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1-Carbonyl-μ-carboxylato-1κC:2κO:2$\kappa O'$-1-η^5-indenyl-2,2,2-triphenyl-1-(triphenylphosphine)irontin

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Abstract. $[FeSn(C_6H_5)_3(C_9H_7)(CO)(CO_2)\{P(C_6H_5)_3\}]$, M_r = 855.33, monoclinic, $P2_1/n$, a = 17.715 (5), b = 13.156 (4), c = 17.749 (5) Å, β = 112.22 (3)°, V = 3829.2 Å^3, Z = 4, D_x = 1.48 g cm^{-3}, Mo $K\alpha$ (λ = 0.71073 Å), μ = 11.1 cm^{-1}, $F(000)$ = 1736, T = 296 K, 7057 unique reflections, R = 0.027, wR = 0.031 for 5480 observed reflections with $I > 3\sigma(I)$. The coordination environment about the Fe atom consists of a triphenylphosphine, the five-membered ring of the indenyl ligand, a carbonyl and a C-bound carboxylate. A triphenyltin unit is bound to the O atoms of the carboxylate group giving a bimetallic complex. The Sn—O bond lengths differ by 0.467 Å which is considerably more than the difference observed for the related cyclopentadienyl analog; the steric demands of the bulky indenyl ligand are responsible for this difference. The geometry about the Sn atom is best described as a distorted trigonal bipyramid.

Introduction. The possibility for thermal activation of CO_2 through bifunctional systems having a highly basic metal center to bind carbon and an acidic center to bind one or both O atoms was suggested previously (Gambarotta, Arena, Floriani & Zanuzzi, 1982). As part of a general effort to synthesize and characterize bimetallic CO_2-bridged compounds (Gibson, Richardson & Ong, 1991; Gibson, Ye & Richardson, 1992) we have prepared the title compound (see Fig. 1); its structure determination and comparisons with two other closely related compounds are presented herein.

Experimental. Under nitrogen, $(\eta^5\text{-}C_9H_7)Fe(CO)_2(PPh_3)^+.I^-$ (2.00 g, 3.25 mmol) and Ph_3SnCl (1.25 g, 3.25 mmol) were dissolved in 15 ml of THF and cooled to 273 K. A solution of KOH (0.73 g, 13.0 mmol) in 2 ml of H_2O was added, with stirring, to this mixture. The mixture was allowed to stir for 10 min and became dark red during this time. Cold (273 K) water, 15 ml, was added and the mixture was then transferred to a separatory funnel to separate the organic layer. This layer was then dried over $MgSO_4$, filtered, and concentrated on a rotary evaporator. Cold ether (30 ml) was then added to precipitate the product as a red-orange powder (1.50 g, 54% yield). A sample of the product was dissolved in CH_2Cl_2 and the solution was carefully layered with pentane and then chilled to 243 K; orange crystals were obtained after 1 week.

X-ray diffraction data were obtained with an Enraf-Nonius CAD-4H diffractometer, Mo $K\alpha$ radiation, incident-beam graphite monochromator, from an orange pyramidal crystal having approximate dimensions 0.23 × 0.32 × 0.40 mm mounted on a glass fiber in a random orientation. The cell dimensions were taken from a least-squares refinement of the setting angles of 25 reflections whose θ angles ranged from 13 to 16°. An orthorhombic C-centered cell (a = 19.775, b = 29.439, c =13.156 Å, α = β = 90, γ = 89.88°) was considered but eliminated due to the lack of mmm symmetry [axial photos; $R_{\rm int}(F^2)$ = 0.54 for observed equivalent reflections]. Data were

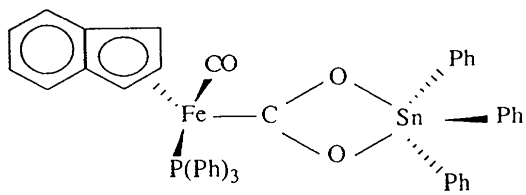

Fig. 1. Sketch of the title complex (Ph = phenyl ring).

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collected using the $\omega/2\theta$-scan technique for $-h$ $+k$ $\pm l$ to a maximum 2θ of 50° over the range 21, 15, 21 for h, k, l. Three standard reflections ($\bar{1}0\,5\,5$, $\bar{2}10$, $06\bar{2}$) were measured every 60 min of exposure time as a check on crystal stability and showed no variation (0.1%).

