# Crystal and Molecular Structure of Di-μ-dimethylstannylene-bis(carbonyl-π-cyclopentadienylcobalt): A Metal Ring Compound

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Crystals of the title compound are triclinic, space group $P\bar{1}$, with $Z = 2$ in a unit cell of dimensions $a = 11{\cdot}23(2)$, $b = 11{\cdot}10(2)$, $c = 7{\cdot}82(1)$ Å, $\alpha = 95{\cdot}7(2)$, $\beta = 97{\cdot}0(2)$, $\gamma = 89{\cdot}1(2)°$. The structure was refined to $R$ 0·085 for 1520 independent reflections measured on a diffractometer. There are two crystallographically distinct molecules in the unit cell, each located astride a centre of inversion; they show no significant differences in their molecular geometry but are differently oriented in the unit cell. Sn and Co atoms alternate around a planar four-membered ring, the Sn atoms having only slightly distorted tetrahedral co-ordination, and Co having octahedral co-ordination if the cyclopentadienyl ring is assumed to occupy three sites. The idealised molecular symmetry is $C_{2h}$ $(2/m)$, with the two-fold axis through the Sn atoms and the mirror through the Co atoms, the CO groups, and bisecting the cyclopentadienyl rings which lie mutually *trans* across the plane of the metal-atom ring. In the $C_5$ ring, the carbon atom in the mirror plane is also diametrically opposite to the CO group attached to the same Co atom. Co–Sn [2·542(2) Å] is significantly shorter than expected, but Co–C(CO), Co–C($\pi$-$C_5H_5$), and C–O are 'normal'; Sn–Co–Sn is 78°. The carbonyl groups occupy *trans* 'axial' positions and are inclined slightly inwards; mean Sn–C 2·20(1) Å, C–Sn–C only a little less than the tetrahedral value.

VERY few cobalt–tin compounds have been examined crystallographically;[1-3] recorded bond lengths range from 2·566(3) to 2·65(1) Å. Plane four-membered rings of metal atoms are also rare.[4,5] However, the title compound is isoelectronic with $[(Me_2Sn)Fe(CO)_4]_2$, the structure of which has been recently reported.[5] Results of the two analyses are here compared. The crystals of $[(Me_2Sn)Co(\pi\text{-}C_5H_5)(CO)]_2$ used for the present investigation were prepared by reaction of dicarbonylcyclopentadienylcobalt with hexamethylditin in a sealed tube at 160 °C.[6]

## EXPERIMENTAL

The crystals were dark red needles showing strong elongation in the $c$ direction, and the lattice parameters (which were measured from a small crystal with Mo-$K_\alpha$ radiation, Weissenberg and precession photographs) are those of a triclinic unit cell with a base which is very nearly square. The crystal used for intensity measurements had dimensions 0·53 × 0·12 × 0·06 mm and was mounted on the needle axis $c$. The intensities of 2413 reflections (reciprocal layers $hk0$—7) were measured on a Buerger–Supper–Pace 0·01°-incrementing two-circle autodiffractometer which utilises equi-inclination geometry and a stationary-background–$\omega$-scan–stationary-background mode of measurement, according to the method described earlier.[7] Each reflection was scanned through an angle of $(2{\cdot}0 + 0{\cdot}4/L)$, where $L$ is the Lorentz correction, at a speed of 1° min$^{-1}$; background counts were taken for 0·5 min. Of the reflections measured, only 1692 satisfied the criterion $\left[N_3 - \frac{t_s}{2t_b}(N_1 + N_2)\right] \Big/ \left[N_3 + \frac{t_s}{2t_b}(N_1 + N_2)\right]^{\frac{1}{2}} > 2{\cdot}0$, and were used in the analysis ($N_1$, $N_2$, and $N_3$ are the first and second background counts and the peak count). Check reflections were incorporated between every 20 measurements and served to monitor the stability of both the apparatus and the crystal.

