

Sn—(peptide N atom) distances are 2.108 (4) Å in (I) and 2.137 (5) Å in (II).

It is noteworthy that the C—Sn—C angle for the Me<sub>2</sub>Sn(AlaHis) complex [143.9 (3)°] is the largest found among closely related R<sub>2</sub>Sn(dipeptide) complexes (Preut, Mundus, Huber & Barbieri, 1986; Huber, Haupt, Preut, Barbieri & Lo Giudice, 1977).

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## Structure of a Ring-Opened 2,5-Dimethylthiophene Complex, ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Ir(CO)(C,S-Me<sub>2</sub>C<sub>4</sub>H<sub>2</sub>S)

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**Abstract.** Carbonyl(2,4-hexadiene-2-thiolato)( $\eta^5$ -pentamethylcyclopentadienyl)iridium, [Ir(C<sub>6</sub>H<sub>8</sub>S)-(C<sub>10</sub>H<sub>15</sub>)(CO)], *M<sub>r</sub>* = 467.6, triclinic, *P*1̄, *a* = 13.694 (4), *b* = 16.519 (5), *c* = 7.740 (2) Å,  $\alpha$  = 102.51 (2),  $\beta$  = 103.43 (2),  $\gamma$  = 81.10 (2)°, *V* = 1652.5 (8) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.880 g cm<sup>-3</sup>, *Mo K $\alpha$* ,  $\lambda$  = 0.71073 Å,  $\mu$  = 81.64 cm<sup>-1</sup>, *F*(000) = 904, *T* = 203 K, *R* = 0.0362 (*wR* = 0.0470), 5822 unique reflections, 3843 with *F<sub>o</sub>*<sup>2</sup> ≥ 3σ(|*F<sub>o</sub>*|<sup>2</sup>). In addition to the  $\eta^5$ -pentamethylcyclopentadienyl and CO ligands, the structure contains a non-planar six-membered ring made up of iridium, and the four C atoms and one S atom of the thiophene. The alternating short–long–short [1.33 (2), 1.48 (2), 1.34 (2) Å] pattern of the C—C bond distances indicates that the four-carbon section of the ring is a diene system.

**Introduction.** Previously we reported (Chen, Daniels & Angelici, 1990*a*) reactions of the isomeric 2,5-dimethylthiophene (2,5-Me<sub>2</sub>T) complexes, Cp\*Ir( $\eta^4$ -

2,5-Me<sub>2</sub>T) and Cp\*Ir(C,S-2,5-Me<sub>2</sub>T), where Cp\* =  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>, with CO to give the title complex Cp\*Ir(CO)(C,S-2,5-Me<sub>2</sub>T). Structures of the related Cp\*Ir(PR<sub>3</sub>)(C,S-2,5-Me<sub>2</sub>T) complexes, where *R* = PMe<sub>2</sub>Ph and PMePh<sub>2</sub>, were described in that communication. The most interesting feature of these complexes was the six-membered ring which included the iridium and the four C atoms and one S atom of the thiophene. Of particular interest in the present structure was the effect of the CO ligand on the ring geometry.

**Experimental.** The title complex Cp\*Ir(CO)(C,S-2,5-Me<sub>2</sub>T) was isolated (Chen, Daniels & Angelici, 1991) as a by-product from the reaction of Cp\*Ir(C,S-2,5-Me<sub>2</sub>T) with Fe(CO)<sub>5</sub> and was identified by its IR and <sup>1</sup>H NMR spectra as being the same as that prepared previously (Chen, Daniels & Angelici, 1990*a*). Crystals were purified from CH<sub>2</sub>Cl<sub>2</sub>/hexane at 193 K. Orange–yellow crystal (0.12 × 0.19 × 0.11 mm).

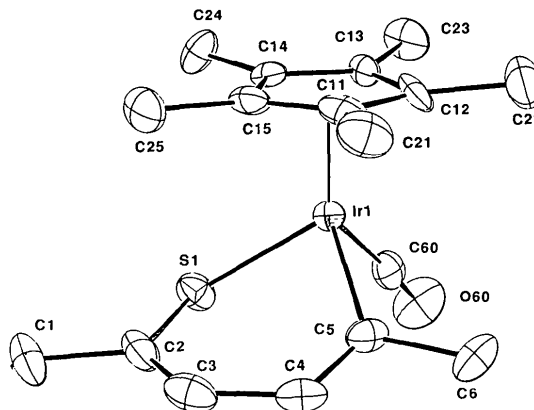
Table 1. Positional parameters and equivalent isotropic atomic displacement coefficients with e.s.d.'s in parentheses

