

The correctness of the space-group choice was checked by using *MISSYM* (Le Page, 1987). The η refinements (Rogers, 1981) gave, with $wR = 0.033$, $\eta = 1.02(3)$ and confirm the proposed chirality. The largest peaks in the final $\Delta\rho$ map were $\pm 1.0(2)e \text{ \AA}^{-3}$. Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from *International Tables X-ray Crystallography* (1974, Vol. IV). The programs used were *PARST* (Nardelli, 1983), *SHELXTL-Plus* (Sheldrick, 1987), *PCK83* (Williams, 1984), *PLATON* (Spek, 1982) and *MISSYM* (Le Page, 1987). The molecule and the numbering scheme are shown in Fig. 1. Positional parameters and the equivalent values of the anisotropic displacement parameters for the non-H atoms are given in Table 1.* Selected bond lengths and bond angles, torsion angles, least-squares

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, complete bond distances and bond angles and a stereoscopic view of the unit cell have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54956 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL0519]

planes, dihedral angles and possible H bonds are given in Table 2.

Related literature. The crystal structure of $(\text{CH}_3)_2\text{Sn}(\text{Br})(\text{CH}_2)_2\text{P}(\text{O})\text{Ph}^t\text{Bu}$ is described by Weichmann, Mügge, Grand & Robert (1982) and literature on triorganotin halides with a pentacoordinated tin centre resulting from the intramolecular coordination of a donor function is given there.

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Structure of *trans*-Carbonylmethylbis(tri-*p*-tolylphosphine)iridium(I), *trans*-[Ir(CO)(CH₃){P(*p*-C₆H₄CH₃)₃}₂]

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Abstract. [Ir(CO)(CH₃){P(C₇H₇)₃}₂], C₄₄H₄₅IrOP₂, $M_r = 843.9$, orthorhombic, *Pna*2₁, $a = 21.654(3)$, $b = 10.581(1)$, $c = 16.820(1)$ Å, $V = 3853.8(6)$ Å³, $Z = 4$, $D_x = 1.455 \text{ g cm}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu(\text{Mo } K\alpha) = 35.62 \text{ cm}^{-1}$, $F(000) = 1696$, $T = 295 \text{ K}$, $R = 5.73$, $wR = 5.01\%$ for 3527 unique data and $R = 3.08$, $wR = 3.82\%$ for 2291 data with $F_o > 6.0\sigma(F_o)$. The central Ir(I) atom has a square-planar coordination environment in which Ir—P(1) = 2.305(3), Ir—P(2) = 2.302(3), Ir—CH₃ = 2.206(13) and Ir—CO = 1.867(17) Å.

Experimental. We have been involved in the structural characterization of a number of simple complexes of Ir^I (Churchill, Fettinger, Rappoli & Atwood, 1987, and references therein). Among the complexes characterized was *trans*-[Ir(CO)(CH₃)-(PPh₃)₂] (Rees, Churchill, Li & Atwood, 1985). This structure suffered from disorder with the methyl and carbonyl ligands scrambled on a statistical basis about the crystallographic inversion center. We now report the results of an X-ray diffraction study of the analogous compound *trans*-[Ir(CO)(CH₃){P(*p*-

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$)

