Trimethylphosphonium *trans*-tetrachloridobis(trimethylphosphane-*κP*)-iridate(III)

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The title compound, $[HP(CH_3)_3][IrCl_4\{(H_3C)_3P\}_2]$, consists of a trimethylphosphonium cation and a tetrachloridobis(trimethylphosphane)iridate(III) anion. The anion has an octahedral arrangement of ligands, with the trimethylphosphane groups occupying *trans* positions. The Ir^{III} atom sits on an inversion center with one $P(CH_3)_3$ ligand and two chloride ligands in the asymmetric unit. The trimethylphosphonium cation is disordered about a twofold rotation axis. The title compound is the first structurally characterized tetrachloridobis(phosphane)iridate complex.

Related literature

The structure of $[((H_3C)_3As)ClPd(\mu\text{-}Cl)_2IrCl_2(P(CH_3)_2\text{-}(C_6H_5))_2]$ can be found in: Briant *et al.* (1981) (CCDC:530747). The structure of $[P(C_6H_5)_4][((H_3C-CH_2)_3P)_2RhCl_4]$ can be found in: Cotton & Kang (1993) (CCDC:632517). Previous work on $((H_3C)_3P)_3IrCl_3$ can be found in: Merola *et al.* (2013).
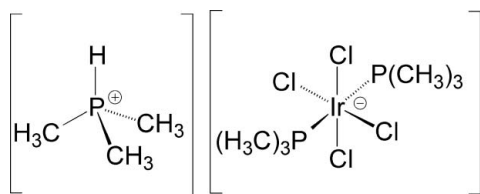
Experimental

Crystal data

$(C_3H_{10}P)[IrCl_4(C_3H_9P)_2]$	$V = 1957.09\ (9)$ Å^3
$M_r = 563.22$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 15.1814\ (5)$ Å	$\mu = 7.60$ mm^{-1}
$b = 9.8502\ (3)$ Å	$T = 100$ K
$c = 13.0943\ (3)$ Å	$0.20 \times 0.13 \times 0.09$ mm
$\beta = 91.843\ (2)°$	

Data collection

Agilent Xcalibur Sapphire3 diffractometer	10332 measured reflections
Absorption correction: Gaussian (*CrysAlis PRO*; Agilent, 2013)	3121 independent reflections
$T_{min} = 0.360$, $T_{max} = 0.570$	2511 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.031$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$	3 restraints
$wR(F^2) = 0.079$	H-atom parameters constrained
$S = 0.98$	$\Delta\rho_{max} = 1.97$ e Å^{-3}
3121 reflections	$\Delta\rho_{min} = -0.93$ e Å^{-3}
97 parameters	

Data collection: *CrysAlis PRO* (Agilent, 2013); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2*.

References

Agilent (2013). *CrysAlis PRO*. Agilent Technologies UK Ltd, Yarnton, England.

Briant, C. E., Rowland, K. A., Webber, C. T. & Mingos, D. M. P. (1981). *J. Chem. Soc. Dalton Trans.* pp. 1515–1519.

Cotton, F. A. & Kang, S. J. (1993). *Inorg. Chem.* **32**, 2336–2342.

Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.

Merola, J. S., Franks, M. A. & Frazier, J. F. (2013). *Polyhedron*, **54**, 67–73.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

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1. Comment

We have been investigating the chemistry of iridium with the strongly electron-donating ligand, trimethylphosphane, for some time. In a recent publication, we discussed how [Ir(COD)(P(CH$_3$)$_3$)$_3$]Cl can be converted into *mer*,tris-(trimethyl-phosphane)trichloroiridium whose crystals tenaciously hold onto many different solvents (Merola *et al.*, 2013). A direct reaction between IrCl$_3$·H$_2$O and P(CH$_3$)$_3$ was attempted to make the same compound in a more direct way, but that reaction did not give a clean product and only a small number of crystals of the title product were obtained.

The title compound crystallizes in the *C*2/*c* space group and the iridium sits on an inversion center. Thus, the iridium (1/2 occupancy), two chlorine atoms and one P(CH$_3$)$_3$ group are unique with the remainder of the [((CH$_3$)$_3$P)$_2$IrCl$_4$] anion being generated by the inversion operator. The cation, trimethylphosphonium, lies slightly offset from a 2-fold rotation axis resulting in a disordered [HP(CH$_3$)$_3$]$^+$ ion where the two sites are generated by the rotation. In aqueous ethanol, reduction of some of the iridium(III)chloride to iridium(I) species will generate HCl and thus lead to the formation of the trimethylphosphonium cation.

This compound is the first crystallographically characterized compound with the [(Me$_3$P)$_2$IrCl$_4$]$^-$ ion. The closest analog in the iridium family is a bis-phenyldimethylphosphane complex of iridium with two terminal chlorines and two chlorines bridging between iridium and palladium (Briant *et al.*, 1981). The closest structure to the title iridium compound in the literature is the rhodium analog with triethylphosphane ligands (Cotton & Kang, 1993).

