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Structure of *trans*-Carbonylchlorobis(tri-*p*-tolylphosphine)iridium(I)

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Abstract. $[IrCl(CO)\{P(C_7H_7)_3\}_2]$, $M_r = 864{\cdot}5$, orthorhombic, $Pna2_1$, $a = 21{\cdot}586\,(2)$, $b = 10{\cdot}603\,(1)$, $c = 16{\cdot}814\,(2)$ Å, $V = 3848{\cdot}3\,(8)$ Å^3, $Z = 4$, $D_x = 1{\cdot}49$ g cm^{-3}, $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}710\,730$ Å, $\mu(\text{Mo } K\alpha) = 38{\cdot}7$ cm^{-1}, $F(000) = 1728$, $T = 297$ K, $R(F) = 3{\cdot}5$, $R(wF) = 3{\cdot}1$% for all 5323 reflections (hkl and $hk\bar{l}$). The central Ir$^{\rm I}$ atom has a square-planar coordination environment in which Ir—P(1) = 2·330 (2), Ir—P(2) = 2·332 (2), Ir—Cl = 2·364 (2) and Ir—CO = 1·817 (8) Å. The tetrahedral bonding to the P atoms is distorted towards C_{3v} from T_d and the phenyl rings are distorted from D_{6h} to C_{2v} symmetry by the electronegative P atoms.

Introduction. We have been involved in the structural characterization of a variety of simple alkyl and alkoxy complexes of Ir$^{\rm I}$, including *trans*-$[Ir(PPh_3)_2(CO)CH_3]$ (Rees, Churchill, Li & Atwood, 1985), *trans*-$[Ir(PPh_3)_2(CO)(OC_6H_5)]$ (Rees, Churchill, Fettinger & Atwood, 1985), *trans*-$[Ir(PPh_3)_2(CO)(OC_6F_5)]$ (Churchill, Fettinger, Rees & Atwood, 1986*c*), $[Ir(PPh_3)_2(CO)_2\{C(=O)OCH_3\}]$ (Churchill, Fettinger, Rees & Atwood, 1986*b*), $[Ir(PPh_3)_2(CO)(CH_3)(CH_3CO_2CH{=}CHCO_2CH_3)]$ (Churchill, Fettinger, Rees & Atwood, 1986*a*) and $[Ir(PPh_3)_2(CO)(CH_3)(CH_3CO_2C{\equiv}CCO_2CH_3)]$ (Rees, Churchill, Fettinger & Atwood, 1987); the species *trans*-$[Ir(PPh_3)_2(CO)(C_6F_5)]$ has also been studied (Clearfield, Gopal, Bernal, Moser & Rausch, 1975). We have recently turned our attention to the related derivatives of the tri-*p*-tolylphosphine ligand and have discovered the tetrahedral Ir$^{\rm I}$ complex $[Ir\{P(C_6H_4\text{-}p\text{-}CH_3)_3\}_2\{C(=O)CH_2C(CH_3)_3\}\{CH_3CO_2C{\equiv}CCO_2CH_3\}]$ (Rappoli, Churchill, Janik, Rees & Atwood, 1987). We now report the results of an X-ray diffraction study on the simple parent molecule of this system, $[Ir\{P(C_6H_4\text{-}p\text{-}CH_3)_3\}_2(CO)Cl]$.

