

A mixed-valence chloride-bridged  
(pincer)Ir<sup>III</sup>–(diene)Ir<sup>I</sup> complexElizabeth M. Pelczar, Thomas J. Emge and Alan S.  
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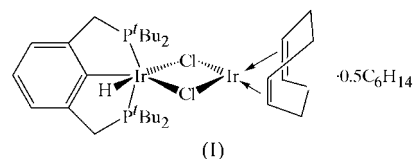
The title compound, [2,6-bis(di-*tert*-butylphosphino)phenyl-1 $\kappa^3$ P, C<sup>1</sup>, P']di- $\mu$ -chlorido-1:2 $\kappa^4$ Cl:Cl-(2 $\eta^4$ -cycloocta-2,5-diene)-hydrido-1 $\kappa$ H-diiridium(I,III) hexane hemisolvate, [Ir<sub>2</sub>(C<sub>8</sub>H<sub>12</sub>)(C<sub>24</sub>H<sub>43</sub>P<sub>2</sub>)Cl<sub>2</sub>H]·0.5C<sub>6</sub>H<sub>14</sub> or [(<sup>*t*</sup>BuPCP)IrH( $\mu_2$ -Cl)<sub>2</sub>Ir(COD)]·[<sup>*t*</sup>BuPCP is  $\kappa^3$ -2,6-(<sup>*t*</sup>Bu<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> and COD is  $\eta^4$ -2,5-cyclooctadiene], is an Ir<sup>III</sup>/Ir<sup>I</sup> dimer bridged by two chloride ions. The Ir<sub>2</sub>Cl<sub>2</sub> framework is nearly planar, with a dihedral angle of 13.04 (4)° between the two Ir centers. The compound was isolated as a hexane hemisolvate. A list of distances found in Ir(PCP) compounds is given.

## Comment

There has been great interest in recent years in the development of pincer complexes (Albrecht & van Koten, 2001; Singleton, 2003; Van der Boom & Milstein, 2003), *i.e.* complexes of tridentate meridionally bound ligands (Moulton & Shaw, 1976). Derivatives of the pincer complex (<sup>*t*</sup>BuPC-2 [<sup>*t*</sup>BuPCP is  $\kappa^3$ -2,6-(<sup>*t*</sup>Bu<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>] (Gupta *et al.*, 1996) have proven highly effective as catalysts for the dehydrogenation of alkanes (Gupta *et al.*, 1996, 1997; Xu *et al.*, 1997; Liu *et al.*, 1999; Zhu *et al.*, 2004; Goldman *et al.*, 2006). The synthetic precursor to (<sup>*t*</sup>BuPCP)IrH<sub>2</sub> (Gupta *et al.*, 1996) is (<sup>*t*</sup>BuPCP)-IrHCl (Moulton & Shaw, 1976). We have previously reported the hexanuclear iridium  $\eta^4$ -2,5-cyclooctadiene complex [(COD)Ir]<sub>2</sub>{ $\eta^6$ -[ $\kappa^4$ -C<sub>6</sub>H<sub>2</sub>(CH<sub>2</sub>P<sup>*t*</sup>Bu<sub>2</sub>)<sub>2</sub>]Ir<sub>2</sub>H<sub>2</sub>Cl<sub>3</sub>]<sub>2</sub> (COD is 1,5-cyclooctadiene), which has been observed as a by-product of the synthesis of the (<sup>*t*</sup>BuPCP)IrHCl complex (Zhang, Emge *et al.*, 2004). We report here another such by-product, an orange-red material that has been identified as (<sup>*t*</sup>BuPCP)-IrH( $\mu_2$ -Cl)<sub>2</sub>Ir(COD), which was isolated as the hexane hemisolvate, (I).

Complex (I) (Fig. 1) is best viewed as the di- $\mu$ -chlorido mixed-valence addition product of (PCP)IrHCl (Moulton & Shaw, 1976) and '(COD)IrCl'. The latter can be viewed as a monomeric unit of the dimer [Ir(COD)Cl]<sub>2</sub>, which has been crystallographically characterized previously (Cotton *et al.*,