*Crystal Data.*—$C_{16}H_{22}O_2Co_2Sn_2$, $M = 601{\cdot}6$, Triclinic, $a = 11{\cdot}23(2)$, $b = 11{\cdot}10(2)$, $c = 7{\cdot}82(1)$ Å, $\alpha = 95{\cdot}7(2)°$, $\beta = 97{\cdot}0(2)$, $\gamma = 89{\cdot}1(2)$, $U = 962$ Å$^3$, $D_m$ (by flotation) = 1·85, $Z = 2$, $D_c = 2{\cdot}08$, $F(000) = 576$. Mo-$K_\alpha$ radiation, $\lambda = 0{\cdot}7107$ Å; $\mu$(Mo-$K_\alpha$) = 20·9 cm$^{-1}$. Space group $P\bar{1}$.

*Structure Solution and Refinement.*—The metal atoms were located (though not immediately) from consideration of the three-dimensional Patterson synthesis. It soon became evident that the asymmetric unit comprised two half-molecules, each half generating the other half of the molecule through the centre of inversion, and that the planar four-membered rings were so orientated that the Co · · · Co diagonal of one ring almost coincides vectorially with the Sn · · · Sn diagonal of the other. This is an interesting point of similarity to the orthorhombic structure of $[Me_2SnFe(CO)_4]_2$, in which there are two crystallographically distinct molecules in converse orientations. Attempts to refine a skeletal structure based on this model led to an atom shift which enlarged the Co–Co distance and diminished the Sn–Sn distance, giving a lozenge-shaped configuration for the metal cluster rather than the square configuration first derived. The two molecules in the unit cell thus sit astride centres of inversion at 0,0,0 and $\frac{1}{2},\frac{1}{2},\frac{1}{2}$; they are required crystallographically to be centrosymmetric, but are not centrosymmetrically related to one another. Indeed, they lie approximately parallel to the $ab$ plane of the unit cell but are rotated *ca.* 90° relative to one another around $c$.

Computation of electron-density difference syntheses now revealed the locations of the carbon and oxygen atoms, and refinement of the whole structure by full-matrix least squares, with separate scale factors for each reciprocal layer and with isotropic thermal parameters for all atoms, gave $R$ 0·113 and $R'$ 0·085. The quantity minimised in the refinement was $\Sigma w\Delta^2$, where $\Delta = |F_o - F_c|$ and $w$ was initially taken as $1/\sigma_F{}^2$ with $\sigma_F$ determined from counting statistics.[7] At this stage the refinement appeared satisfactory for all atoms except the carbon atom of the carbonyl group in molecule (2) (for which a very high thermal parameter was given). Examination of a recalculated electron-density difference synthesis, however, showed a well defined peak near by, in a chemically plausible location; this position was used for subsequent refinement, in which also

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[1] B. P. Biryukov, O. P. Solodova, and Yu. T. Struchkov, *J. Struct. Chem.*, 1968, **9**, 171.

[2] F. P. Boer, J. H. Tsai, and J. J. Flynn, jun., *J. Amer. Chem. Soc.*, 1970, **92**, 6092.

[3] F. P. Boer and J. J. Flynn, jun., *J. Amer. Chem. Soc.*, 1971, **93**, 6495.

[4] J. C. Zimmer and M. Huber, *Compt. rend.*, 1968, **267**, *C*, 1685.

[5] C. J. Gilmore and P. Woodward, *J.C.S. Dalton*, 1972, 1387.

[6] E. W. Abel and S. Moorhouse, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 905.

[7] C. J. Gilmore, P. A. Tucker, and P. Woodward, *J. Chem. Soc.* (*A*), 1971, 1337.