$$B_{eq} = (1/3) \sum_i \sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$B_{eq}$ (Å <sup>2</sup> )
Ir(1)	0.24186 (3)	0.42651 (2)	0.09746 (5)	1.499 (8)
Ir(2)	0.21426 (3)	0.86672 (2)	0.55736 (5)	1.539 (8)
S(1)	0.1626 (2)	0.3924 (2)	-0.2084 (4)	2.19 (6)
S(2)	0.1997 (2)	0.9480 (2)	0.3349 (4)	2.47 (6)
C(1)	0.1547 (9)	0.2457 (8)	-0.453 (1)	3.0 (3)
C(2)	0.2258 (8)	0.2977 (7)	-0.301 (1)	2.1 (2)
C(3)	0.3231 (8)	0.2736 (7)	-0.246 (1)	2.6 (2)
C(4)	0.3978 (8)	0.3219 (8)	-0.108 (1)	2.8 (3)
C(5)	0.3803 (7)	0.3857 (6)	0.025 (1)	1.9 (2)
C(6)	0.4700 (8)	0.4275 (9)	0.142 (2)	3.6 (3)
C(11)	0.2789 (7)	0.3363 (6)	0.289 (1)	1.7 (2)
C(12)	0.2707 (7)	0.4208 (6)	0.393 (1)	1.7 (2)
C(13)	0.1675 (8)	0.4567 (6)	0.341 (1)	1.9 (2)
C(14)	0.1130 (7)	0.3955 (6)	0.207 (1)	1.9 (2)
C(15)	0.1833 (7)	0.3230 (6)	0.173 (1)	1.6 (2)
C(21)	0.3691 (8)	0.2735 (8)	0.314 (1)	2.6 (2)
C(22)	0.3483 (9)	0.4598 (8)	0.548 (1)	2.8 (3)
C(23)	0.1226 (8)	0.5409 (7)	0.425 (2)	2.9 (3)
C(24)	0.0038 (8)	0.4037 (8)	0.118 (2)	3.0 (3)
C(25)	0.1577 (8)	0.2408 (7)	0.050 (1)	2.4 (2)
C(31)	0.333 (1)	1.0430 (8)	0.275 (2)	4.2 (3)
C(32)	0.3224 (8)	0.9610 (7)	0.325 (1)	2.5 (2)
C(33)	0.4032 (8)	0.9035 (8)	0.356 (1)	2.8 (3)
C(34)	0.4029 (8)	0.8203 (7)	0.394 (1)	2.3 (2)
C(35)	0.3348 (8)	0.7926 (7)	0.459 (1)	2.1 (2)
C(36)	0.3462 (9)	0.7016 (8)	0.473 (2)	3.2 (3)
C(41)	0.2357 (8)	0.8451 (7)	0.843 (1)	2.1 (2)
C(42)	0.1415 (7)	0.8971 (6)	0.799 (1)	1.7 (2)
C(43)	0.1621 (7)	0.9736 (6)	0.764 (1)	1.6 (2)
C(44)	0.2692 (7)	0.9694 (7)	0.784 (1)	2.0 (2)
C(45)	0.3157 (8)	0.8917 (7)	0.835 (1)	2.2 (2)
C(51)	0.249 (1)	0.7656 (8)	0.910 (2)	3.5 (3)
C(52)	0.0394 (8)	0.8766 (8)	0.811 (2)	3.3 (3)
C(53)	0.0884 (8)	1.0481 (7)	0.725 (2)	2.8 (3)
C(54)	0.3256 (8)	1.0390 (7)	0.771 (2)	3.0 (3)
C(55)	0.4254 (9)	0.8641 (9)	0.885 (2)	3.1 (3)
C(60)	0.2574 (9)	0.5303 (7)	0.065 (1)	2.6 (2)
C(61)	0.1294 (8)	0.7949 (7)	0.397 (1)	2.3 (2)
O(60)	0.2646 (8)	0.5928 (6)	0.035 (1)	4.9 (3)
O(61)	0.0762 (6)	0.7521 (6)	0.295 (1)	4.2 (2)

Table 2. Selected bond distances (Å) and bond angles (°) with e.s.d.'s in parentheses