	x	y	z	U_{eq}^*
Ir(1)	9048 (1)	8693 (1)	10000	35 (1)
P(1)	9879 (1)	9796 (3)	9499 (3)	36 (1)
P(2)	8261 (1)	7587 (3)	10603 (3)	34 (1)
C(1)	8491 (7)	9841 (16)	9556 (10)	61 (5)
O(1)	8153 (6)	10483 (15)	9252 (11)	119 (7)
C(2)	9691 (6)	7199 (13)	10387 (8)	45 (4)
C(11)	8018 (4)	6275 (10)	9929 (15)	36 (3)
C(12)	8170 (5)	5026 (11)	10106 (9)	35 (4)
C(13)	7984 (7)	4138 (14)	9567 (10)	58 (5)
C(14)	7685 (6)	4388 (16)	8895 (10)	58 (5)
C(15)	7523 (7)	5641 (16)	8757 (11)	63 (6)
C(16)	7701 (7)	6575 (12)	9261 (9)	53 (5)
C(17)	7495 (10)	3383 (16)	8296 (14)	98 (9)
C(21)	8395 (6)	6852 (12)	11588 (7)	35 (4)
C(22)	7981 (6)	5998 (13)	11901 (8)	48 (5)
C(23)	8064 (7)	5492 (13)	12641 (8)	51 (5)
C(24)	8571 (7)	5831 (15)	13097 (8)	50 (5)
C(25)	8991 (6)	6659 (14)	12781 (8)	53 (5)
C(26)	8906 (6)	7174 (12)	12040 (8)	43 (4)
C(27)	8655 (10)	5288 (22)	13945 (10)	89 (9)
C(31)	7535 (6)	8428 (12)	10777 (7)	36 (4)
C(32)	6962 (6)	7849 (13)	10745 (10)	56 (5)
C(33)	6420 (7)	8523 (16)	10871 (10)	59 (6)
C(34)	6450 (7)	9812 (17)	11037 (10)	47 (5)
C(35)	6996 (7)	10351 (16)	11109 (10)	61 (6)
C(36)	7543 (6)	9692 (13)	10974 (9)	48 (5)
C(37)	5842 (8)	10547 (19)	11099 (12)	80 (7)
C(41)	10314 (6)	9107 (12)	8666 (8)	42 (4)
C(42)	10231 (7)	7871 (13)	8451 (9)	55 (5)
C(43)	10540 (8)	7377 (15)	7808 (10)	70 (6)
C(44)	10940 (7)	8092 (15)	7341 (9)	59 (5)
C(45)	11030 (7)	9315 (15)	7565 (9)	55 (5)
C(46)	10721 (7)	9849 (17)	8205 (9)	55 (5)
C(47)	11256 (11)	7526 (20)	6642 (11)	92 (8)
C(51)	10457 (6)	10142 (12)	10284 (7)	36 (4)
C(52)	10228 (6)	10355 (15)	11036 (9)	51 (5)
C(53)	10602 (7)	10727 (15)	11640 (8)	54 (5)
C(54)	11218 (7)	10933 (12)	11541 (9)	47 (5)
C(55)	11438 (7)	10713 (13)	10757 (11)	57 (6)
C(56)	11076 (6)	10301 (14)	10128 (12)	60 (7)
C(57)	11611 (8)	11358 (16)	12217 (10)	74 (6)
C(61)	9708 (5)	11369 (12)	9127 (8)	39 (4)
C(62)	9417 (6)	11520 (14)	8390 (8)	49 (5)
C(63)	9248 (7)	12704 (14)	8103 (10)	57 (5)
C(64)	9357 (6)	13777 (14)	8572 (10)	52 (5)
C(65)	9619 (6)	13615 (13)	9276 (9)	50 (5)
C(66)	9790 (7)	12456 (13)	9578 (10)	52 (5)
C(67)	9148 (8)	15081 (15)	8267 (11)	71 (6)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

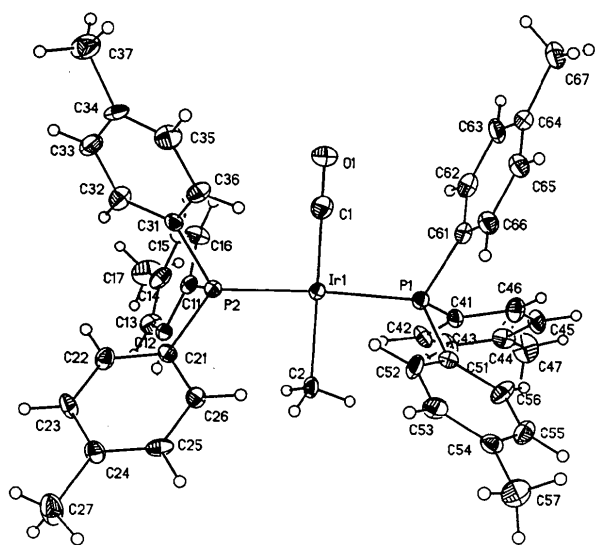
Table 2. Selected distances (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses

Ir(1)—P(1)	2.305 (3)	Ir(1)—P(2)	2.302 (3)
Ir(1)—C(1)	1.867 (17)	Ir(1)—C(2)	2.206 (13)
P(1)—C(41)	1.838 (14)	P(1)—C(51)	1.856 (13)
P(1)—C(61)	1.816 (13)	P(2)—C(11)	1.868 (18)
P(2)—C(21)	1.853 (13)	P(2)—C(31)	1.830 (13)
C(1)—O(1)	1.122 (22)		
P(1)—Ir(1)—P(2)	175.1 (1)	P(1)—Ir(1)—C(1)	91.6 (5)
P(2)—Ir(1)—C(1)	91.7 (5)	P(1)—Ir(1)—C(2)	88.7 (3)
P(2)—Ir(1)—C(2)	88.5 (3)	C(1)—Ir(1)—C(2)	172.8 (6)
Ir(1)—P(1)—C(41)	118.5 (4)	Ir(1)—P(1)—C(51)	111.5 (4)
C(41)—P(1)—C(51)	106.0 (6)	Ir(1)—P(1)—C(61)	115.5 (4)
C(41)—P(1)—C(61)	101.8 (6)	C(51)—P(1)—C(61)	101.6 (6)
Ir(1)—P(2)—C(11)	108.6 (6)	Ir(1)—P(2)—C(21)	119.4 (4)
C(11)—P(2)—C(21)	106.0 (7)	Ir(1)—P(2)—C(31)	117.3 (4)
C(11)—P(2)—C(31)	102.5 (5)	C(21)—P(2)—C(31)	101.2 (6)
Ir(1)—C(1)—O(1)	175.9 (16)		

C₆H₄CH₃)₃}]₂, which has an ordered structure, thereby allowing the direct determination of both Ir—CH₃ and Ir—CO bond lengths in this class of compound.

A colorless crystal of approximate orthogonal dimensions 0.20 \times 0.20 \times 0.25 mm was sealed into a thin-walled glass capillary and was mounted and accurately aligned on a Siemens *R3m/V* automated four-circle diffractometer. Determination of unit-cell parameters and the orientation matrix and data collection [Mo *K* α ; $2\theta = 6.0$ – 50.0° ; $[(\sin\theta)/\lambda]_{\max} = 0.539 \text{ \AA}^{-1}$] were performed using the Siemens *P3* program package. Data for the octants $hk\bar{l}$ and $h\bar{k}l$ were collected (h 0–25, k –12–12, l –20–0). 7259 data were collected. These data were corrected for Lorentz and polarization factors and for the effects of absorption. The data were merged to produce 3527 independent reflections ($R_{\text{int}} = 3.91\%$). The systematic absences $0kl$ for $k + l = 2n + 1$ and $h0l$ for $h = 2n + 1$ are consistent with the non-centrosymmetric space group *Pna2*₁ or the centrosymmetric space group *Pnam*. Intensity statistics favored the non-centrosymmetric space group; this was confirmed by successful solution and refinement of the structure in space group *Pna2*₁.

All crystallographic calculations were carried out on a VAX3100 workstation using the *SHELXTL-Plus* program package (Siemens, 1990). The analytical scattering factors for neutral atoms were corrected for both the f' and the f'' components of anomalous dispersion. The Ir atom was located by direct methods; all other non-H atoms were located from difference-Fourier maps. H atoms of the *p*-tolyl and the methyl ligands were located from these maps and were placed in idealized positions with $d(\text{C—H}) = 0.96 \text{ \AA}$ (Churchill, 1973). Shifts in their positions were fixed to be equal to those of their attached C atoms; their isotropic thermal parameters were refined, but only one such parameter was used for all three H atoms on a given methyl group. All non-H atoms were refined with anisotropic thermal parameters, leading to convergence $[(\Delta/\sigma)_{\max} = 0.001]$ with

Fig. 1. ORTEP view of *trans*-[Ir(CO)(CH₃){P(*p*-C₆H₄CH₃)₃}]₂.