2. Experimental

Trimethylphosphane (0.19 g, 2.55 mmol) and IrCl$_3$.H$_2$O (0.100 g, 0.80 mmol) were refluxed in 95% aqueous ethanol for 3 hr. At the end of that time, the solvent was removed under reduced pressure yielding 0.20 g of a dark, brown, sticky powder. ^{1}H NMR spectroscopy indicated that a number of different species were present, possibly with various numbers of PMe$_3$ and chloride on iridium as well as a mixture of iridium(III) and iridium(I) species. Attempts to separate different complexes were unsuccessful. A small portion of the solid was dissolved in dichloromethane and the solvent was allowed to evaporate slowly. After evaporation, a very few crystals of the title compound suitable for X-ray diffraction were formed and used for this experiment.

3. Refinement

The trimethylphosphonium cation is disordered about a twofold axis and was modeled with each trimethylphosphonium fragment at 50% occupancy. P—C distances within the disordered fragment were restrained to be similar (esd 0.02 Å). Methyl carbon atoms C4 and C5 of the two disordered moieties do overlap substantially and were constrained to have identical ADPs. H atoms were placed at calculated positions and refined using a model in which the hydrogen rides on the atom to which it is attached. For methyl hydrogen atoms U_{iso}(H) = 1.5U_{eq}(C). The phosphonium H atom was treated

with an idealized tetrahedral geometry (AFIX 13) with $U_{iso}(H) = 1.5U_{eq}(P)$.

Computing details

Data collection: *CrysAlis PRO* (Agilent, 2013); cell refinement: *CrysAlis PRO* (Agilent, 2013); data reduction: *CrysAlis PRO* (Agilent, 2013); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: OLEX2 (Dolomanov *et al.*, 2009); software used to prepare material for publication: OLEX2 (Dolomanov *et al.*, 2009).
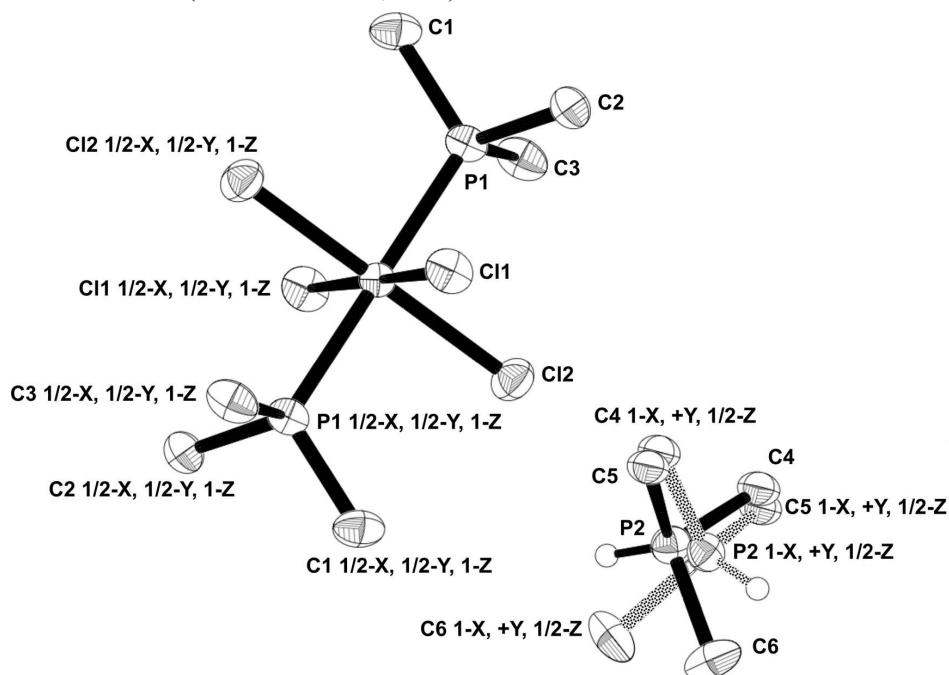
Figure 1

The thermal ellipsoid representation of the fully grown anion/cation pair with atoms labeled with the symmetry operation generating them. Each trimethylphosphonium fragment has 50% occupancy with one fragment indicated by different shading. With the exception of the P—H hydrogen atoms, H atoms are omitted for clarity. The displacement ellipsoids are shown at the 50% probability level.