Ir(1)—S(1)	2.349 (3)	Ir(2)—C(61)	1.85 (1)
Ir(1)—C(5)	2.07 (1)	S(1)—C(2)	1.76 (1)
Ir(1)—C(11)	2.25 (1)	S(2)—C(32)	1.75 (1)
Ir(1)—C(12)	2.25 (1)	C(1)—C(2)	1.53 (1)
Ir(1)—C(13)	2.27 (1)	C(2)—C(3)	1.33 (2)
Ir(1)—C(14)	2.294 (9)	C(3)—C(4)	1.48 (2)
Ir(1)—C(15)	2.23 (1)	C(4)—C(5)	1.34 (2)
Ir(1)—C(60)	1.84 (1)	C(5)—C(6)	1.51 (2)
Ir(2)—S(2)	2.359 (3)	C(31)—C(32)	1.52 (2)
Ir(2)—C(35)	2.09 (1)	C(32)—C(33)	1.35 (2)
Ir(2)—C(41)	2.26 (1)	C(33)—C(34)	1.47 (2)
Ir(2)—C(42)	2.25 (1)	C(34)—C(35)	1.33 (2)
Ir(2)—C(43)	2.26 (1)	C(35)—C(36)	1.51 (2)
Ir(2)—C(44)	2.24 (1)	C(60)—O(60)	1.13 (1)
Ir(2)—C(45)	2.27 (1)	C(61)—O(61)	1.14 (1)
S(1)—Ir(1)—C(5)	89.1 (3)	Ir(1)—C(5)—C(4)	125.5 (8)
S(1)—Ir(1)—C(60)	90.0 (4)	Ir(1)—C(5)—C(6)	116.9 (9)
C(5)—Ir(1)—C(60)	87.3 (5)	C(4)—C(5)—C(6)	117. (1)
Ir(1)—S(1)—C(2)	107.3 (4)	Ir(2)—C(35)—C(34)	125.1 (9)
Ir(2)—S(2)—C(32)	106.9 (5)	Ir(2)—C(35)—C(36)	115.8 (8)
S(1)—C(2)—C(1)	111.9 (9)	C(34)—C(35)—C(36)	119. (1)
S(1)—C(2)—C(3)	124. (1)	S(2)—Ir(2)—C(35)	88.8 (3)
C(1)—C(2)—C(3)	124. (1)	S(2)—Ir(2)—C(61)	90.5 (4)
C(2)—C(3)—C(4)	127. (1)	C(35)—Ir(2)—C(61)	88.0 (5)
C(3)—C(4)—C(5)	128. (1)	S(2)—C(32)—C(31)	114.9 (9)
S(2)—C(32)—C(33)	124.0 (9)	Ir(1)—C(60)—O(60)	176. (1)
C(31)—C(32)—C(33)	121. (1)	Ir(2)—C(61)—O(61)	178. (1)
C(32)—C(33)—C(34)	127. (1)		

Fig. 1. ORTEP drawing of Cp\*Ir(CO)(C,S-2,5-Me<sub>2</sub>T).

Enraf-Nonius CAD-4 diffractometer, 203 K, graphite monochromator, automatic search routine located and centered 25 reflections,  $20 < 2\theta < 38^\circ$ , from which the unit cell was derived. 11721 reflections were collected,  $\theta$ - $2\theta$  scans ( $4 < 2\theta < 50^\circ$ ,  $-17 < h < 17$ ,  $-20 < k < 20$ ,  $-10 < l < 10$ ), 5822 unique reflections, 3843 reflections used in refinement [ $F_o^2 \geq 3\sigma(F_o^2)$ ],  $R_{int} = 0.024$ . Three intensity standards (344, 353, 442) showed a total decay of 15.8%. Empirical absorption correction applied,  $\psi$  scan for each of seven reflections near  $\chi = 90^\circ$ , normalized transmission 1.00–0.858. Intensity statistics suggested the centrosymmetric triclinic space group. Two Ir atoms were located from direct methods, remaining atoms from difference Fourier synthesis.  $F$  magnitudes were used to refine positions, anisotropic temperature factors and a scale factor. H atoms were not included. 361 parameters,  $R = 0.036$ ,  $wR = 0.047$ ,  $w = 4I/[\sigma^2(I) + 0.005I^2]$ ,  $S = 1.11$ .  $(\Delta/\sigma)_{max} = 0.01$ ,  $\Delta\rho_{max} = 2.2 \text{ e } \text{Å}^{-3}$  located 1.04 Å from atom Ir(2). Atomic scattering factors and  $f'$ ,  $f''$  values were from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were performed using the Enraf-Nonius Structure Determination Package.