anisotropic thermal parameters ($B_{33}$ constant) were introduced for the metal atoms, following clear evidence for such thermal motion on the electron-density maps. Finally, hydrogen atoms for the cyclopentadienyl rings were included at calculated positions (C–H 1·1 Å, *B* 3·5) but neither co-ordinates nor thermal parameters for these hydrogen atoms were refined. The weight ascribed to each structure amplitude was also reassessed according to the scheme $1/w = \sigma_F{}^2 + F_o + 0{\cdot}002(F_o)^2$ in which the multiplier 0·002 was obtained from an analysis of the variance of $\Delta$ with *F* and with sin $\theta/\lambda$. Convergence was obtained at *R* 0·061 and *R′* 0·074; in the final cycle the mean shift to error ratio was 0·004 and the ' error of fit ' $\{= [\Sigma w\Delta^2/(n_o - n_v)]^{\frac{1}{2}}$, where $n_o$ = number of observations and $n_v$ = number of variables} was 1·10, as compared with an ideal value of unity. In view of the small size of the crystal and the relatively low linear-absorption coefficient no absorption correction was applied. Atomic scattering factors were taken from ref. 8. A final electron-density difference synthesis showed no peaks $>0{\cdot}6$ nor $< -0{\cdot}5$ eÅ$^{-3}$. Final atomic positional and thermal parameters with their standard deviations are in Table 1, bond lengths and angles in Table 2, and some least-squares planes in Table 3.

TABLE 1

Atomic positional and thermal parameters with estimated standard deviations in parentheses

| Atom | *x/a* | *y/b* | *z/c* | *B*/Å$^2$ |
|---|---|---|---|---|
| Molecule (1) | | | | |
| Sn(1) | 0·1379(1) | 0·0331(1) | 0·0691(2) | |
| C(16) | 0·280(2) | 0·072(2) | −0·083(3) | 5·8(5) |
| C(17) | 0·229(2) | 0·052(2) | 0·340(3) | 6·4(6) |
| Co(1) | −0·0427(2) | 0·1725(2) | 0·0283(3) | |
| C(10) | −0·069(2) | 0·146(2) | 0·227(3) | 3·8(4) |
| O(10) | −0·085(1) | 0·126(1) | 0·371(2) | 6·4(4) |
| C(11) | 0·001(1) | 0·231(2) | −0·200(3) | 4·8(5) |
| C(12) | 0·051(2) | 0·310(2) | −0·053(3) | 4·9(5) |
| C(13) | −0·041(1) | 0·362(2) | 0·025(3) | 4·2(4) |
| C(14) | −0·148(2) | 0·315(2) | −0·060(3) | 4·6(4) |
| C(15) | −0·122(2) | 0·236(2) | −0·203(3) | 4·4(4) |
| Molecule (2) | | | | |
| Sn(2) | 0·5211(1) | 0·3590(1) | 0·5157(2) | |
| C(26) | 0·560(2) | 0·215(2) | 0·305(3) | 6·9(6) |
| C(27) | 0·525(2) | 0·261(2) | 0·745(3) | 6·0(5) |
| Co(2) | 0·3251(2) | 0·4716(2) | 0·4475(3) | |
| C(20) | 0·350(2) | 0·447(2) | 0·239(3) | 6·2(6) |
| O(20) | 0·367(2) | 0·435(2) | 0·095(3) | 7·9(4) |
| C(21) | 0·273(2) | 0·485(2) | 0·693(3) | 5·7(5) |
| C(22) | 0·216(2) | 0·580(2) | 0·595(3) | 5·6(5) |
| C(23) | 0·142(2) | 0·512(2) | 0·460(3) | 4·8(5) |
| C(24) | 0·163(2) | 0·387(2) | 0·469(3) | 4·6(4) |
| C(25) | 0·242(2) | 0·374(2) | 0·619(3) | 5·4(5) |
| Hydrogen atoms of the cyclopentadienyl rings (not refined) | | | | |
| H(11) | 0·053 | 0·186 | −0·301 | 3·5 |
| H(12) | 0·147 | 0·322 | 0·001 | 3·5 |
| H(13) | −0·027 | 0·426 | 0·139 | 3·5 |
| H(14) | −0·234 | 0·351 | −0·032 | 3·5 |
| H(15) | −0·189 | 0·176 | −0·292 | 3·5 |
| H(21) | 0·332 | 0·505 | 0·833 | 3·5 |
| H(22) | 0·225 | 0·680 | 0·616 | 3·5 |
| H(23) | 0·077 | 0·546 | 0·369 | 3·5 |
| H(24) | 0·124 | 0·314 | 0·370 | 3·5 |
| H(25) | 0·278 | 0·289 | 0·649 | 3·5 |