A total of 7586 reflections were collected of which 7057 were unique; 5480 were considered observed with $I > 3\sigma(I)$, where I was determined from counting statistics (1577 unobserved reflections). $R_{\rm int}(F)$ = 0.018 for 724 reflections. The structure was solved by the Patterson technique (Sn atom) and subsequent least-squares and difference Fourier cycles; H atoms were included in calculated positions (C—H = 0.97 Å) with isotropic thermal parameters set to 1.3 times the value of $B_{\rm eq}$ of the bonded atom. H-atom parameters were not refined. Data were corrected for Lorentz and polarization factors as well as absorption (ψ scans) with transmission coefficients ranging from 0.975 to 0.999.

An isotropic extinction parameter could not be refined. The structure was refined in full-matrix least squares where the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, $w = [\sigma(F)^2 + (0.005F)^2 + 0.2]^{-1}$ (Killean & Lawrence, 1969). Atomic scattering factors used were those of Cromer & Waber (1974) and were corrected for anomalous-dispersion effects (Cromer, 1974). The model converged (maximum Δ/σ < 0.01) for 5480 reflections and 478 variables with R = 0.027, wR = 0.031, S = 1.16 and the highest peak on a difference Fourier map of 0.59 (6) e Å^{-3} associated with the Sn atom. All calculations were performed on a VAXstation 3100 computer using *MolEN* (Fair, 1990). Final positional and equivalent isotropic thermal parameters for non-H atoms are given in Table 1.*

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$B_{\rm eq} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (2ab\cos\gamma)\beta_{12} + (2ac\cos\beta)\beta_{13} + (2bc\cos\alpha)\beta_{23}]$.