Experimental. A canary-yellow colored crystal with approximate orthogonal dimensions of 0·30 × 0·30 × 0·40 mm was sealed into a thin-walled glass capillary in an inert (Ar) atmosphere and was mounted and aligned accurately on a Syntex $P2_1$ automated four-circle diffractometer. Determination of unit-cell parameters and the crystal orientation matrix and data collection [Mo $K\alpha$; $2\theta = 4{\cdot}5$–$45{\cdot}0°$; $[(\sin\theta)/\lambda]_{\max} = 0{\cdot}539$ Å^{-1}] were performed as has previously been described in detail (Churchill, Lashewycz & Rotella, 1977). Three standard reflections (in approximately mutually orthogonal directions in space) were measured before each batch of 97 data; no fluctuations nor decay were observed. Diffraction data were corrected for absorption (by interpolation in 2θ and φ between a set of close-to-axial ψ scans in which $T_{\max}/T_{\min} = 1{\cdot}09$–$1{\cdot}14$). The systematic absences $0kl$ for $k + l = 2n + 1$ and $h0l$ for $h = 2n + 1$ ($00l$ for $l = 2n + 1$) are consistent with the non-centrosymmetric space group $Pna2_1$ or the centrosymmetric space group $Pnam$. Data for the octants hkl and $hk\bar{l}$ were collected ($h\,0\rightarrow23$, $k\,0\rightarrow12$, $l\,{-20}\rightarrow20$), corrected for Lorentz and polarization factors and reduced to observed structure-factor amplitudes. Any reflection with a net intensity less than zero was assigned an $|F_o|$ value of zero. Intensity statistics favored the non-centrosymmetric case; this was confirmed by the successful solution and refinement of the structure in the non-centrosymmetric space group.

The coordinates of the Ir atom were determined from a three-dimensional Patterson map. The positions of all remaining non-H atoms were located from a series of difference-Fourier syntheses. H atoms on the methyl groups of the *p*-tolyl ligands were located directly and input in idealized positions; H atoms of the aromatic rings were input in calculated trigonal positions based upon externally bisecting geometry with $d(\text{C—H}) = 0{\cdot}95$ Å (Churchill, 1973). All H atoms were assigned a thermal parameter of $U = 0{\cdot}076$ Å^2. Full-matrix least-squares refinement of positional parameters for all non-H atoms, anisotropic thermal parameters for the $IrP_2(CO)Cl$ fragment and isotropic thermal parameters

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Table 1. *Final fractional atomic coordinates and isotropic thermal parameters*

E.s.d.'s are given in parentheses.