Anisotropic thermal parameters for Sn and Co †

| Atom | $B_{11}$ | $B_{22}$ | $B_{33}$ (constant) | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|
| Sn(1) | 3·6(1) | 3·3(1) | 3·4(1) | 0·1(1) | 0·3(1) | −0·0(1) |
| Sn(2) | 3·4(1) | 3·4(1) | 3·9(1) | 0·6(1) | 0·5(1) | 0·4(1) |
| Co(1) | 3·8(1) | 2·4(1) | 2·5(1) | 0·5(1) | 0·2(1) | 0·3(1) |
| Co(2) | 2·8(1) | 3·6(1) | 2·0(1) | 0·3(1) | 0·4(1) | 0·3(1) |

† These were used in the form: $-\frac{1}{4}[B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl]$.

TABLE 2

Interatomic distances (Å) and bond angles (°) *

| Molecule (1) | | Molecule (2) | |
|---|---|---|---|
| (*a*) Metal ring | | | |
| Sn(1)–Co(1) | 2·538(5) | Sn(2)–Co(2) | 2·539(5) |
| Sn(1)–Co(1′) | 2·544(5) | Sn(2)–Co(2′) | 2·546(5) |
| Mean 2·542(2) | | | |
| (i) Metal–methyl groups | | | |
| Sn(1)–C(16) | 2·17(3) | Sn(2)–C(26) | 2·23(3) |
| Sn(1)–C(17) | 2·21(3) | Sn(2)–C(27) | 2·19(3) |
| Mean 2·20(1) | | | |
| (ii) Metal–carbonyl group | | | |
| Co(1)–C(10) | 1·66(2) | Co(2)–C(20) | 1·68(2) |
| Mean 1·67(1) | | | |
| C(10)–O(10) | 1·21(2) | C(20)–O(20) | 1·17(3) |
| Mean 1·19(3) | | | |
| (iii) Metal–cyclopentadienyl carbon atoms | | | |
| Co(1)–C(11) | 2·07(2) | Co(2)–C(21) | 2·07(2) |
| Co(1)–C(12) | 2·08(2) | Co(2)–C(22) | 2·08(3) |
| Co(1)–C(13) | 2·11(2) | Co(2)–C(23) | 2·11(2) |
| Co(1)–C(14) | 2·09(2) | Co(2)–C(24) | 2·09(2) |
| Co(1)–C(15) | 2·11(2) | Co(2)–C(25) | 2·12(2) |
| Mean 2·09(1) | | | |
| (iv) Carbon–carbon ring | | | |
| C(11)–C(12) | 1·47(3) | C(21)–C(22) | 1·50(3) |
| C(12)–C(13) | 1·35(3) | C(22)–C(23) | 1·40(3) |
| C(13)–C(14) | 1·41(3) | C(23)–C(24) | 1·39(3) |
| C(14)–C(15) | 1·40(3) | C(24)–C(25) | 1·40(3) |
| C(15)–C(11) | 1·36(3) | C(25)–C(21) | 1·34(3) |
| Mean 1·40(2) | | | |
| (*b*) Intramolecular non-bonded distances | | | |
| Sn(1) · · · Sn(1′) | 3·222(5) | Sn(2) · · · Sn(2′) | 3·191(5) |
| Co(1) · · · Co(1′) | 3·929(7) | Co(2) · · · Co(2′) | 3·960(7) |
| C(16) · · · C(17) | 3·44(4) | C(26) · · · C(27) | 3·45(4) |
| C(17) · · · C(10) | 3·51(4) | C(26) · · · C(20) | 3·50(4) |
| C(16) · · · H(11) | 3·18(3) | C(27) · · · H(21) | 3·53(3) |
| C(16) · · · H(12) | 3·17(3) | C(27) · · · H(25) | 2·81(3) |
| (*c*) Bond angles | | | |
| Molecule (1) | | Molecule (2) | |
| Co(1)–Sn(1)–Co(1′) | 101·30(13) | Co(2)–Sn(2)–Co(2′) | 102·26(12) |
| Sn(1)–Co(1)–Sn(1′) | 78·70(13) | Sn(2)–Co(2)–Co(2′) | 77·74(12) |
| C(16)–Sn(1)–C(17) | 103·8(10) | C(26)–Sn(2)–C(27) | 102·9(11) |
| Co(1)–Sn(1)–C(16) | 113·1(7) | Co(2)–Sn(2)–C(26) | 114·0(8) |
| Co(1)–Sn(1)–C(17) | 112·2(7) | Co(2)–Sn(2)–C(27) | 113·5(7) |
| Co(1′)–Sn(1)–C(16) | 112·0(7) | Co(2′)–Sn(2)–C(26) | 111·0(8) |
| Co(1′)–Sn(1)–C(17) | 114·9(7) | Co(2′)–Sn(2)–C(27) | 113·5(7) |
| C(15)–C(11)–C(12) | 106·2(19) | C(25)–C(21)–C(22) | 111·3(22) |
| C(11)–C(12)–C(13) | 108·0(21) | C(21)–C(22)–C(23) | 100·8(21) |
| C(12)–C(13)–C(14) | 108·5(20) | C(22)–C(23)–C(24) | 112·1(21) |
| C(13)–C(14)–C(15) | 108·1(19) | C(23)–C(24)–C(25) | 107·2(21) |
| C(14)–C(15)–C(11) | 109·2(20) | C(24)–C(25)–C(21) | 108·2(22) |
| Sn(1)–Co(1)–C(10) | 87·1(8) | Sn(2)–Co(2)–C(20) | 86·2(9) |
| Sn(1′)–Co(1)–C(10) | 85·6(7) | Sn(2′)–Co(2)–C(20) | 87·6(9) |
| Co(1)–C(10)–O(10) | 178·2(19) | Co(2)–C(20)–O(20) | 178·4(23) |
| C(10)–Co(1)–C(11) | 171·7(10) | C(20)–Co(2)–C(21) | 172·1(11) |