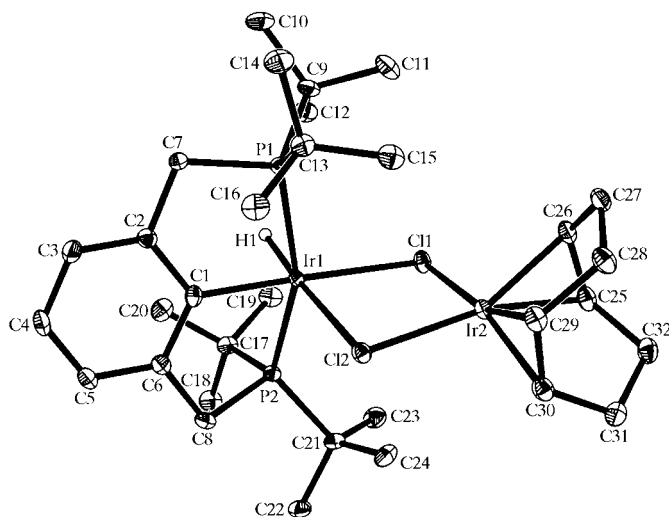
1986). The hydride was found in this complex using electron difference maps. The Ir–H distance, which is known from neutron diffraction measurements to be 1.60 Å (Eckert *et al.*, 1995; Bau *et al.*, 1993, 1984; Garlaschelli *et al.*, 1985) and found on difference Fourier maps here at 1.60 Å, refines to a much shorter distance (~1.37 Å), but still along the difference Fourier map Ir–H vector, because of the close proximity to the metal atom ( $Z = 77$ ). In such cases, it is preferable to restrain the distance to 1.60 Å, as was done here, using the *SHELXL97* command 'DFIX 1.60. 01' (Sheldrick, 1997).



The pincer-bound Ir1 atom is best considered as being formally in the +3 oxidation state. The Ir1–Cl distance (Table 1) is similar to the Ir–C distance found in other PCP complexes of either Ir<sup>I</sup> or Ir<sup>III</sup> (Table 2). The Ir–P bond lengths (average 2.327 Å; Table 1) are consistent with the Ir–P bond lengths in reported PCP complexes of Ir<sup>III</sup> (Table 2), but somewhat outside the range reported for PCP complexes of Ir<sup>I</sup> (2.27–2.30 Å; Table 2). As in other (PCP)Ir complexes, the P–Ir–P angle is decidedly nonlinear (Gupta *et al.*, 1997; Zhang *et al.*, 2005, 2006; Ghosh *et al.*, 2007). Both P atoms are bent away from the Cl ligand *cis* to the PCP aryl C–Ir bond, as seen by the corresponding P1–Ir1–Cl2 and P2–Ir1–Cl2 angles given in Table 1. The COD-bound Ir2 atom is formally in the +1 oxidation state and can be viewed as approximately square planar if one considers the centers of the coordinating C=C double bonds as single coordination points.

The Ir(COD)Cl<sub>2</sub> portion of (I) has a geometry consistent with either Ir(COD)Cl<sub>2</sub> part of [Ir(COD)Cl]<sub>2</sub>. However, presumably due to the steric bulk of the <sup>*t*</sup>BuPCP ligand, the considerable folding about the Cl··Cl vector observed in [Ir(COD)Cl]<sub>2</sub> is not present in compound (I). The dihedral angle between the Cl<sub>2</sub>–Ir1 and Cl<sub>2</sub>–Ir2 portions of the central Ir<sub>2</sub>Cl<sub>2</sub> group is only 13.04 (4)°, compared with the dihedral angle of 86° in [Ir(COD)Cl]<sub>2</sub> (Cotton *et al.*, 1986). This gives rise to a significantly greater Ir··Ir distance; in [Ir(COD)Cl]<sub>2</sub> this distance is 2.910 (1) Å, while in (I) the value is 3.6754 (2) Å.

The Ir–Cl bond lengths for the trivalent Ir1 atom are noticeably longer (average 2.55 Å) than those for the monovalent Ir2 atom (average 2.40 Å) or those found in the [Ir(COD)Cl]<sub>2</sub> dimer (average 2.40 Å) (Cotton *et al.*, 1986). As seen in Table 1, the specific values of the Ir2–Cl distances are fairly similar. The two Ir1–Cl distances, however, are substantially different, with the bond to the Cl atom *trans* to the strong *trans*-influence hydride ligand being substantially longer than that *trans* to the PCP aryl C atom. Not surprisingly, the Ir1–Cl distances in (I) are longer than the Ir–Cl


**Figure 1**

The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms, with the exception of the iridium hydride ligand, have been omitted for clarity.

distances in (PCP)Ir complexes with terminal chloride ligands (Table 2).