$R = 5.73$, $wR = 5.01\%$ and $GOF = 0.81$ for all 3527 reflections [$R = 3.08$, $wR = 3.82\%$ for those 2291 data for which $F_o > 6.0\sigma(F)$]. The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$ where $w = 1/[\sigma^2(F) + 0.0012F^2]$. A final difference Fourier map showed no unusual features, having a residual electron density in the range -0.59 to $+0.97 \text{ e } \text{Å}^{-3}$ close to the position of the Ir atom and no other features above $0.50 \text{ e } \text{Å}^{-3}$. The absolute configuration was determined by η refinement [$\eta = +1.07$ (6) for the initially chosen coordinates]. Final atom coordinates appear in Table 1.* The molecular structure and atomic labeling scheme are shown in Fig. 1; this is an *ORTEP* plot (Johnson, 1976). Selected bond lengths and bond angles are collected in Table 2. The structure is ordered and there are no abnormally short intermolecular distances.

Related literature. In the following discussion corresponding values of bond lengths and angles from the related structural determination of disordered *trans*-[CH₃(CO)Ir(PPh₃)₂] (Rees, Churchill, Li & Atwood, 1985) are listed in curly brackets for ease of comparison. It should be noted that in the earlier determination the Ir—CO and Ir—CH₃ distances were estimated and that the molecule lay at a crystallographic inversion center and so was rigorously

* Lists of anisotropic thermal parameters, H-atom positions, structure factors, C—C distances and C—C—C angles within the *p*-tolyl ligands have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54965 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR0014]

square planar. The central Ir(I) atom in the present complex is in a square-planar environment with *trans* tri-*p*-tolylphosphine ligands [Ir—P(1) = 2.305 (3), Ir—P(2) = 2.302 (3) Å {2.300 (1) Å}, P(1)—Ir—P(2) = 175.1 (1)° {180°}]. The Ir—CO bond length is 1.867 (17) Å {1.835 Å} with C(1)—O(1) = 1.122 (22) Å {1.14 Å, assumed}. The Ir—CH₃ distance is 2.206 (13) Å {2.17 Å} and is *trans* to the carbonyl ligand with C(1)—Ir—C(2) = 172.8 (6)° {180°}.

Distances and angles within the *p*-tolyl ligands are normal, with P—C bond lengths ranging from 1.816 (13) through 1.868 (18) Å {1.825 (3)–1.834 (3) Å}, averaging $1.844 \pm 0.019 \text{ Å}$ { $1.830 \pm 0.005 \text{ Å}$ }. The present complex is isomorphous with *trans*-carbonylchlorobis(tri-*p*-tolylphosphine)iridium-(I) (Churchill, Fettinger, Rappoli & Atwood, 1987).

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Structure of 1,1-Dioxo-2,4,4,6-tetraphenyl-4*H*-thiopyran Benzene Solvate

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Abstract. C₂₉H₂₂O₂S_{1/2}C₆H₆, $M_r = 473.61$, monoclinic, $P2_1/c$, $a = 9.029$ (4), $b = 13.265$ (4), $c = 21.426$ (11) Å, $\beta = 92.62$ (4)°, $V = 2564$ (2) Å³, $Z = 4$, $D_x = 1.227 \text{ g cm}^{-3}$, $\lambda(\text{Cu } K\alpha) = 1.54184 \text{ Å}$, $\mu = 12.95 \text{ cm}^{-1}$, $F(000) = 996$, $T = 294 \text{ K}$, $R = 0.052$ for 3161 unique observed reflections. The central ring

adopts a boat conformation with S1 and C4 displaced by 0.108 (6) and 0.041 (6) Å, respectively, out of the least-squares plane through the remaining ring atoms. The phenyl rings at C2 and C6 make dihedral angles of 58.2 (2) and -44.7 (3)°, respectively, with this least-squares plane. The orientations of the