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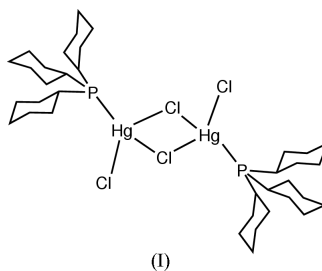
## Key indicators

Single-crystal X-ray study  
*T* = 100 K  
Mean  $\sigma(\text{C}-\text{C})$  = 0.006 Å  
*R* factor = 0.031  
*wR* factor = 0.075  
Data-to-parameter ratio = 22.4For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Di- $\mu$ -chloro-bis[chloro(tricyclohexylphosphine- $\kappa$ P)mercury(II)]

In the title compound,  $[\text{Hg}_2\text{Cl}_4(\text{C}_{18}\text{H}_{33}\text{P})_2]$ , there are two independent centrosymmetric  $\text{Hg}^{\text{II}}$  dimers, the asymmetric unit containing half of each. The coordination about each Hg atom is highly distorted tetrahedral, three sites being occupied by one terminal and two bridging Cl atoms, and the remaining site by the P atom of a tricyclohexylphosphine ligand ( $\text{PCy}_3$ ). The Hg atoms in the dimers are 3.792 (3) and 3.940 (3) Å apart and are thus non-bonded.

## Comment

Recently, interest has increased in the synthesis and photo-physical properties of cyclometallated complexes (Glusac *et al.*, 2002). 2-Phenylpyridine (phpy) is a widely used ligand for the preparation of cyclometallated complexes, such as those of iridium, ruthenium and osmium, which have applications as phosphors in organic light-emitting sensors and as luminescent labels for biomolecules (Zhu *et al.*, 2002; Gong *et al.*, 2003). The transmetallation of *ortho*-mercurated aryl derivatives into metal compounds has been a useful way to synthesize cyclometallated compounds of the later metals (Ryabov *et al.*, 2003). In order to understand the reaction mechanism, the reaction of  $\text{Os}(\text{PCy}_3)_3\text{Cl}_2$  and  $\text{Hg}(\text{phpy})_2$  (Black *et al.*, 1993) in dichloromethane was carried out, resulting in the isolation of  $\text{Os}(\text{phpy})(\text{PCy}_3)_2\text{Cl}_2$  together with  $[\text{HgCl}(\mu\text{-Cl})(\text{PCy}_3)]_2$  in an almost stoichiometric yield. An attempt to obtain single crystals of the osmium-*phpy* complex failed. However, the title mercury- $\text{PCy}_3$  complex, (I), has been characterized by single-crystal X-ray diffraction and its structure is reported here.

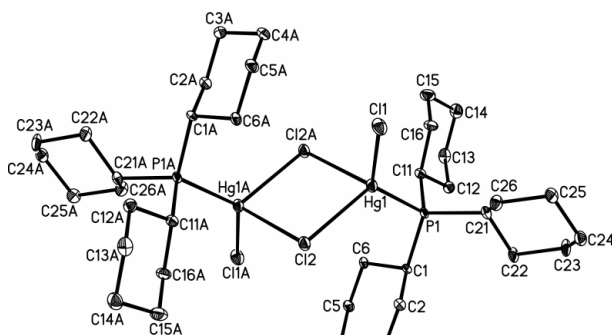


In (I), there are two independent centrosymmetric  $\text{Hg}^{\text{II}}$  dimers, molecules *A* and *B*, with slightly different conformations, the asymmetric unit containing half of each molecule (Fig. 1 and Table 1). There are a few differences in bonding parameters between these two molecules, exhibited by the bridging  $\text{Cl}^-$  ligands. The four-membered  $\text{Hg}_2\text{Cl}_2$  chelate ring is necessarily planar, with smaller angles at the Hg atoms. In molecule *A*, the ring contains a pair of long and short Hg-Cl(bridging) bonds,  $\text{Hg1}-\text{Cl2}$  2.6049 (10) and  $\text{Hg1}-\text{Cl2}^{\text{i}}$

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**Figure 1**

A view of one of the two independent molecules of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Atoms labelled with the suffix A are at the symmetry position  $(2 - x, 2 - y, 1 - z)$ .

2.7614 (10) Å [symmetry code: (i)  $2 - x, 2 - y, 1 - z$ ], with a Cl2–Hg1–Cl2<sup>i</sup> angle of 85.57 (3)°. In molecule B, the ring contains a pair of almost equal Hg–Cl(bridging) bonds, Hg2–Cl3 2.6765 (10) and Hg2–Cl3<sup>ii</sup> 2.6412 (10) Å [symmetry code: (ii)  $2 - x, 1 - y, -z$ ], with a Cl3–Hg2–Cl3<sup>ii</sup> angle of 89.02 (3)°.

The coordination about each Hg<sup>II</sup> atom is highly distorted tetrahedral, three sites being occupied by two bridging and one terminal Cl<sup>−</sup> anions and the remaining one by the P atom of the PCy<sub>3</sub> ligand. The terminal Hg–Cl bond lengths [Hg1–Cl1 2.4108 (11) and Hg2–Cl4 2.3950 (12) Å] are obviously shorter than the bridging Hg–Cl bond distances. Accordingly, the angles around Hg involving the terminal Cl<sup>−</sup> anions are larger than those involving the bridging Cl<sup>−</sup> anions.