The geometries of both weaker and significant C—H...Cl interactions are described in Table 3, where it is shown that the intramolecular Cl...H distances are as short as 2.66 Å from atom Cl2 to the PCP methyl atom H16A and as short as 2.79 Å from atom Cl1 to the COD methylene atom H26. There are two weak intermolecular (COD)C—H...Cl2 interactions (last two entries in Table 3). The hexane solvent molecule lies across the inversion center at  $y = \frac{1}{2}$  in a channel that propagates along the crystallographic  $b$  axis. As a result, each solvent molecule is surrounded by the methyl and methylene groups of six Ir<sub>2</sub> dimer complexes. The packing of the Ir dimer complexes and the hexane solvent molecules yields only long C—H...H—C contacts (>2.54 Å) and the nearest Cl atom to any H atom on the hexane solvent is quite remote (>5 Å).

## Experimental

The synthesis was performed under an argon atmosphere using standard Schlenk and glove-box techniques. <sup>t</sup>BuPCP-H was synthesized according to the method of Moulton & Shaw (1976). <sup>t</sup>BuPCP-H (2.000 g, 5.068 mmol) was dissolved in toluene (100 ml) to which [Ir(COD)Cl]<sub>2</sub> (1.660 g, 2.472 mmol) was added, and the resulting solution was refluxed under argon for 2 d. The solution was cooled to room temperature and the solvent was removed by vacuum, followed by addition of hexane (50 ml) to the resulting solid. The red solution was pipetted away from the yellow insoluble material and filtered through glass wool before being placed in a freezer for one week. The resulting solid material (0.4299 g) contained large red crystals of complex (I), as well as a significant amount of microcrystalline (<sup>t</sup>BuPCP)IrHCl. Further details and <sup>31</sup>P{<sup>1</sup>H} NMR data are given in the archived CIF.

## Crystal data

[Ir<sub>2</sub>(C<sub>8</sub>H<sub>12</sub>)(C<sub>24</sub>H<sub>43</sub>P<sub>2</sub>)Cl<sub>2</sub>H]<sup>-</sup>·  
0.5C<sub>6</sub>H<sub>14</sub>  
 $M_r = 1001.09$   
Monoclinic,  $P2_1/c$   
 $a = 14.8424$  (7) Å  
 $b = 11.6735$  (5) Å  
 $c = 22.0589$  (10) Å

$\beta = 99.416$  (1)°  
 $V = 3770.5$  (3) Å<sup>3</sup>  
 $Z = 4$   
Mo  $K\alpha$  radiation  
 $\mu = 7.30$  mm<sup>-1</sup>  
 $T = 100$  (2) K  
 $0.19 \times 0.12 \times 0.08$  mm

## Data collection

Bruker SMART CCD area-detector  
diffractometer  
Absorption correction: multi-scan  
(SADABS in SAINT-Plus;  
Bruker, 2003)  
 $T_{\min} = 0.361$ ,  $T_{\max} = 0.558$

42778 measured reflections  
11498 independent reflections  
10259 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.033$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$   
 $wR(F^2) = 0.062$   
 $S = 1.00$   
11498 reflections

383 parameters  
H-atom parameters constrained  
 $\Delta\rho_{\max} = 2.04$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -1.03$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Ir1—C1	2.012 (3)	Ir2—C26	2.090 (3)
Ir1—P1	2.326 (1)	Ir2—C30	2.100 (3)
Ir1—P2	2.328 (1)	Ir2—C25	2.108 (3)
Ir1—Cl1	2.507 (1)	Ir2—C29	2.113 (3)
Ir1—Cl2	2.591 (1)	Ir2—Cl1	2.383 (1)
Ir1—H1	1.59	Ir2—Cl2	2.407 (1)
C1—Ir1—P1	83.27 (9)	P2—Ir1—Cl2	96.29 (3)
C1—Ir1—P2	81.21 (9)	Cl1—Ir1—Cl2	79.98 (2)
P1—Ir1—P2	158.83 (3)	C1—Ir1—H1	87
C1—Ir1—Cl1	176.79 (9)	P1—Ir1—H1	79
P1—Ir1—Cl1	97.23 (3)	P2—Ir1—H1	86
P2—Ir1—Cl1	99.07 (3)	Cl1—Ir1—H1	96
C1—Ir1—Cl2	96.80 (9)	Cl2—Ir1—H1	176
P1—Ir1—Cl2	99.77 (3)	Cl1—Ir2—Cl2	86.33 (3)

The hydride H atom was refined with a restrained Ir—H distance of 1.60 (1) Å and with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{Ir1})$ , then with a fixed position during the final cycle of refinement. All other nonmethyl H atoms were constrained to their respective idealized  $sp^2$  or  $sp^3$  geometries of 0.95 and 0.99 Å, respectively, and given  $U_{\text{iso}}(\text{H})$  values of 1.2 times  $U_{\text{eq}}$  of the atom to which they are bonded. The methyl H atoms were given  $U_{\text{iso}}(\text{H})$  values of 1.5 times  $U_{\text{eq}}$  of the C atom to which they are bonded (C—H = 0.98 Å) and allowed to rotate as a rigid group to the angle that maximized the sum of the electron density at the three calculated H-atom positions.