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Crystal data

$(C_3H_{10}P)[IrCl_4(C_3H_9P)_2]$	$F(000) = 1088$
$M_r = 563.22$	$D_x = 1.912$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 15.1814$ (5) Å	Cell parameters from 4635 reflections
$b = 9.8502$ (3) Å	$\theta = 4.5–31.7°$
$c = 13.0943$ (3) Å	$\mu = 7.60$ mm^{-1}
$\beta = 91.843$ (2)°	$T = 100$ K
$V = 1957.09$ (9) Å^3	Prism, clear light brown
$Z = 4$	$0.20 \times 0.13 \times 0.09$ mm

Data collection

Agilent Xcalibur Sapphire3 diffractometer	10332 measured reflections
Radiation source: Enhance (Mo) X-ray Source	3121 independent reflections
Graphite monochromator	2511 reflections with $I > 2\sigma(I)$
Detector resolution: 16.0355 pixels mm⁻¹	$R_{int} = 0.031$
ω and π scans	$\theta_{max} = 32.0°$, $\theta_{min} = 4.1°$
Absorption correction: gaussian	$h = -22 \rightarrow 17$
(*CrysAlis PRO*; Agilent, 2013)	$k = -14 \rightarrow 14$
$T_{min} = 0.360$, $T_{max} = 0.570$	$l = -18 \rightarrow 19$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.028$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.079$	
$S = 0.98$	H-atom parameters constrained
3121 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0438P)^2 + 4.5906P]$
97 parameters	where $P = (F_o^2 + 2F_c^2)/3$
3 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 1.97$ e Å⁻³
	$\Delta\rho_{min} = -0.93$ e Å⁻³

Special details

Experimental. Absorption correction: CrysAlisPro (Agilent, 2013) Numerical absorption correction based on gaussian integration over a multifaceted crystal model

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	$U_{iso}*/U_{eq}$	Occ. (<1)
Ir1	0.2500	0.2500	0.5000	0.02041 (7)	
Cl1	0.10488 (6)	0.33083 (11)	0.52340 (8)	0.0362 (2)	
Cl2	0.26795 (8)	0.22552 (10)	0.67847 (7)	0.0333 (2)	
P1	0.31064 (7)	0.46585 (10)	0.51853 (7)	0.02636 (19)	
C1	0.4083 (3)	0.4741 (4)	0.6014 (3)	0.0372 (9)	
H1A	0.3929	0.4501	0.6713	0.056*	
H1B	0.4323	0.5665	0.6007	0.056*	
H1C	0.4526	0.4104	0.5772	0.056*	
C2	0.2402 (3)	0.5911 (4)	0.5739 (3)	0.0380 (9)	
H2A	0.2182	0.5566	0.6385	0.057*	
H2B	0.1903	0.6101	0.5266	0.057*	
H2C	0.2737	0.6748	0.5866	0.057*	
C3	0.3468 (3)	0.5433 (4)	0.4021 (3)	0.0315 (8)	
H3A	0.3740	0.6314	0.4178	0.047*	
H3B	0.2961	0.5563	0.3549	0.047*	
H3C	0.3900	0.4842	0.3703	0.047*	
P2	0.50757 (18)	0.99525 (19)	0.22786 (14)	0.0272 (4)	0.50
H2	0.5366	0.9618	0.1652	0.033*	0.50

C4	0.5875 (7)	1.0818 (16)	0.3085 (10)	0.0316 (17)	0.50
H4A	0.6290	1.0156	0.3386	0.047*	0.50
H4B	0.5575	1.1293	0.3632	0.047*	0.50
H4C	0.6197	1.1476	0.2678	0.047*	0.50
C5	0.4190 (7)	1.1060 (16)	0.1915 (11)	0.0316 (17)	0.50
H5A	0.3785	1.0591	0.1436	0.047*	0.50
H5B	0.4425	1.1871	0.1587	0.047*	0.50
H5C	0.3873	1.1328	0.2523	0.047*	0.50
C6	0.4725 (6)	0.8538 (9)	0.3010 (7)	0.042 (2)	0.50
H6A	0.5236	0.7979	0.3207	0.063*	0.50
H6B	0.4305	0.7995	0.2599	0.063*	0.50
H6C	0.4440	0.8864	0.3625	0.063*	0.50

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ir1	0.02394 (11)	0.02238 (11)	0.01471 (10)	0.00069 (6)	−0.00252 (7)	0.00009 (6)
Cl1	0.0274 (4)	0.0375 (5)	0.0434 (5)	0.0035 (4)	0.0001 (4)	−0.0059 (4)
Cl2	0.0483 (6)	0.0369 (5)	0.0145 (4)	−0.0021 (4)	−0.0047 (4)	0.0010 (3)
P1	0.0321 (5)	0.0243 (4)	0.0223 (4)	−0.0017 (4)	−0.0043 (4)	0.0002 (3)
C1	0.043 (2)	0.031 (2)	0.036 (2)	−0.0080 (17)	−0.0141 (18)	−0.0007 (17)
C2	0.052 (3)	0.0272 (19)	0.035 (2)	0.0029 (18)	−0.0015 (19)	−0.0082 (16)
C3	0.034 (2)	0.031 (2)	0.0292 (18)	−0.0034 (15)	0.0006 (15)	0.0042 (15)
P2	0.0301 (11)	0.0283 (8)	0.0233 (13)	−0.0010 (8)	0.0010 (11)	0.0018 (6)
C4	0.030 (2)	0.021 (5)	0.044 (2)	0.000 (3)	−0.0014 (19)	0.001 (4)
C5	0.030 (2)	0.021 (5)	0.044 (2)	0.000 (3)	−0.0014 (19)	0.001 (4)
C6	0.036 (4)	0.040 (5)	0.050 (5)	−0.014 (4)	−0.014 (4)	0.020 (4)

