Table 1. *Final atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($Å^2 \times 10^3$), *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Pt(1)	1159 (1)	2101 (1)	1183 (1)	41 (1)
S(1)	1477 (2)	4937 (7)	694 (1)	57 (2)
S(2)	957 (2)	968 (6)	374 (1)	57 (2)
S(3)	792 (3)	−964 (6)	1510 (1)	63 (2)
S(4)	1433 (2)	3664 (6)	1918 (1)	52 (2)
S(5)	933 (2)	−561 (6)	2251 (1)	57 (2)
C(1)	1248 (7)	3403 (23)	204 (5)	49 (8)
C(2)	1277 (8)	4046 (27)	−325 (5)	57 (8)
C(3)	636 (14)	5407 (58)	−482 (8)	134 (20)
C(4)	1398 (26)	2306 (50)	−649 (8)	186 (30)
C(5)	1896 (20)	5650 (69)	−353 (9)	157 (26)
C(6)	1263 (7)	1903 (26)	2365 (4)	50 (7)
C(7)	1392 (7)	2581 (18)	2908 (4)	43 (7)
C(8)	758 (10)	3977 (31)	3026 (6)	70 (10)
C(9)	1461 (14)	666 (34)	3243 (6)	92 (13)
C(10)	2078 (11)	3893 (35)	2993 (6)	81 (12)

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

Pt–S(1)	2·322 (4)	C(1)–C(2)	1·51 (2)
Pt–S(2)	2·323 (3)	C(2)–C(3)	1·50 (3)
Pt–S(3)	2·238 (4)	C(2)–C(4)	1·43 (3)
Pt–S(4)	2·248 (3)	C(2)–C(5)	1·54 (3)
S(1)–C(1)	1·667 (13)	C(6)–C(7)	1·54 (1)
S(2)–C(1)	1·687 (14)	C(7)–C(8)	1·53 (2)
S(3)–S(5)	2·037 (5)	C(7)–C(9)	1·50 (2)
S(4)–C(6)	1·694 (13)	C(7)–C(10)	1·52 (2)
S(5)–C(6)	1·668 (15)		
S(1)–Pt–S(2)	73·0 (1)	C(1)–C(2)–C(3)	109 (1)
S(3)–Pt–S(4)	93·6 (1)	C(1)–C(2)–C(4)	115 (1)
Pt–S(1)–C(1)	88·3 (5)	C(1)–C(2)–C(5)	108 (1)
Pt–S(2)–C(1)	87·9 (4)	C(6)–C(7)–C(8)	107 (1)
Pt–S(3)–S(5)	106·1 (2)	C(6)–C(7)–C(9)	112 (1)
Pt–S(4)–C(6)	109·0 (5)	C(6)–C(7)–C(10)	110 (1)
S(3)–S(5)–C(6)	108·1 (4)		
S(4)–C(6)–S(5)	123·2 (7)		

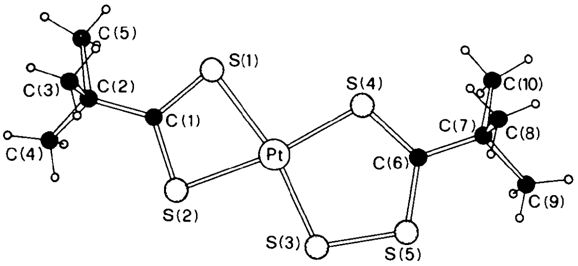

Fig. 1. A perspective view of the molecular structure with the labelling scheme.

Similar results have been observed in the analogous (dithiocumato)(trithioperoxycumato)platinum(II) by Fackler (1983).

Finally, the *tert*-butyl group does not seem to have any influence on the geometry of the rings and it behaves like the aryl substituent in the easy formation of dithio–trithio complexes.

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trans-(Acetylacetonato)dichloro(1,5-cyclooctadiene)iridium(III), $[IrCl_2(C_5H_7O_2)(C_8H_{12})]$

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Abstract. $M_r = 470{\cdot}4$, orthorhombic, $Pnam$, $a = 13{\cdot}822$ (4), $b = 17{\cdot}117$ (5), $c = 11{\cdot}653$ (6) Å, $U = 2757{\cdot}0$ Å^3, $Z = 8$, $D_x = 2{\cdot}27$ Mg m^{-3}, λ(Mo $K\bar{\alpha}$) = 0·71069 Å, $\mu = 10{\cdot}36$ mm^{-1}, $F(000) = 1792$, $T = 133$ (2) K. Final $R = 0{\cdot}030$ for 2904 observed reflections. Mean bond lengths are Ir–Cl 2·348, Ir–O 2·022, Ir–C 2·182 and C=C 1·369 Å. The molecular dimensions are compared with those in acetylacetonato(1,5-cyclooctadiene)iridium(I).