**Discussion.** Fractional coordinates of all non-H atoms are listed in Table 1.† Bond distances and selected bond angles are given in Table 2. The crystal contains two independent Cp\*Ir(CO)(C,S-2,5-Me<sub>2</sub>T) molecules with almost the same intramolecular geometries but intermolecular contacts indicate that each resides in a unique environment. The ORTEP drawing of one molecule is shown in Fig. 1. For the molecule that is not shown, the C(41)–C(45) atoms

† Lists of structure factors, anisotropic thermal parameters, bond distances and angles, and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55361 (32 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH0574]

are in the Cp\* ring while C(51)–C(55) are the corresponding CH<sub>3</sub> groups. The six-membered-ring atoms are Ir(2), S(2) and C(32)–C(35); C(31) and C(36) are the CH<sub>3</sub> carbons attached to C(32) and C(35), respectively; the CO ligand consists of C(61) and O(61).

The most notable feature of the structure is the six-membered ring. In the molecule Cp\*Ir(S,S-2,5-Me<sub>2</sub>T), which does not contain a CO ligand, this ring is planar and the three C–C distances in it are the same within experimental error (Chen, Daniels & Angelici, 1990*b*). These distances, together with other data, were interpreted to indicate that the six-membered ring in Cp\*Ir(C,S-2,5-Me<sub>2</sub>T) is a  $\pi$ -delocalized system (Chen, Daniels & Angelici, 1990*a*). In Cp\*Ir(CO)(C,S-2,5-Me<sub>2</sub>T), the C–C bond distances have alternating lengths with C(2)–C(3) and C(4)–C(5) being short (1.34 Å) as compared with C(3)–C(4) (1.47 Å). This indicates localized  $\pi$  bonding at C(2)–C(3) and C(4)–C(5). Moreover, the six-membered ring is no longer planar as shown by the fact that C(5) is 0.30 Å above the plane defined by S(1), C(1), C(2), C(3), C(4) toward Ir(1), while the Ir(1) is 1.19 Å out of this plane.

These distortions from planarity are similar to those in the PMe<sub>2</sub>Ph analog, Cp\*Ir(PMe<sub>2</sub>Ph)(C,S-2,5-Me<sub>2</sub>T), which was also assigned a  $\pi$ -localized structure. Although the bond distances in Cp\*Ir(CO)(C,S-2,5-Me<sub>2</sub>T) and Cp\*Ir(PMe<sub>2</sub>Ph)(C,S-2,5-Me<sub>2</sub>T) are the same within experimental error, the Ir is further (1.19 *versus* 0.69 Å) out of the plane defined by S(1), C(1), C(2), C(3), C(4) in Cp\*Ir(CO)(C,S-2,5-Me<sub>2</sub>T).

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## Structure of Copper(II) 3-Cyanobenzoate

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**Abstract.** [Cu(C<sub>8</sub>H<sub>4</sub>NO<sub>2</sub>)<sub>2</sub>], *M<sub>r</sub>* = 355.8, triclinic, *P* $\bar{1}$ , *a* = 6.545 (4), *b* = 10.235 (5), *c* = 12.174 (6) Å,  $\alpha$  = 74.40 (3),  $\beta$  = 85.02 (4),  $\gamma$  = 78.64 (3)°, *V* = 769.6 (7) Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 1.535 Mg m<sup>-3</sup>,  $\lambda(\text{Mo K}\alpha)$  = 0.71069 Å,  $\mu$  = 1.440 mm<sup>-1</sup>, *F*(000) = 358, room temperature, *R* = 0.029 for 1213 unique reflections having  $|F| > 4\sigma(|F|)$ . The Cu atoms are coordinated by four O atoms from four carboxylate groups, one N atom from a cyano substituent and another Cu atom in a distorted octahedral arrange-

ment. There are six coordination distances: four of 1.957 (3), 1.964 (3), 1.965 (3) and 1.975 (3) Å with the four carboxylate O atoms, one of 2.191 (4) Å with the N atom, and the largest of 2.664 (2) Å with the neighbouring Cu atom. The dimeric units formed by Cu-atom pairs are linked through the aromatic ligands building a polymeric chain structure.

**Introduction.** In the course of our studies on copper(II) arylcarboxylates (Cueto, Gramlich, Petter, Rys