Geometric parameters (Å, º)

Ir1—Cl1[i]	2.3717 (9)	C3—H3B	0.9800
Ir1—Cl1	2.3717 (9)	C3—H3C	0.9800
Ir1—Cl2	2.3564 (9)	P2—H2	1.0000
Ir1—Cl2[i]	2.3564 (9)	P2—C4	1.798 (10)
Ir1—P1	2.3264 (10)	P2—C5	1.785 (12)
Ir1—P1[i]	2.3264 (10)	P2—C6	1.781 (7)
P1—C1	1.811 (4)	C4—H4A	0.9800
P1—C2	1.800 (4)	C4—H4B	0.9800
P1—C3	1.807 (4)	C4—H4C	0.9800
C1—H1A	0.9800	C5—H5A	0.9800
C1—H1B	0.9800	C5—H5B	0.9800
C1—H1C	0.9800	C5—H5C	0.9800
C2—H2A	0.9800	C6—H6A	0.9800
C2—H2B	0.9800	C6—H6B	0.9800
C2—H2C	0.9800	C6—H6C	0.9800
C3—H3A	0.9800		
Cl1—Ir1—Cl1[i]	180.0	P1—C1—H1C	109.5
Cl2[i]—Ir1—Cl1[i]	89.11 (4)	H1A—C1—H1B	109.5

Cl2—Ir1—Cl1[i]	90.89 (4)	H1A—C1—H1C	109.5
Cl2[i]—Ir1—Cl1	90.89 (4)	H1B—C1—H1C	109.5
Cl2—Ir1—Cl1	89.11 (4)	P1—C2—H2A	109.5
Cl2—Ir1—Cl2[i]	180.0	P1—C2—H2B	109.5
P1—Ir1—Cl1	92.63 (3)	P1—C2—H2C	109.5
P1[i]—Ir1—Cl1	87.37 (3)	H2A—C2—H2B	109.5
P1[i]—Ir1—Cl1[i]	92.63 (3)	H2A—C2—H2C	109.5
P1—Ir1—Cl1[i]	87.37 (3)	H2B—C2—H2C	109.5
P1[i]—Ir1—Cl2[i]	87.56 (3)	P1—C3—H3A	109.5
P1—Ir1—Cl2[i]	92.44 (3)	P1—C3—H3B	109.5
P1—Ir1—Cl2	87.56 (3)	P1—C3—H3C	109.5
P1[i]—Ir1—Cl2	92.44 (3)	H3A—C3—H3B	109.5
P1[i]—Ir1—P1	180.0	H3A—C3—H3C	109.5
C1—P1—Ir1	114.66 (14)	H3B—C3—H3C	109.5
C1—P1—C3	102.8 (2)	C4—P2—H2	109.3
C2—P1—Ir1	115.48 (15)	C5—P2—H2	109.3
C2—P1—C1	102.3 (2)	C5—P2—C4	110.8 (4)
C2—P1—C3	104.5 (2)	C6—P2—H2	109.3
C3—P1—Ir1	115.34 (14)	C6—P2—C4	105.2 (6)
P1—C1—H1A	109.5	C6—P2—C5	112.7 (5)
P1—C1—H1B	109.5		
Cl1[i]—Ir1—P1—C1	−45.68 (17)	Cl2—Ir1—P1—C1	45.32 (17)
Cl1—Ir1—P1—C1	134.32 (17)	Cl2[i]—Ir1—P1—C1	−134.68 (17)
Cl1—Ir1—P1—C2	15.72 (17)	Cl2[i]—Ir1—P1—C2	106.72 (17)
Cl1[i]—Ir1—P1—C2	−164.28 (17)	Cl2—Ir1—P1—C2	−73.28 (17)
Cl1—Ir1—P1—C3	−106.51 (15)	Cl2—Ir1—P1—C3	164.50 (15)
Cl1[i]—Ir1—P1—C3	73.49 (15)	Cl2[i]—Ir1—P1—C3	−15.50 (15)

Symmetry code: (i) −*x*+1/2, −*y*+1/2, −*z*+1.