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Table 1. *Atomic coordinates (with e.s.d.'s in parentheses) and equivalent isotropic thermal parameters* (Å^2)

	$n = 1$				$n = 2$			
	x	y	z	U_{eq}*	x	y	z	U_{eq}*
Ir(n)	0·13353 (2)	0·12818 (2)	0·25	0·0110	0·10488 (2)	0·63935 (2)	0·25	0·0115
Cl(n1)	0·1631 (2)	−0·0065 (1)	0·25	0·0218	−0·0617 (1)	0·6130 (1)	0·25	0·0163
Cl(n2)	0·0474 (2)	0·2467 (1)	0·25	0·0190	0·2722 (2)	0·6147 (1)	0·25	0·0214
O(n1)	0·0403 (3)	0·1014 (3)	0·3777 (4)	0·0169	0·1068 (3)	0·5594 (2)	0·3776 (4)	0·0160
C(n1)	−0·0453 (4)	0·0763 (3)	0·3565 (6)	0·0227	0·1086 (4)	0·4861 (3)	0·3557 (6)	0·0229
C(n2)	−0·0856 (7)	0·0642 (6)	0·25	0·0239	0·1094 (6)	0·4498 (5)	0·25	0·0189
C(n3)	−0·1040 (5)	0·0604 (5)	0·4610 (7)	0·0452	0·1101 (6)	0·4364 (4)	0·4601 (7)	0·0407
C(n4)	0·2541 (5)	0·1206 (4)	0·1287 (7)	0·0218	0·1529 (4)	0·7284 (4)	0·1278 (5)	0·0110
C(n5)	0·2184 (5)	0·1957 (4)	0·1284 (6)	0·0258	0·0542 (5)	0·7286 (4)	0·1305 (8)	0·0401
C(n6)	0·3476 (6)	0·0994 (6)	0·1865 (8)	0·0208	0·2132 (6)	0·7895 (5)	0·1852 (7)	0·0133
C(n7)	0·2710 (6)	0·2621 (5)	0·1851 (8)	0·0340	−0·0055 (7)	0·7890 (6)	0·1880 (12)	0·1550

* $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{23} + 2U_{13} + 2U_{12})$.

Table 2. *Bond lengths* (Å) *and angles* (°) (*with e.s.d.'s in parentheses*)

	$n = 1$	$n = 2$		$n = 1$	$n = 2$		$n = 1$	$n = 2$
Ir(n)–Cl(n1)	2·341 (1)	2·347 (1)	O(n1)–C(n1)	1·283 (5)	1·281 (4)	C(n4)–C(n6)	1·502 (7)	1·495 (6)
Ir(n)–Cl(n2)	2·352 (1)	2·350 (1)	C(n1)–C(n2)	1·376 (5)	1·379 (5)	C(n5)–C(n7)	1·503 (7)	1·483 (8)
Ir(n)–O(n1)	2·021 (3)	2·021 (3)	C(n1)–C(n3)	1·489 (6)	1·484 (6)	C(n6)–C(n6′)	1·479 (12)	1·511 (10)
Ir(n)–C(n4)	2·189 (4)	2·189 (4)	C(n4)–C(n5)	1·376 (6)	1·364 (6)	C(n7)–C(n7)′	1·512 (12)	1·445 (17)
Ir(n)–C(n5)	2·173 (4)	2·182 (4)						

	$n = 1$	$n = 2$		$n = 1$	$n = 2$		$n = 1$	$n = 2$
O(n1)–Ir(n)–O(n1)′	94·9 (1)	94·8 (1)	O(n1)–C(n1)–C(n3)	114·0 (4)	113·4 (4)	C(n6)–C(n4)–C(n5)	122·3 (5)	123·1 (4)
Cl(n1)–Ir(n)–O(n1)	83·6 (1)	83·3 (1)	C(n1)–C(n2)–C(n1)′	128·8 (5)	126·5 (5)	C(n4)–C(n5)–C(n7)	122·1 (4)	124·6 (5)
Cl(n2)–Ir(n)–O(n1)	82·7 (1)	82·3 (1)	C(n2)–C(n1)–C(n3)	119·3 (4)	118·3 (4)	C(n5)–C(n7)–C(n7)′	116·1 (5)	116·9 (5)
Ir(n)–O(n1)–C(n1)	121·4 (3)	121·1 (3)	C(n4)–C(n6)–C(n6)′	116·6 (5)	116·5 (5)	Cl(n1)–Ir(n)–Cl(n2)	159·7 (1)	158·6 (1)
O(n1)–C(n1)–C(n2)	126·8 (4)	128·3 (4)						