	x	y	z	$B_{\rm eq}$
Sn	0.96496 (1)	0.50428 (2)	0.72248 (1)	2.757 (4)
Fe	0.94649 (3)	0.16985 (3)	0.78915 (3)	2.442 (9)
P	0.97339 (5)	0.11568 (6)	0.68333 (5)	2.47 (2)
O1	1.1067 (2)	0.1341 (2)	0.9108 (2)	5.60 (8)
O2	0.9189 (1)	0.3580 (2)	0.7091 (1)	3.22 (5)
O3	1.0366 (1)	0.3547 (2)	0.8106 (1)	3.43 (5)
C1	1.0445 (2)	0.1484 (3)	0.8605 (2)	3.44 (8)
C2	0.9745 (2)	0.3068 (2)	0.7700 (2)	2.80 (7)
C3	0.8339 (2)	0.0769 (3)	0.7632 (2)	3.51 (8)
C4	0.8191 (2)	0.1831 (3)	0.7420 (2)	3.71 (8)
C5	0.8537 (2)	0.2398 (3)	0.8142 (2)	4.00 (8)
C6	0.8958 (2)	0.1738 (3)	0.8785 (2)	3.99 (8)
C7	0.8816 (2)	0.0719 (3)	0.8481 (2)	3.63 (8)
C8	0.9027 (3)	−0.0234 (3)	0.8874 (3)	5.1 (1)
C9	0.8757 (3)	−0.1087 (3)	0.8424 (3)	6.3 (1)
C10	0.8287 (2)	−0.1038 (3)	0.7587 (3)	5.7 (1)
C11	0.8082 (2)	−0.0149 (3)	0.7186 (2)	4.70 (9)
C21	0.9721 (2)	0.5681 (2)	0.8355 (2)	3.01 (7)
C22	1.0451 (2)	0.5828 (3)	0.9010 (2)	4.36 (9)
C23	1.0457 (3)	0.6179 (3)	0.9739 (2)	5.1 (1)
C24	0.9741 (3)	0.6364 (3)	0.9845 (2)	5.0 (1)
C25	0.9020 (2)	0.6233 (3)	0.9204 (2)	5.0 (1)
C26	0.9009 (2)	0.5902 (3)	0.8463 (2)	3.98 (9)
C31	1.0645 (2)	0.5253 (2)	0.6846 (2)	3.09 (7)
C32	1.1446 (2)	0.5147 (3)	0.7375 (2)	4.59 (9)
C33	1.2081 (2)	0.5356 (3)	0.7135 (3)	5.5 (1)
C34	1.1923 (2)	0.5668 (4)	0.6355 (3)	5.7 (1)
C35	1.1134 (3)	0.5771 (4)	0.5820 (2)	5.6 (1)
C36	1.0499 (2)	0.5571 (3)	0.6063 (2)	4.19 (9)
C41	0.8590 (2)	0.5717 (3)	0.6315 (2)	3.14 (7)
C42	0.7961 (2)	0.5165 (3)	0.5766 (2)	4.4 (1)
C43	0.7303 (2)	0.5648 (4)	0.5188 (3)	5.2 (1)
C44	0.7258 (2)	0.6679 (4)	0.5153 (2)	4.9 (1)
C45	0.7865 (3)	0.7244 (3)	0.5700 (2)	4.9 (1)
C46	0.8529 (2)	0.6765 (3)	0.6272 (2)	3.95 (9)
C51	1.0203 (2)	−0.0105 (2)	0.6951 (2)	2.91 (7)
C52	1.0220 (2)	−0.0724 (3)	0.7587 (2)	3.82 (9)
C53	1.0586 (2)	−0.1680 (3)	0.7689 (3)	4.8 (1)
C54	1.0928 (2)	−0.2007 (3)	0.7163 (3)	5.3 (1)
C55	1.0922 (2)	−0.1400 (3)	0.6533 (3)	5.2 (1)
C56	1.0562 (2)	−0.0450 (3)	0.6428 (2)	4.26 (9)
C61	1.0460 (2)	0.1891 (3)	0.6555 (2)	3.05 (7)
C62	1.1195 (2)	0.2160 (3)	0.7161 (2)	4.19 (9)
C63	1.1789 (2)	0.2639 (4)	0.6975 (3)	5.7 (1)
C64	1.1669 (3)	0.2868 (4)	0.6200 (3)	6.6 (1)
C65	1.0944 (3)	0.2618 (4)	0.5585 (3)	7.0 (1)
C66	1.0340 (2)	0.2135 (4)	0.5759 (2)	5.2 (1)
C71	0.8841 (2)	0.1080 (3)	0.5882 (2)	3.00 (7)
C72	0.8390 (2)	0.1970 (3)	0.5610 (2)	3.62 (8)
C73	0.7683 (2)	0.1956 (3)	0.4923 (2)	4.28 (9)
C74	0.7413 (2)	0.1067 (4)	0.4503 (2)	5.1 (1)
C75	0.7855 (3)	0.0193 (3)	0.4754 (2)	5.1 (1)
C76	0.8576 (2)	0.0192 (3)	0.5445 (2)	3.97 (9)

Discussion. Fig. 2 gives a view of the molecule with the atomic numbering focused on the bonding mode of the bridging CO_2 ligand to the two metal centers. Selective bond lengths and angles are given in Table 2.

The structure exhibits several differences when compared to (η^5-C_5H_5)Fe(CO)(PPh_3)CO_2SnPh_3 (Gibson *et al.*, 1991) and (η^5-C_5H_5)Re(NO)(PPh_3)CO_2SnPh_3 (Senn, Gladysz, Emerson & Larsen, 1987); the latter two compounds are structurally very similar. The O—Sn bonds in the indenyl complex differ by 0.467 (3) Å [2.069 (2) and 2.536 (2) Å] and thus exhibit the distorted bidentate bonding characteristic of monomeric triaryltin organocarboxylates (Holmes, Day, Chandrasekhar, Vollano & Holmes, 1986) whereas the cyclopentadienyliron and rhenium complexes show a much smaller difference in the carboxyl O—Sn bond lengths. It should be noted also that the difference in the carboxyl C—O bond lengths of 0.100 (4) Å [1.336 (3) and 1.236 (3) Å] in the indenyl compound is larger than in the μ_2-η^2-CO_2-bridged compound (η^5-C_5H_5)Fe(CO)(PPh_3)CO_2Re$(CO)_4$(PPh_3) [0.072 (4) Å; 1.226 (3) and 1.298 (3) Å] (Gibson *et al.*, 1992) in which only one carboxyl O atom is bound to the Re atom. The Fe—C—O bond angles in the

* Lists of structure factors, anisotropic thermal parameters, bond lengths, bond angles, torsion angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71154 (37 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST0609]

Table 2. *Selected bond lengths* (Å) *and angles* (°)