Data collection: SMART (Bruker, 2005); cell refinement: SMART; data reduction: SAINT-Plus (Bruker, 2003); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 2003); software used to prepare material for publication: SHELXTL.

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**Table 2**  
Selected bond distances (Å) of (<sup>t</sup>BuPCP)Ir<sup>I</sup> and (<sup>t</sup>BuPCP)Ir<sup>III</sup> complexes.

( <sup>t</sup> BuPCP)Ir complex	Ir—C(aryl)	Ir—P1	Ir—P2	Ir—Cl
<b>Ir<sup>I</sup> complexes</b>				
(PCP)Ir(NH <sub>3</sub> ) <sup>a</sup>	2.013 (4)	2.2737 (14)	2.2610 (13)	
(PCP)Ir(CO) <sup>b</sup>	2.102 (8)	2.298 (2)	2.291 (2)	
(PCP)IrN≡NIr(PCP) <sup>c</sup>	2.0534 (18)	2.2989 (5)	2.3028 (5)	
	2.0511 (18)	2.29855	2.3001 (5)	
(PCP)IrN <sub>2</sub> <sup>c†</sup>	2.0445	2.2891	2.2921	
<b>Ir<sup>III</sup> complexes</b>				
(PCP)Ir(H)(NHPh) <sup>a</sup>	2.049 (2)	2.2917 (14)	2.3429 (11)	
(PCP)Ir(H)(NHPh)(CO) <sup>a</sup>	2.077 (2)	2.3422 (6)	2.3338 (5)	
(PCP)Ir(H)(NH <sub>2</sub> )(CN <sup>t</sup> Bu) <sup>a</sup>	2.077 (4)	2.3075 (11)	2.3111 (12)	
(PCP)Ir(H)(κ <sup>2</sup> -O <sub>2</sub> COH) <sup>d</sup>	2.04 (2)	2.321 (5)	2.331 (5)	
(PCP)Ir(H)[C(O)OH] <sup>d</sup>	2.07 (2)	2.323 (5)	2.291 (6)	
(PCP)Ir(HgPh)Cl <sup>e</sup>	2.027 (3)	2.3238 (8)	2.3068 (8)	2.4599 (7)
(PCP)Ir(H)(κ <sup>2</sup> -O,C-nitrophenyl) <sup>f‡</sup>	2.028	2.3266	2.3307	
(PCP)Ir(H)(κ <sup>2</sup> -O,C-acetylphenyl) <sup>f</sup>	2.0261 (17)	2.3209 (5)	2.3079 (5)	
(PCP)Ir(H)(κ <sup>2</sup> -O,O-NO <sub>2</sub> CH <sub>2</sub> ) <sup>g</sup>	2.0283 (17)	2.3117 (5)	2.3185 (5)	
(PCP)Ir(H)(κ <sup>1</sup> -O-ONOCH <sub>2</sub> ) <sup>g</sup>	2.042 (6)	2.3325 (16)	2.3349 (16)	
(PCP)Ir(H)(CO)(CH <sub>2</sub> NO <sub>2</sub> ) <sup>g</sup>	2.091 (3)	2.3447 (9)	2.3499 (9)	
(PCP)Ir(H)(CH <sub>2</sub> NO <sub>2</sub> )(CNC <sub>6</sub> H <sub>11</sub> ) <sup>g</sup>	2.090 (2)	2.3374 (5)	2.3399 (5)	
(PCP)IrH <sub>2</sub> <sup>h</sup>	2.124 (13)	2.308 (2)	2.308 (2)	
(PCP)Ir(H)(OH) <sup>i</sup>	2.01 (2)	2.304 (4)	2.303 (4)	
(PCP)Ir <sup>+</sup> [C(O)CH <sub>3</sub> ] <sup>j</sup>	2.076 (11)	2.354 (3)	2.370 (3)	
<i>trans</i> -(PCP)Ir(H)(CH <sub>3</sub> )(CO) <sup>j</sup>	2.095 (3)	2.3215 (9)	2.3246 (9)	
<i>cis</i> -(PCP)Ir(H)(CH <sub>3</sub> )(CO) <sup>j</sup>	2.095 (5)	2.3256 (12)	2.3316 (11)	
<i>cis</i> -(PCP)Ir(H)(CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> )(CO) <sup>j</sup>	2.121 (2)	2.3403 (6)	2.3403 (6)	
(PCP)Ir(η <sup>2</sup> -PhCCCHPh) <sup>k</sup>	2.072 (2)	2.3054 (6)	2.3272 (7)	
(PCP)Ir(H)(CCPh) <sup>k§</sup>	2.062	2.294	2.293	
(PCP)Ir(CCPh)(PhCCH <sub>2</sub> )(CO) <sup>k</sup>	2.0901 (18)	2.3876 (5)	2.4317 (5)	
(PCP)Ir[C(H)=C(H)Ph]Cl <sup>k</sup>	2.0303 (18)	2.3405 (5)	2.3361 (5)	2.4628 (4)
(PCP)Ir[C(H)=C(H)Ph](CO)Cl <sup>k</sup>	2.0478 (15)	2.4115 (4)	2.3817 (4)	2.4812 (4)
(PCP)Ir[C(H)=C(H)Ph](CCC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> )(CO) <sup>k</sup>	2.090 (4)	2.3878 (11)	2.3683 (11)	
(PCP)Ir(CCPh)[C(Me)C(H)Ph] <sup>k</sup>	2.068 (9)	2.344 (2)	2.328 (2)	
(PCP)Ir(CCPh)[PhC(H)CC(H)C(H)Ph](CO) <sup>k</sup>	2.092 (3)	2.4194 (7)	2.4136 (7)	
<i>trans</i> -(PCP)Ir(H)(CH <sub>3</sub> )(CNC <sub>6</sub> H <sub>11</sub> ) <sup>¶</sup>	2.078	2.3035	2.3075	
<i>trans</i> -(PCP)Ir(H)(CH <sub>3</sub> )(CN <sup>t</sup> Bu) <sup>¶</sup>	2.081 (2)	2.3065 (6)	2.3067 (6)	
<i>cis</i> -(PCP)Ir(H)(CH <sub>3</sub> )(CNC <sub>2</sub> H <sub>5</sub> ) <sup>¶</sup>	2.0962 (19)	2.3062 (5)	2.3064 (5)	
<i>para</i> -NO <sub>2</sub> -(PCP)IrHCl <sup>m</sup>	2.015 (3)	2.3138 (12)	2.3111 (12)	2.4395 (9)