Introduction. Recently (Robertson, Tucker & Whimp, 1981) we have been interested in the differences in olefinic coordination between the +I and +III oxidation states of rhodium and iridium. The title compound (1) was easily prepared by heating acetylacetonato(1,5-cyclooctadiene)iridium(I) (2) in chloroform and provides the opportunity for a structural comparison with (2) (Tucker, 1981).

Experimental. Pale-yellow parallelepipedal crystals from chloroform; orthorhombic, systematic absences $0kl$, $k + l = 2n + 1$, $h0l$, $h = 2n + 1$, space group *Pnam* (non-standard setting of *Pnma*, *International Tables for X-ray Crystallography,* 1969) confirmed by structure refinement. Cell dimensions (photographic) at 294 K, $a = 14·106$ (7), $b = 17·416$ (17), $c = 11·929$ (7) Å, $U = 2930·5$ Å^3, $Z = 8$, D_m (by flotation in ZnBr$_2$ solution) = 2·14 (2), $D_x = 2·13$ Mg m^{-3}. Bounding forms {001}, {010} and {110}; Philips PW1100/20 diffractometer with Philips NCD1 LN$_2$ gas-flow low-temperature attachment; Mo $K\bar{\alpha}$ radiation; $2\theta_{max} = 60°$. Cell dimensions at 133 K from repeated half-shutter centring of 25 reflections with $8 < 2\theta < 33°$. 8752 data (quadrant $+h + k + l$ measured twice, $h\,0 \to 19$, $k\,0 \to 23$, $l\,0 \to 16$) excluding standards (12,0,0, 0,0,12 and 0,16,0, checked every 60 reflections); data scaled by smoothing cumulative sum of differences curve for the standards; averaged to give 2904 unique data with $I > 3\sigma(I)$; corrected for absorption (Sheldrick, 1976); $R_{av} = \sum|F^2 - \langle F^2\rangle|/\sum F^2 = 0·039$ (= 0·054 for all data). Structure solved from Patterson and Fourier syntheses, refined by full-matrix least squares minimizing $\sum w(|F_o| - |F_c|)^2$ with $w = [\sigma_s^2(F_o) + 0·002|F_o|^2]^{-1}$; anisotropic thermal parameters for non-H atoms; H atoms located from difference synthesis, coordinates refined; four overall isotropic thermal parameters (olefinic H, methylene H, methyl H and acetylacetonato H) refined; final $R = 0·030$, $R_w = 0·040$; $(\Delta/\sigma)_{max} = 0·6$ [H(272)], $(\Delta/\sigma)_{av} = 0·08$; $\Delta\rho_{max} = 0·84$ e Å^{-3} near Ir, 0·36 e Å^{-3} elsewhere; atomic scattering amplitudes with dispersion corrections from *International Tables for X-ray Crystallography* (1974); computer programs *PWREDU* (McLaughlin, 1982; McLaughlin, Taylor & Whimp, 1977), *SHELX*76 (Sheldrick, 1976), *ORTEP*II (Johnson, 1971).

Discussion. Final atomic coordinates for non-H atoms are listed in Table 1 and principal bond lengths and bond angles are listed in Table 2.* The atom-numbering is defined in Fig. 1 and the crystal-packing arrangement is illustrated in the stereopair of Fig. 2. The two independent molecules, which are separated by normal

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* Lists of observed and calculated structure amplitudes, anisotropic thermal parameters, H-atom coordinates, distances and angles involving H atoms and least-squares-planes' data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39111 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

van der Waals contacts, each have crystallographic mirror symmetry, the mirror plane bisecting the Ir(acetylacetonate) ring. Their molecular geometries differ only in the orientation of the acetylacetonato methyl group.