Sn—O2	2.069 (2)	Fe—C3	2.234 (3)
Sn—O3	2.536 (2)	Fe—C4	2.097 (3)
Sn—C21	2.134 (3)	Fe—C5	2.074 (4)
Sn—C31	2.130 (4)	Fe—C6	2.097 (4)
Sn—C41	2.150 (3)	Fe—C7	2.233 (4)
Fe—P	2.223 (1)	O2—C2	1.336 (3)
Fe—C1	1.742 (3)	O3—C2	1.236 (3)
Fe—C2	1.933 (3)		
O2—Sn—O3	55.42 (7)	C1—Fe—C2	91.6 (1)
O2—Sn—C21	110.8 (1)	Fe—P—C51	115.3 (1)
O2—Sn—C31	115.0 (1)	Fe—P—C61	117.3 (1)
O2—Sn—C41	95.9 (1)	Fe—P—C71	114.3 (1)
O3—Sn—C21	83.5 (1)	C51—P—C61	100.1 (2)
O3—Sn—C31	90.8 (1)	C51—P—C71	104.6 (1)
O3—Sn—C41	151.0 (1)	C61—P—C71	103.4 (2)
C21—Sn—C31	118.9 (1)	Sn—O2—C2	103.8 (2)
C21—Sn—C41	105.6 (1)	Sn—O3—C2	84.7 (2)
C31—Sn—C41	107.5 (1)	Fe—C2—O2	116.9 (2)
P—Fe—C1	95.1 (1)	Fe—C2—O3	127.1 (2)
P—Fe—C2	90.0 (1)	O2—C2—O3	115.9 (3)

carboxyl ligand are also highly distorted in the indenyl complex in comparison to the cyclopentadienyliron and rhenium complexes or to tin organocarboxylates; the latter compounds show nearly equal Fe—C—O angles while the indenyl complex shows a difference of 10.2 (3)° [116.9 (2) and 127.1 (2)°]. The distortions which occur in the indenyl complex are the result of severe steric interactions between the six-membered ring of the indenyl ligand and a phenyl ring of the phosphine ligand bound to the Fe atom. Note that these distortions occur in spite of the usual 'slipped' nature (O'Connor & Casey, 1987) of the five-membered ring in the indenyl ligand in bonding to the Fe atom, which shifts this center away from the arene ring in the indenyl ligand.

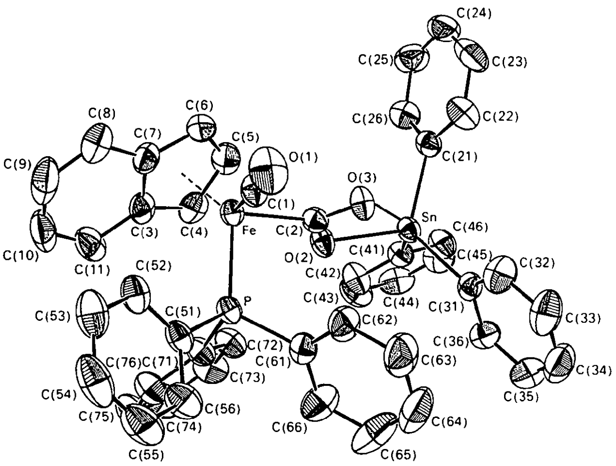

Fig. 2. *ORTEP* (Johnson, 1965) plot showing the atomic numbering system. The thermal ellipsoids are drawn at the 50% probability level.

Whereas the Sn atom in tin organocarboxylates and the cyclopentadienyl-substituted iron or rhenium complexes lies in the plane of the atoms of the bridging carboxyl group, the Sn atom is pushed significantly out of this plane in the indenyl complex, a further change prompted by the steric effects of the indenyl ligand. The geometry about the Sn atom is also distorted more than in the cyclopentadienyl complexes; the sum of the equatorial bond angles is 344.7 (2)° as compared to 349.8 (2)° in the cyclopentadienyl iron compound and 351.2 (2)° in the cyclopentadienyl rhenium complex. Displacement of the Sn atom from the equatorial plane was 0.28 (1) Å towards the indenyl unit. The angle between the O2—C2—O3 plane and the Fe—C1—O1 vector is 8 (3)°, comparable to the value of 9 (3)° in the cyclopentadienyl iron compound.

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