† The asymmetric unit cell of (PCP)IrN<sub>2</sub> consisted of four individual molecules; the values shown here are averaged and standard deviations have been omitted. ‡ The unit cell of (PCP)Ir(H)(κ<sup>2</sup>-O,C-nitrophenyl) consisted of two inequivalent molecules; the values shown here are averaged and standard deviations have been omitted. § The unit cell of (PCP)Ir(H)(CCPh) contained two inequivalent molecules; the values shown here are averaged and standard deviations have been omitted. ¶ *trans*-(PCP)Ir(H)(CH<sub>3</sub>)(CNC<sub>6</sub>H<sub>11</sub>) was found for two different phases; the values shown here are averaged and standard deviations have been omitted. References: (a) Kanzelberger *et al.* (2003); (b) Morales-Morales, Redon *et al.* (2001); (c) Ghosh *et al.* (2006); (d) Lee *et al.* (2003); (e) Zhang *et al.* (2001); (f) Zhang, Kanzelberger *et al.* (2004); (g) Zhang *et al.* (2006); (h) Gupta *et al.* (1997); (i) Morales-Morales, Lee *et al.* (2001); (j) Kanzelberger (2004); (k) Ghosh *et al.* (2007); (l) Zhang *et al.* (2005); (m) Grimm *et al.* (2000).

**Table 3**  
Hydrogen-bond and short-contact geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
C12—H12B...Cl1	0.98	2.93	3.785 (4)	147
C15—H15C...Cl2	0.98	2.80	3.628 (4)	143
C16—H16A...Cl2	0.98	2.66	3.551 (4)	152
C24—H24B...Cl2	0.98	2.79	3.295 (3)	113
C24—H24C...Cl1	0.98	2.91	3.782 (3)	149
C24—H24B...Cl2	0.98	2.79	3.295 (3)	113
C26—H26...Cl1	0.94	2.79	3.165 (3)	105
C27—H27B...Cl1 <sup>†</sup>	0.99	2.81	3.659 (3)	144
C30—H30...Cl2	0.87	2.93	3.264 (3)	105
C32—H32A...Cl1 <sup>†</sup>	0.99	2.90	3.865 (3)	166

Symmetry code: (i)  $-x + 2, y + \frac{1}{2}, -z + \frac{1}{2}$ .

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA3042). Services for accessing these data are described at the back of the journal.

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