	x	y	z	U_{eq}(Å^2)
Ir	0·09594 (1)	0·12893 (2)	$\frac{1}{4}$	0·030
P(1)	0·17602 (7)	0·24119 (15)	0·31024 (10)	0·029
P(2)	0·01141 (7)	0·01735 (15)	0·19990 (10)	0·031
Cl	0·02823 (8)	0·29527 (17)	0·28484 (11)	0·051
C(1)	0·14921 (33)	0·01053 (72)	0·21232 (47)	0·052
O(1)	0·18267 (26)	−0·06209 (62)	0·18774 (43)	0·091
C(11)	0·16132 (28)	0·31352 (57)	0·40749 (35)	0·030 (1)
C(12)	0·10852 (30)	0·28631 (62)	0·45088 (40)	0·041 (2)
C(13)	0·10048 (32)	0·33859 (66)	0·52603 (44)	0·047 (2)
C(14)	0·14320 (33)	0·41944 (65)	0·55928 (41)	0·045 (2)
C(15)	0·19577 (31)	0·44632 (64)	0·51557 (41)	0·045 (2)
C(16)	0·20462 (31)	0·39470 (59)	0·44100 (38)	0·040 (2)
C(17)	0·13699 (39)	0·47049 (82)	0·64296 (49)	0·065 (2)
C(21)	0·24876 (28)	0·15798 (53)	0·32756 (35)	0·031 (1)
C(22)	0·30607 (31)	0·21481 (61)	0·31999 (40)	0·043 (2)
C(23)	0·36138 (34)	0·14772 (67)	0·33388 (43)	0·049 (2)
C(24)	0·35941 (31)	0·02539 (69)	0·35264 (39)	0·040 (2)
C(25)	0·30269 (34)	−0·03465 (69)	0·36111 (43)	0·050 (2)
C(26)	0·24801 (31)	0·03052 (65)	0·34940 (40)	0·043 (2)
C(27)	0·41963 (41)	−0·04886 (85)	0·35968 (54)	0·069 (2)
C(31)	0·19917 (22)	0·36996 (47)	0·24467 (61)	0·033 (1)
C(32)	0·18480 (25)	0·49467 (50)	0·25874 (46)	0·039 (1)
C(33)	0·20184 (33)	0·58766 (64)	0·20491 (42)	0·047 (2)
C(34)	0·23314 (34)	0·55832 (70)	0·13660 (45)	0·051 (2)
C(35)	0·24723 (37)	0·43591 (76)	0·12163 (49)	0·060 (2)
C(36)	0·22991 (33)	0·33989 (61)	0·17404 (42)	0·046 (2)
C(37)	0·25024 (48)	0·65925 (86)	0·07704 (61)	0·084 (3)
C(41)	−0·03282 (29)	0·08491 (58)	0·11740 (38)	0·036 (2)
C(42)	−0·02783 (33)	0·21235 (67)	0·09944 (42)	0·049 (2)
C(43)	−0·06001 (35)	0·26439 (71)	0·03478 (43)	0·053 (2)
C(44)	−0·09688 (32)	0·18979 (70)	−0·01323 (44)	0·049 (2)
C(45)	−0·10231 (32)	0·06388 (70)	0·00508 (44)	0·049 (2)
C(46)	−0·07071 (33)	0·01021 (66)	0·06916 (40)	0·043 (2)
C(47)	−0·12997 (43)	0·24509 (84)	−0·08453 (53)	0·072 (2)
C(51)	−0·04444 (27)	−0·01619 (55)	0·27848 (33)	0·033 (2)
C(52)	−0·10709 (28)	−0·03582 (60)	0·26731 (39)	0·045 (2)
C(53)	−0·14381 (34)	−0·07375 (70)	0·33025 (43)	0·049 (2)
C(54)	−0·12059 (32)	−0·09490 (62)	0·40553 (41)	0·042 (2)
C(55)	−0·05855 (34)	−0·07574 (68)	0·41714 (42)	0·048 (2)
C(56)	−0·02072 (33)	−0·03480 (67)	0·35443 (42)	0·046 (2)
C(57)	−0·16107 (40)	−0·13885 (77)	0·47407 (52)	0·067 (2)
C(61)	0·03015 (28)	−0·14112 (55)	0·16270 (36)	0·033 (1)
C(62)	0·05906 (33)	−0·15536 (63)	0·08865 (41)	0·043 (2)
C(63)	0·07520 (33)	−0·27316 (66)	0·06065 (41)	0·046 (2)
C(64)	0·06543 (31)	−0·38058 (62)	0·10617 (39)	0·042 (2)
C(65)	0·03774 (32)	−0·36574 (63)	0·18061 (40)	0·045 (2)
C(66)	0·02084 (31)	−0·24755 (63)	0·20881 (39)	0·042 (2)
C(67)	0·08335 (37)	−0·50961 (78)	0·07600 (47)	0·060 (2)

For the first six atoms, $U_{eq} = [\frac{1}{3}(B_{11} + B_{22} + B_{33})]/8\pi^2$.

for atoms of the *p*-tolyl groups led to convergence $[(\Delta/\sigma) \leq 0\cdot10]$ with $R(F) = 3\cdot5$, $R(wF) = 3\cdot1\%$ and GOF = 1·27 for all 5323 reflections $[R(F) = 2\cdot5$ and $R(wF) = 2\cdot9\%$ for those 4544 data with $|F_o| > 6\sigma(|F_o|)]$. A final difference-Fourier map was 'clean' with $|\Delta\rho| \leq 0\cdot24$ e Å^{-3}. A listing of atomic coordinates is given in Table 1.

The analytical form of the appropriate neutral-atom scattering factors was corrected for both the real (f') and imaginary (if'') components of anomalous dispersion using the values compiled in *International Tables for X-ray Crystallography* (1974). [It should be noted that the results reported are for the correct crystal chirality; inversion of the atomic coordinates and refinement yielded $R(F) = 6\cdot7$ and $R(wF) = 7\cdot8\%$.] Computer programs used: Syntex *XTL* system (locally modified).

The function minimized during the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = (\sigma|F_o|)^2 + (0\cdot015|F_o|)^2$. An empirical correction for secondary extinction was also applied to the data in the form $|F_{o,\rm corr}| = |F_{o,\rm uncorr}|(1\cdot0 + gI_o)$; the value determined for g was $3\cdot9 \times 10^{-8}$.