The Hg atoms in the dimers are 3.792 (3) and 3.940 (3) Å apart and are thus non-bonded. The average Hg–P bond length of 2.4052 (10) Å is slightly shorter than that in [HgBr<sub>2</sub>{(2-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Hg}] [2.462 (3) Å; Bennett *et al.*, 2002], possibly due to the stronger  $\sigma$ -donor bond between Hg and P in the tricyclohexylphosphine ligand.

## Experimental

An equimolar mixture of Os(PCy<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub> and Hg(phpy)<sub>2</sub> in dichloromethane was stirred overnight at room temperature. The solvent was pumped off, and the residue was washed with hexane and then extracted with diethyl ether. The extracted solution was concentrated to give a purple–red oily product. The light-green solid remaining after the extraction was recrystallized from dichloromethane–diethyl ether to give block crystals of (I) in 97% yield. Analysis: <sup>31</sup>P NMR (CDCl<sub>3</sub>, p.p.m.): 52.2; MS (FAB):  $m/z$  550 (1/2[M]<sup>+</sup> + 1), 479 ([Hg(PCy<sub>3</sub>) + 1]; analysis calculated for C<sub>18</sub>H<sub>33</sub>Cl<sub>2</sub>PHg: C 39.2, H 5.98%; found: C 40.2, H 5.39%.

### Crystal data

[Hg<sub>2</sub>Cl<sub>4</sub>(C<sub>18</sub>H<sub>33</sub>P)<sub>2</sub>]  
 $M_r = 551.90$   
 Triclinic,  $P\bar{1}$   
 $a = 10.7825$  (7) Å  
 $b = 13.8572$  (9) Å  
 $c = 14.5242$  (10) Å  
 $\alpha = 85.633$  (1)°  
 $\beta = 80.182$  (1)°  
 $\gamma = 69.582$  (1)°  
 $V = 2003.7$  (2) Å<sup>3</sup>

$Z = 4$   
 $D_x = 1.830$  Mg m<sup>−3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 2685 reflections  
 $\theta = 2.3$ – $27.9$ °  
 $\mu = 8.02$  mm<sup>−1</sup>  
 $T = 100$  (2) K  
 Prism, light green  
 $0.32 \times 0.26 \times 0.22$  mm

### Data collection

Bruker SMART CCD area-detector  
 diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1997a)  
 $T_{\min} = 0.089$ ,  $T_{\max} = 0.171$   
 23 115 measured reflections

9306 independent reflections  
 8459 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.029$   
 $\theta_{\max} = 28.3$ °  
 $h = -14 \rightarrow 14$   
 $k = -17 \rightarrow 18$   
 $l = -18 \rightarrow 19$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.031$   
 $wR(F^2) = 0.075$   
 $S = 1.04$   
 9306 reflections  
 415 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0349P)^2 + 5.287P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.005$   
 $\Delta\rho_{\max} = 2.74$  e Å<sup>−3</sup>  
 $\Delta\rho_{\min} = -1.24$  e Å<sup>−3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Hg1–P1	2.4102 (10)	Hg2–Cl4	2.3950 (12)
Hg1–Cl1	2.4108 (11)	Hg2–Cl3 <sup>ii</sup>	2.6412 (10)
Hg1–Cl2	2.6049 (10)	Hg2–Cl3	2.6765 (10)
Hg1–Cl2 <sup>i</sup>	2.7614 (10)		
P1–Hg1–Cl1	133.54 (4)	Cl4–Hg2–Cl3 <sup>ii</sup>	93.95 (4)
P1–Hg1–Cl2	119.53 (3)	P2–Hg2–Cl3 <sup>ii</sup>	110.82 (3)
Cl1–Hg1–Cl2	101.19 (4)	Cl4–Hg2–Cl3	100.92 (4)
P1–Hg1–Cl2 <sup>i</sup>	99.41 (3)	P2–Hg2–Cl3	104.84 (4)
Cl1–Hg1–Cl2 <sup>i</sup>	105.46 (4)	Cl3 <sup>ii</sup> –Hg2–Cl3	89.02 (3)
Cl2–Hg1–Cl2 <sup>i</sup>	85.57 (3)	Hg1–Cl2–Hg1 <sup>i</sup>	94.43 (3)
Cl4–Hg2–P2	144.18 (4)	Hg2 <sup>ii</sup> –Cl3–Hg2	90.98 (3)

Symmetry codes: (i)  $2 - x, 2 - y, 1 - z$ ; (ii)  $2 - x, 1 - y, -z$ .

All H atoms were found in difference density maps, but were then placed in calculated positions ( $C-H = 0.99$ – $1.00$  Å) and included in the refinement using a riding-model approximation, with  $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$ . The largest peak in the final difference maps is in the vicinity of the Hg atoms.

Data collection: SMART (Bruker, 1998); cell refinement: SMART; data reduction: SAINT-Plus (Bruker, 1998); program(s) used to solve structure: SHELXTL (Sheldrick, 1997b); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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