* Estimated standard deviations include all cell parameter errors.

Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20665 (7 pp.,).* All

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, index issue. (Items less than 10 pp. are supplied as full-size copies.)

[8] H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, 1959, **12**, 600.

computations were carried out by use of the '*X*-Ray '67' suite of crystallographic programmes.[9]

TABLE 3

Equations of best least-squares planes, defined by atomic positions and, in square brackets, distances of atoms (Å) from these planes *

Plane (1):
Co–Sn ring of molecule (1) $-3\cdot341x - 2\cdot051y + 7\cdot660z = 0\cdot0$
[Sn(1) 0·001, Sn(1′) 0·001, Co(1) −0·001, Co(1′) −0·001]

Plane (2):
Co–Sn ring of molecule (2) $-2\cdot368x + 0\cdot523y + 7\cdot700z = 2\cdot928$
[Sn(2) −0·001, Sn(2′) −0·001, Co(2) 0·001, Co(2′) 0·001]

Plane (3):
$\pi$-$C_5H_5$ ring of molecule (1) $0\cdot640x + 9\cdot051y - 5\cdot134z = 3\cdot109$
[C(11) 0·005, C(12) 0·024, C(13) −0·042, C(14) 0·045, C(15) −0·032]

Plane (4):
$\pi$-$C_5H_5$ ring of molecule (2) $9\cdot328x + 1\cdot064y - 5\cdot107z = -0\cdot458$
[C(21) −0·032, C(22) 0·041, C(23) −0·037, C(24) 0·016, C(25) 0·013]

Plane (5):
$SnMe_2$ of molecule (1) $-2\cdot605x - 10\cdot705y + 0\cdot245z = 0\cdot012$

Plane (6):
$SnMe_2$ of molecule (2) $10\cdot571x + 2\cdot159y + 0\cdot677z = 6\cdot727$

Plane (7):
Co(CO) of molecule (1) $10\cdot331x + 2\cdot319y + 1\cdot587z = 0\cdot000$
[Co(1) −0·006, Co(1′) 0·000, C(10) 0·014, O(10) −0·008]