Discussion. The molecular structure and atomic labelling scheme are shown in Fig. 1. Selected bond lengths and angles are collected in Table 2. The structure is ordered and there are no abnormally short intermolecular distances.

The central Ir$^{\rm I}$ atom is in a square-planar coordination environment with *trans* tri-*p*-tolylphosphine ligands [Ir—P(1) = 2·330 (2), Ir—P(2) = 2·332 (2) Å, P(1)—Ir—P(2) = 175·19 (6)°]. The Ir—CO bond length is 1·817 (8) Å with C(1)—O(1) = 1·134 (10) Å and Ir—C(1)—O(1) = 178·8 (7)°. The chloride ligand has Ir—Cl = 2·364 (2) Å and is *trans* to the carbonyl ligand, with Cl—Ir—C(1) = 173·36 (24)°.

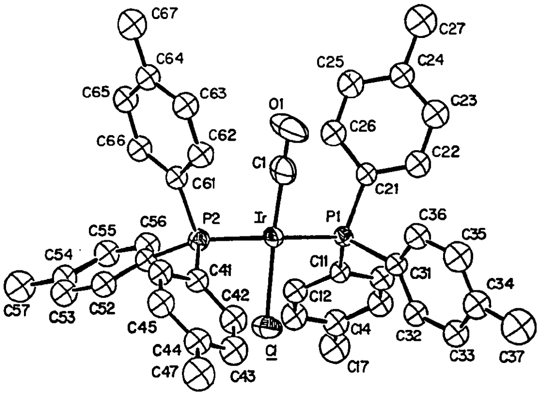

Fig. 1. A view of the molecule showing the atom numbering.

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

Ir—P(1)	2·330 (2)	P(1)—C(11)	1·834 (6)
Ir—P(2)	2·332 (2)	P(1)—C(21)	1·824 (6)
Ir—Cl	2·364 (2)	P(1)—C(31)	1·825 (8)
Ir—C(1)	1·817 (8)	P(2)—C(41)	1·830 (7)
C(1)—O(1)	1·134 (10)	P(2)—C(51)	1·824 (6)
		P(2)—C(61)	1·838 (6)
P(1)—Ir—P(2)	175·19 (6)	Ir—P(1)—C(11)	118·2 (2)
P(1)—Ir—Cl	88·27 (6)	Ir—P(1)—C(21)	117·4 (2)
P(1)—Ir—C(1)	92·00 (24)	Ir—P(1)—C(31)	108·8 (2)
P(2)—Ir—Cl	89·10 (6)	Ir—P(2)—C(41)	118·9 (2)
P(2)—Ir—C(1)	91·07 (24)	Ir—P(2)—C(51)	110·8 (2)
Cl—Ir—C(1)	173·36 (24)	Ir—P(2)—C(61)	114·5 (2)
Ir—C(1)—O(1)	178·8 (7)		
C(11)—P(1)—C(21)	102·1 (3)	C(12)—C(11)—C(16)	118·0 (6)
C(11)—P(1)—C(31)	105·9 (3)	C(22)—C(21)—C(26)	117·1 (6)
C(21)—P(1)—C(31)	102·9 (3)	C(32)—C(31)—C(36)	118·1 (6)
C(41)—P(2)—C(51)	106·3 (3)	C(42)—C(41)—C(46)	118·1 (6)
C(41)—P(2)—C(61)	102·4 (3)	C(52)—C(51)—C(56)	117·7 (6)
C(51)—P(2)—C(61)	102·4 (3)	C(62)—C(61)—C(66)	118·4 (6)
P(1)—C(11)—C(12)	121·7 (5)	P(2)—C(41)—C(42)	120·4 (5)
P(1)—C(11)—C(16)	120·3 (5)	P(2)—C(41)—C(46)	121·6 (5)
P(1)—C(21)—C(22)	123·0 (5)	P(2)—C(51)—C(52)	125·3 (5)
P(1)—C(21)—C(26)	119·9 (5)	P(2)—C(51)—C(56)	116·7 (5)
P(1)—C(31)—C(32)	123·5 (5)	P(2)—C(61)—C(62)	119·9 (5)
P(1)—C(31)—C(36)	118·2 (5)	P(2)—C(61)—C(66)	121·5 (5)