The olefinic functionalities are less strongly bound to Ir in (1) than in (2) (Tucker, 1981) reflecting poorer π back-donation from the less electron-rich Ir^{III} centre. Thus Ir—C is significantly longer [2·183 Å (1), 2·092 Å (2), $\Delta/\sigma \sim 22$] and C=C significantly shorter [1·370 Å (1), 1·400 Å (2), $\Delta/\sigma \sim 4$] in (1) than in (2). However, the angle of bend-back of the olefin, α (Stalick & Ibers, 1970), is rather similar in (1) (31 and 36°), (2) (40 and 45°) and acetylacetonato(1,5-cyclooctadiene)rhodium(I) [(3), 43 and 26°]. Other mean bond lengths and angles in the cyclooctadiene ring are unexceptional and do not differ significantly from those in (2) and (3). The imposition of crystallographic mirror symmetry on the cyclooctadiene ring results in an ideal boat conformation which is sterically less favourable than the skewed boat conformation adopted in the free ligand (Hedberg & Hedberg, 1964) and in (3) (Tucker, Scutcher & Russell, 1975). It may be, therefore, that the large anisotropic thermal parameters for the methylene C atoms (see Fig. 1) result from statistical disordering of each of these atoms between two closely spaced sites rather than from genuine vibration. Unfortunately it has not proven possible to produce a stable refinement of such a model. A similar situation pertains in (2) although the crystallographic mirror plane in that molecule bisects the olefinic bond.

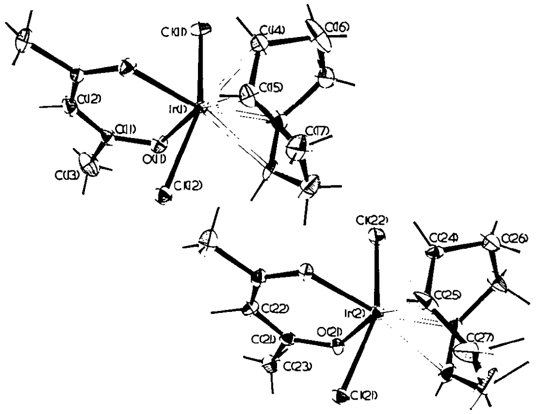

Fig. 1. *ORTEP* drawing (Johnson, 1971) of the two independent molecules showing the atom labelling. Ellipsoids are drawn to include 50% probability and H atoms are scaled arbitrarily for clarity.

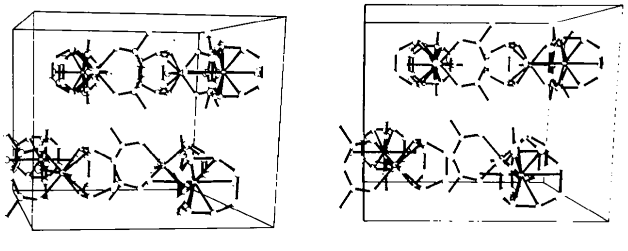

Fig. 2. Stereoscopic drawing of the molecular packing viewed roughly along **c**.

The Ir(acetylacetonate) ring is approximately planar with deviations from the best plane of less than 0·11 Å There are significant differences in the ring geometry between (1) and (2) but their origin is unclear. In (1) the metal—O bond is shorter [Ir—O 2·021 Å (1), 2·042 Å (2), $\Delta/\sigma \sim 7$] and the ligand bite angle is larger [O—Ir—O 94·8° (1), 91·6° (2), $\Delta/\sigma \sim 32$] with, concomitantly, a smaller ring angle at O [Ir—O—C, 121·2° (1), 124·4° (2), $\Delta/\sigma \sim 12$]. Other differences of marginal significance are O—C—CH_3 [113·7° (1), 115·0° (2), $\Delta/\sigma \sim 3$] and C(CH_3)—C(H) [1·376 Å (1), 1·391 Å (2), $\Delta/\sigma \sim 3$].

The steric demand of the cyclooctadiene ligand, above and below the Ir coordination plane defined by O(n1) and the midpoint of the C(n4)=C(n5) bond, is obviously greater than that of the acetylacetonate ligand. Consequently the chloride ligands are positioned over the acetylacetonate ring and the Cl—Ir—Cl angle (mean 159·1°) is markedly non-linear. The marginally shorter Ir—Cl (*trans* to chloride) bond in (1) (mean 2·348 Å) relative to equivalent distances in *mer*-$Cl_3(PMe_2Ph)_3Ir$ (2·361 Å; Robertson & Tucker, 1981) and Cl_3[bis(diphenylphosphino)stilbene]Ir (2·358 Å; Robertson, Tucker & Whimp, 1981) may be related to this non-linearity.

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