Plane (8):
Co(CO) and C of $\pi$-$C_5H_5$ molecule (2) $-1\cdot478x + 10\cdot947y - 1\cdot251z = 4\cdot098$
[Co(2) 0·022, Co(2′) −0·001, C(20) 0·039, O(20) −0·040, C(21) −0·021]

Angles between planes (°)

| | | | | | |
|---|---|---|---|---|---|
| (1)–(2) | 14·3 | (1)–(3) | 45·2 | (2)–(4) | 44·9 |
| (1)–(5) | 89·2 | (2)–(6) | 88·3 | (1)–(7) | 89·5 |
| (2)–(8) | 89·9 | (7)–(8) | 87·3 | | |

* *x*, *y*, *z* are fractional crystal co-ordinates.

## DISCUSSION

The structure of $[(\pi\text{-}C_5H_5)Co(CO)SnMe_2]_2$ can be viewed as the fusion of two octahedral $(\pi\text{-}C_5H_5)Co(CO)$ moieties (the cyclopentadienyl group occupying three of the octahedral sites) through tetrahedral $SnMe_2$ bridges; the CO groups occupy *trans* axial positions relative to the plane of the metal atom ring. A stereoscopic view of the molecule is given in Figure 1. The symmetry approximates closely to $C_{2h}$ $(2/m)$, although for each of the two crystallographically distinct molecules the required symmetry is only $C_i$ $(\bar{1})$. For both molecules the two-fold axis passes through the two tin atoms, while the mirror plane contains the two cobalt atoms and bisects the cyclopentadienyl rings. The carbon atom of the $C_5$ ring which lies in the mirror plane also lies diametrically opposite to the carbonyl group of the cobalt atom to which they are both bonded. If the configuration of the cobalt valencies is regarded as octahedral, then one axial site is occupied by the carbonyl ligand, one axial and two equatorial sites by the cyclopentadienyl ligand, and the other two equatorial sites are distorted towards one another to accommodate the tetrahedral $SnMe_2$ bridges. Figure 2 shows the relationship of the cyclopentadienyl ligand to the cobalt atom and its bonded fragments by a perspective view along the vector between Co and the centroid of the cyclopentadienyl ring. The valencies of the tin atom remain close to tetrahedral. The two crystallographically distinct molecules do not differ significantly in their molecular geometry, and therefore throughout this discussion mean values will be used; individual values are all in Table 2.

*The* $Co_2Sn_2$ *Ring*.—The planar metal nucleus of the molecule, which comprises a four-membered ring of alternating Co and Sn atoms, has angles at Co and Sn of 78 and 102°. Its angular geometry is thus almost identical to that found in the isoelectronic compound $[(Me_2Sn)Fe(CO)_4]_2$ [5] where the corresponding angles were 77 and 103°. Any expectation that the cyclopentadienyl ring might 'constrain' the valencies of the cobalt atom to remain closer to the ideal octahedral value of 90° is thus not fulfilled. The Co–Sn distance, however, is 2·54(2) Å, whereas in $[(Me_2Sn)Fe(CO)_4]_2$ Fe–Sn is 2·64 Å, although the radii of octahedral iron and cobalt would not be expected to differ by >0·01 Å.[10] Now, it is well established that the length of the bond between a transition-metal atom and a tin atom varies markedly

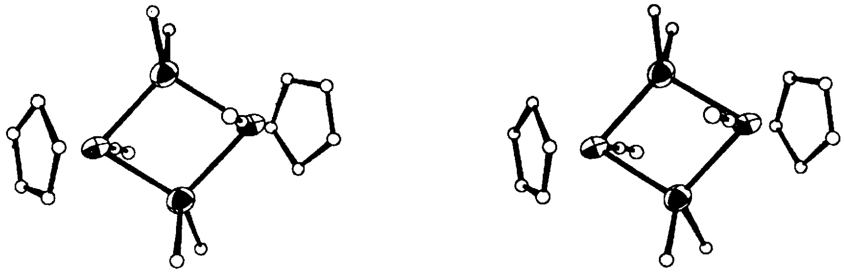

FIGURE 1 Stereoscopic drawing of the configuration of the molecule

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[9] J. M. Stewart, F. A. Kundell, and J. C. Baldwin, '*X*-Ray '67', a suite of Fortran programs for crystallographic computation, adapted for use on an Atlas computer, University of Maryland, U.S.A. Report TR 67 58, 1967.

