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An unexpected product: di-μ-iodo-bis-{[2-(N-diphenylphosphinomethyl-N-cyclo-hexylamino)pyridine]iodomercury(II)}

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The title compound, $[Hg_2I_4(C_{24}H_{27}N_2P)_2]$, is found to be a symmetric doubly iodide-bridged dimer, with the phosphine ligands attached *trans* to the two Hg atoms [Hg—P = 2.4726 (12) Å]. The molecule has a centre of symmetry at the centre of the four-membered ring formed by the two Hg and two bridging I atoms.

Comment

Pyridylphosphines continue to generate much interest as excellent ligands for stabilizing many transition-metal coordination and organometallic complexes (Espinet & Soulantica, 1999). One important property of these ligands is that they can stabilize metal ions in a variety of valence states and geometries. Hence, a metal–metal bond between an electron-rich metal (soft base) and a high-oxidation-state metal (Lewis acid) is easily formed (Zhang & Cheng, 1996). Recently, we designed and synthesized a new pyridylphosphine ligand, namely 2-(N-diphenylphosphinomethyl-N-cyclohexylamino)-pyridine, *L*, and obtained a hetero-binuclear complex containing an Fe—Cu bond (Cui *et al.*, 2001). However, when *trans*-Fe(CO)$_3$L$_2$ was reacted with HgI$_2$, instead of the desired compound containing an Fe—Hg bond, the title compound, (I), was unexpectedly formed.

(I)
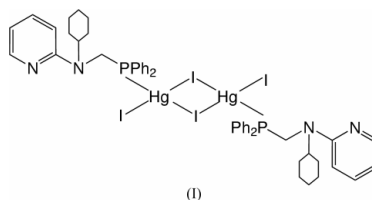
In (I), each Hg atom is four-coordinated by two bridging I atoms (Fig. 1), [Hg1—I1 2.8036 (4) Å and Hg1–I1^i 2.9667 (4) Å], one terminal I atom [Hg1—I2 2.7699 (4) Å] and one P atom from the ligand *L* [Hg1–P4 2.4723 (11) Å]. There is significant distortion from tetrahedral geometry, the angles about the metal ranging from 94.047 (10) to 127.87 (3)° (Table 1).

The title compound may be compared with the series (PPh$_3$)$_2$Hg$_2$X$_4$ which have the same molecular structure as (I) (X = Cl, Br, I), but with replacement of ligand *L* by triphenylphosphine (Bell *et al.*, 1980, 1989*b*; Bowmaker *et al.*, 1993). As in (I), the complex with X = Cl is centrosymmetric, whereas the bromo and iodo complexes are non-centrosymmetric. While the larger X_{br}—Hg—X_{br} angles (X_{br} is bridging halogen) and Hg—X distances in the iodide complex may be readily attributed to the increasing size of the halogen, no
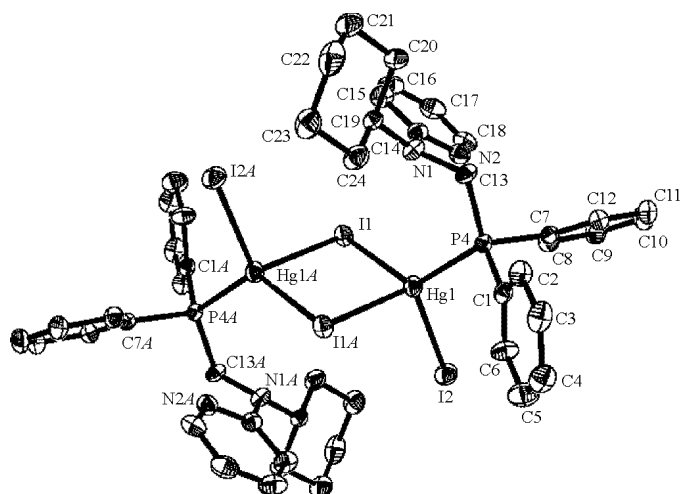
Figure 1
A view of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Suffix *A* corresponds to symmetry code (i) in Table 1

ready explanation is available for the substantial asymmetry of the Hg—X_{br} distances found in the iodide complex. In contrast to $(R_3P)_2HgX_2$ complexes, in which the P—Hg—P angle is an effective indicator of the σ-donating ability of both the phosphine and the halogen (Allen *et al.*, 1985; Bell *et al.*, 1989a), the P—Hg—X_t angles (X_t is terminal halogen) in the present complex, which might, on the basis of the stronger σ-donor properties of iodide compared to chloride and bromide, have been anticipated to be larger than in the chloride and bromide, are, in fact, very similar. The relative σ-donating ability of the halides is, however, reflected in the Hg—P distance. Thus the significantly larger distance found in the iodide complex may be attributed to the greater σ-donor ability of iodide compared to chloride and bromide.

Experimental

The synthesis was carried out under an Ar atmosphere. To a solution of *trans*-Fe(CO)$_3L_2$ (0.23 g, 0.25 mmol) was added solid HgI$_2$ (0.11 g, 0.25 mmol). After stirring for 5 min, the solid disappeared. The mixture was filtered and the solvent was removed. The residue was recrystallized from CH$_2$Cl$_2$/CH$_3$OH and gave 0.17 g (85%) of a dark yellow solid.

Crystal data

[Hg$_2$I$_4$(C$_{24}$H$_{27}$N$_2$P)$_2$]	$D_x = 2.170$ Mg m^{-3}
$M_r = 1657.67$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 634
$a = 12.5386$ (7) Å	reflections
$b = 16.1113$ (9) Å	$\theta = 2.8$–25.3°
$c = 12.6488$ (7) Å	$\mu = 8.58$ mm^{-1}
$\beta = 96.773$ (1)°	$T = 298$ (2) K
$V = 2537.4$ (2) Å^3	Plate, dark yellow
$Z = 2$	$0.40 \times 0.35 \times 0.05$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	5142 independent reflections
	4365 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.041$
Absorption correction: multi-scan	$\theta_{max} = 26.4°$
(*SADABS*; Sheldrick, 1996)	$h = -15 \rightarrow 15$
$T_{min} = 0.52$, $T_{max} = 0.96$	$k = -18 \rightarrow 20$
11685 measured reflections	$l = -11 \rightarrow 15$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0458P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.030$	$+ 0.249P]$
$wR(F^2) = 0.076$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.98$	$(\Delta/\sigma)_{max} = 0.002$
5142 reflections	$\Delta\rho_{max} = 1.49$ e Å^{-3}
271 parameters	$\Delta\rho_{min} = -1.15$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Hg1—P4	2.4723 (11)	Hg1—I1	2.8036 (4)
Hg1—I2	2.7699 (4)	Hg1—I1^i	2.9667 (4)
P4—Hg1—I2	115.61 (3)	I2—Hg1—I1^i	105.587 (13)
P4—Hg1—I1	127.87 (3)	I1—Hg1—I1^i	94.047 (10)
I2—Hg1—I1	105.332 (13)	Hg1—I1—Hg1^i	85.953 (10)
P4—Hg1—I1^i	104.03 (3)		

Symmetry code: (i) $2 - x, 2 - y, 1 - z$.

All H atoms were positioned geometrically, with C—H = 0.96 Å. They were treated as riding atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$. The maximum and minimum electron-density peaks are located 0.92 and 0.88 Å from Hg1, respectively.

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

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