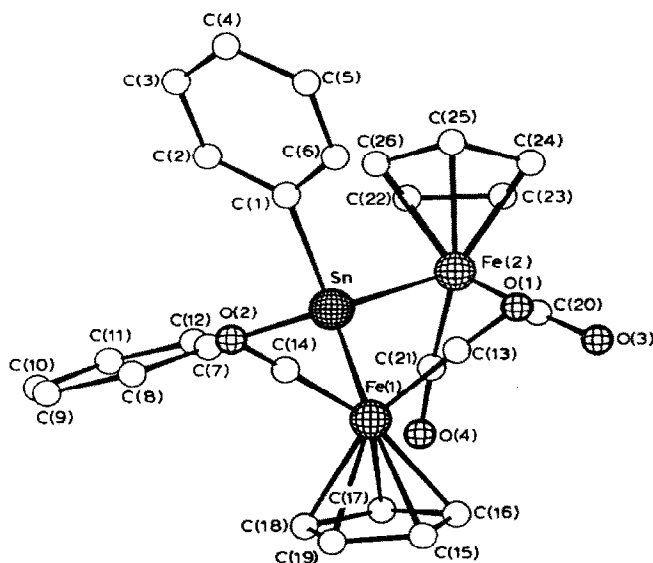


Fig. 1. A molecular diagram of the bis-(dicarbonyl- η^5 -cyclopentadienyliron)diphenyltin complex with the numbering of the atoms.

Table 2. Relevant bond distances (Å) and angles (°)

Sn-Fe(1)	2.579(1)	Fe(1)-C(13)	1.721(5)	C(13)-O(1)	1.164(6)
Sn-Fe(2)	2.586(1)	Fe(1)-C(14)	1.748(5)	C(14)-O(2)	1.149(6)
Sn-C91)	2.156(5)	Fe(2)-C(20)	1.731(6)	C(20)-O(3)	1.155(7)
Sn-C(7)	2.156(5)	Fe(2)-C(21)	1.730(6)	C(21)-O(4)	1.157(7)
Fe(1)-Sn-Fe(2)	118.6(1)	Fe(2)-Sn-C(1)	109.5(2)	Sn-Fe(1)-C(13)	86.6(3)
Fe(1)-Sn-C(1)	107.7(2)	Fe(2)-Sn-C(7)	109.8(2)	Sn-Fe(1)-C(14)	85.7(3)
Fe(1)-Sn-C(7)	108.9(2)	C(1)-Sn-C(7)	100.8(3)	Sn-Fe(2)-C(20)	89.3(3)
				Sn-Fe(2)-C(21)	87.8(3)

Table 3. Fe-Sn and A-Sn bond distances (Å) and bond angles (°) around the tin atom in related complexes. A stands for carbon atom unless indicated otherwise (VI: $\text{Ph}_3\text{SnFe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)$)

Compound	R	Fe-Sn	A-Sn	Fe-Sn-Fe	A-Sn-A	Ref.
I	Cl	2.492(8)	2.43(1)	94.1(6)	128.6(3) [A = Cl]	2
II	C_5H_5	2.2571(2)	2.17(2)	115.9(1)	95.2(8)	4
III	ONO	2.568(5)	2.14(1)	126.3(1)	67.4(2) [A = O]	3
IV	Me	2.602(4)	2.18(1)	123.4(1)	104.7(8)	3
V	Ph	2.583(4)	2.156(5)	118.6(1)	100.8(3)	this work
VI	Ph	2.536(3)	2.13(3)	-	105(2)	7

are probably due to extra steric interactions at the central Sn atom upon further substitution of a phenyl group with a large $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]$ group.

The structural parameters of the title compound exhibit less distortion from the tetrahedral angle than the bis- η^1 -cyclopentadienyl complex data used in the original Mössbauer/structure comparison article. The relevant angles about tin for the diphenyl complex are 119 and 101°, whereas those for the bis-cyclopentadienyl complex are 116 and 95°. The real geometry of the diphenyl complex better fits the Mössbauer data, reinforcing to a greater extent the ideas of Bancroft et al. [5]. The "increase" of the C-Sn-C angle from 95 to 101° suggests more *s*-character in the Sn-C bond. The previously discussed value of 95° is very similar to that of the related dichlorotin complex, $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2\text{SnCl}_2$, i.e. 94.1° where significant reduction in *s*-character is expected for the Sn-Cl bond from Mössbauer data.

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References

- 1 K.H. Pannell and J.R. Rice, *J. Organomet. Chem.*, 341 (1988) 415.
- 2 J. O'Connor and E.R. Corey, *Inorg. Chem.*, 6 (1967) 968.
- 3 B.P. Biryukov and Yu.T. Struchkov, *Zh. Strukt. Khim.*, 9 (1968) 488.
- 4 B.P. Biryukov and Yu.T. Struchkov, *Zh. Strukt. Khim.*, 10 (1969) 95.
- 5 G.M. Bancroft, K.D. Butler, A.T. Rake and B. Dale, *J. Chem. Soc., Dalton Trans. (London)*, (1972) 2025 and references therein.
- 6 A.N. Nesmeyanov, K.N. Anisimov, N.E. Kolobova and V.V. Skripkin, *Izv. Akad. Nauk S.S.S.R. (Ser. Khim.)*, (1966) 1292.
- 7 R.F. Bryant, *J. Chem. Soc. (London) (A)*, (1967) 192.