[10] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1963.

according to the electronegativity of the groups attached to the tin atom, as also does the deviation from ideal tetrahedral angularity around the tin atom.[11-14] These ideas are difficult to apply to $[(\pi\text{-}C_5H_5)Co(CO)(SnMe_2)]_2$ because of the constraints imposed on the geometry of the bonds around the tin atom by ring formation, and indeed, it is not feasible to predict what bond length is to be expected for the Co–Sn bond in $[(\pi\text{-}C_5H_5)Co(CO)(SnMe_2)]_2$ by comparison with other established cobalt–tin structures, since so few have been studied. But since in comparing $[(\pi\text{-}C_5H_5)Co(CO)(SnMe_2)]_2$ with $[(Me_2Sn)Fe(CO)_4]_2$ the external substituents on the tin atom are the same for both compounds, and the ring angles are virtually identical, any differences in the metal–metal bond lengths greater than *ca.* 0·01 Å can therefore be ascribed to the nature of the substituents on the transition-metal atom. Evidence has been given elsewhere[5] for believing the Sn–Fe bond in $[(Me_2Sn)Fe(CO)_4]_2$ to be a single bond relatively free from $\pi$ interactions between *d* orbitals on the component atoms. We can now assert, by comparison, that in $[(\pi\text{-}C_5H_5)Co(CO)(SnMe_2)]_2$ there must be considerable $\pi$ character in the Co–Sn bond. In $Co(CO)_4Sn(Ph_2)Mn(CO)_5$, where $\pi$ interactions are likely to be small, the Co–Sn bond length [2·66(1) Å][1] is not significantly different from the Fe–Sn bond length in $[(Me_2Sn)Fe(CO)_4]_2$. That some degree of multiple bonding does occur in $[(\pi\text{-}C_5H_5)Co(CO)(SnMe_2)]_2$ is not surprising when the chemical nature of the cyclopentadienyl ligand is compared with that of the carbonyl ligand from the viewpoint of electron donation and acceptance. Metal–carbonyl bonds are characterised by considerable back-donation of electrons from filled *d* orbitals on the metal into empty antibonding ($\pi^*$) orbitals on the carbonyl group,[15] whereas such back-donation is not essential for the formation of cyclopentadienyl–metal bonds.

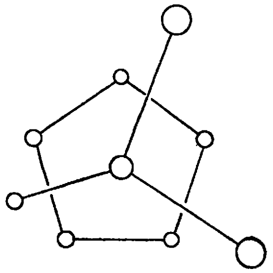

FIGURE 2 The relationship between the cyclopentadienyl ring and the rest of the molecule: a view perpendicular to the $C_5$ plane