P—C bond lengths range from 1·824 (6) through 1·838 (6) Å, averaging 1·829 ± 0·006 Å. The tetrahedral environment about the P atoms is distorted from T_d toward C_{3v}, with Ir—P—C(*ipso*) angles of 108·8 (2)–118·9 (2)° (average = 114·8°) and C(*ipso*)—P—C(*ipso'*) angles of 102·1 (3)–106·3 (3)° (average = 103·7°). Internal angles at the *ipso* C atoms [C(n1), n = 1–6] range from 117·1 (6) through 118·4 (6)° [average = 117·9 (5)°]. The six-membered carbocyclic rings are all distorted from D_{6h} to C_{2v} symmetry owing to the electronegative P atoms on the *ipso* C atoms (*cf.* Churchill & De Boer, 1975; Domenicano, Vaciago & Coulson, 1975).*

The current structural study is of additional interest insofar as the complex studied represents an analogue of Vaska's compound, *trans*-[$Ir(PPh_3)_2(CO)Cl$] (Vaska & Di Luzio, 1961; Vaska, 1968), a complex of pivotal importance in the discovery of oxidative addition reactions of transition-metal complexes. To the best of our knowledge, no structural study of Vaska's compound has appeared in the primary literature. An account of the analogous Rh^I species, *trans*-[$Rh(PPh_3)_2(CO)Cl$], has appeared (Del Pra, Zanotti & Segala, 1979); this study was beset with difficulties and the structure is probably disordered. An account of the crystal structure of the tri-*o*-tolylphosphine derivative, *trans*-[$Ir\{P(C_6H_4\text{-}o\text{-}CH_3)_3\}_2(CO)Cl$], has appeared (Brady, DeCamp, Flynn, Schneider, Scott, Vaska & Werneke, 1975); this also exhibits CO/Cl disorder. Bond lengths are similar to those in the current study [Ir—P = 2·338 (5) Å, Ir—Cl = 2·43 (1) Å, Ir—CO = 1·67 (4) Å] but are of intrinsically lower precision and accuracy.

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* Lists of structure factors, anisotropic thermal parameters, C—C distances, C—C—C angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44006 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The Structures of $Bi_2(CH_3COO)_6.3SC(NH_2)_2.H_2O$ and $Bi(CH_3COO)_3.3SC(NH_2)_2$

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Abstract. Compound *A*: $Bi_2(CH_3COO)_6.3SC(NH_2)_2.H_2O$, $M_r = 1018·61$, triclinic, $P\bar{1}$, $a = 11·450$ (7), $b = 11·553$ (5), $c = 11·885$ (4) Å, $\alpha = 95·44$ (4), $\beta = 91·45$ (4), $\gamma = 85·05$ (4)°, $V = 1559$ (2) Å^3, $Z = 2$, $D_m = 2·154$, $D_x = 2·170$ (3) Mg m^{-3}, Mo $K\alpha$ radiation, $\lambda = 0·7107$ Å, $\mu = 11·08$ mm^{-1}, $T = 295$ K, $F(000) = 964$, $R(F) = 0·041$ for 2549 unique reflections. Compound *B*: $Bi(CH_3COO)_3.3SC(NH_2)_2$, $M_r = 614·48$, monoclinic, $P2_1/n$, $a = 8·437$ (1), $b = 15·065$ (2), $c = 15·843$ (2) Å, $\beta = 94·00$ (1)°, $V = 2008·8$ (8) Å^3, $Z = 4$, $D_m = 2·04$, $D_x = 2·033$ (1) Mg m^{-3}, Mo $K\alpha$ radiation, $\lambda = 0·7107$ Å, $\mu = 9·1$ mm^{-1}, $T = 295$ K, $F(000) = 1184$, $R(F) = 0·029$ for 3525 unique reflections. The structure of compound *A* is built from two different dimeric ionic groups: $[Bi_2(CH_3COO)_8]^{2-}$ and $[Bi_2(CH_3COO)_4\{SC$-

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