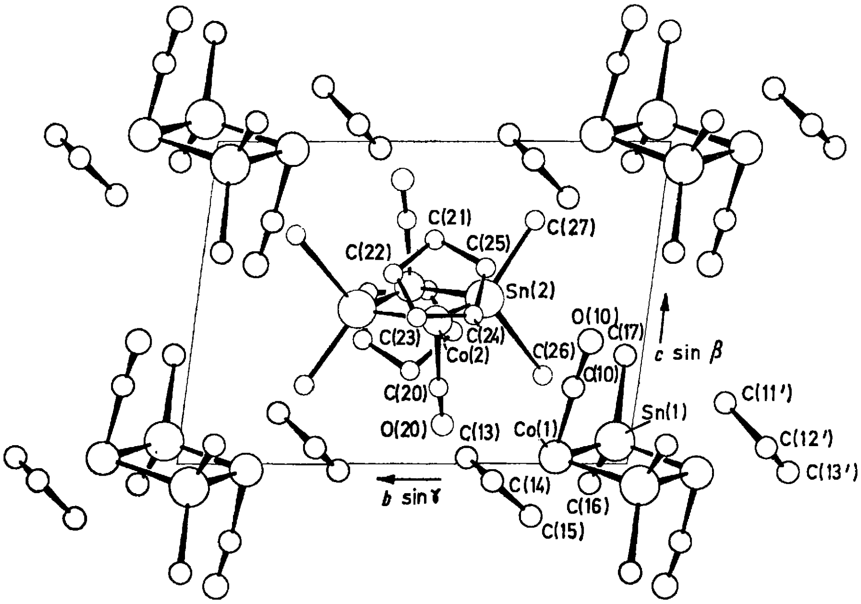

FIGURE 3 The contents of the triclinic unit cell seen in projection along *a* looking away from the origin. The two different orientations of the molecule relative to the centres of inversion at 0,0,0 and ½,½,½ are clearly seen

*The Ligands on the Cobalt Atom.*—Each cobalt atom carries one cyclopentadienyl ligand and one carbonyl group. The mean Co–C($\pi$-$C_5H_5$) distance [2·09(1) Å] agrees well with reported values, *e.g.* 2·08(3) in $(\pi\text{-}C_5H_5)Co[(CF_3)_4C_5O]$,[16] 2·08(3) in $(\pi\text{-}C_5H_5)Co(C_5H_4Ph)$,[17] and 2·06(4) Å in $(\pi\text{-}C_5H_5)(CO)_2CoHgCl_2$.[18] The mean bond length C–C in the cyclopentadienyl ring is 1·40(2) Å,

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and the plane of this ring makes an angle of 45° with the $Co_2Sn_2$ plane. For the carbonyl groups, the mean Co–C and C–O distances are 1·67(1) and 1·19(3) Å, *cf.* 1·80(2) and 1·10(2) in $Co_3(CO)_9(CMe)$,[19] 1·71(2) and 1·18(2) in $Ph_2Sn[Co(CO)_2(C_7H_8)]_2$,[2] and 1·78(1) and 1·14(1) Å in $Cl_2Sn[Co(CO)_2(C_7H_8)]_2$.[2] In the last two compounds the differences between corresponding bonds are alleged to be significant and to be a consequence of the electronegativity of the ligand attached to the central tin atom; this is certainly possible. In our case, the magnitude of the standard deviations would preclude any correlations of this kind.

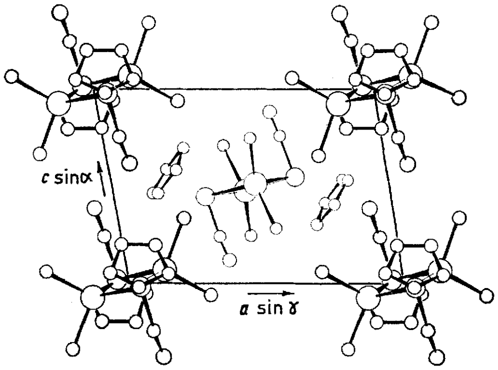

FIGURE 4 The contents of the triclinic unit cell seen in projection along *b* looking away from the origin

*The Ligands on the Tin Atom.*—Each tin atom carries two methyl groups; the mean Sn–C bond length [2·20(1) Å] is close to that found in $[Me_2SnFe(CO)_4]_2$ [2·22(7) Å], and to the sum of the covalent radii for $Sn^{IV}(sp^3)$ and $C(sp^3)$.[20] The angle between the two Sn–C(Me) bonds [103(1)°] is rather less than the tetrahedral value, which is perhaps surprising in view of the constraint (to 102°) applied to the vertically opposite Co–Sn–Co angle by the ring. It is possible, however, that the molecular packing (Figures 3 and 4) is of some importance in determining this angle, since the carbon atoms of the methyl groups, the oxygen atoms of the carbonyl groups, and the carbon atoms of the cyclopentadienyl ligands are all approximately equidistant from one another.

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