Mercury(II) Halide Complexes of Tertiary Phosphines. Part XIII*. Crystal Structure of $[Ph_3P{\cdot}HgI_2]_2$

NORMAN A. BELL**, LORRAINE A. MARCH and IAN W. NOWELL†
Department of Chemistry, Sheffield City Polytechnic, Pond Street, Sheffield, S1 1WB, U.K.

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Abstract

Crystals of the complex $[Ph_3PHgI_2]_2$ are monoclinic, space group $P2_1/c$ with $a = 19.299(4)$, $b = 11.130(3)$, $c = 19.102(2)$ Å, $\beta = 90.50(1)°$. The structure was solved using the heavy atom method and refined to a final R value of 0.094 for 2984 observed diffractometer data. The complex is found to be a halogen-bridged dimer with the phosphine ligands attached *trans* to the two mercury atoms. The double halogen bridge is very asymmetric. The greater donor ability of iodide compared to chloride does not appear to have a major effect on the structure adopted.

Introduction

Our studies of a wide range of tertiary phosphine complexes of mercury(II) halides of 1:1 and 2:1 stoichiometry, $(R_3P)_nHgX_2$ ($n = 1, 2$; X = Cl, Br, I) have shown that the structures adopted are very dependent on the nature of the phosphine (in particular its σ-donor ability and steric requirement), the nature of the halogen and also the tendency of mercury to acquire linear coordination. The 2:1 complexes studied thus far [1–5] all have essentially a monomeric pseudotetrahedral constitution with widely varying degrees of distortion from a regular shape. The extent of interaction between phosphorus and mercury in these complexes has been monitored from NMR studies by the magnitude of ^1J(Hg–P) and from crystallographic studies by the size of the P–Hg–P angle which has been shown to vary from 158.5(5)° for a strong σ-donor phosphine as in $(Et_3P)_2HgCl_2$ [2] down to 128.6(1)° for the weaker donor complex $[(2\text{-}C_4H_3S)_3P]_2HgCl_2$ [3].

In contrast the 1:1 complexes exhibit a bewildering array of structural types, ranging from dimers through tetramers to five-coordinate polymers, though all except one form of $[Pr_3P{\cdot}HgI_2]_2$ [6] can be considered to be based on a centrosymmetric halogen-bridged dimeric arrangement, present either as a discrete entity or associated to give the polymeric arrangement [5, 7–12]. In these complexes strong σ-donors favour extended association and result in short Hg–P bonds, causing an opening of the P–Hg–$Cl_{terminal}$ bond angle whereas weaker donors produce dimers with longer Hg–P bonds and smaller P–Hg–Cl angles [5].

We have earlier reported the structure of $[Ph_3PHgCl_2]_2$ in full and preliminary X-ray data indicated that the bromide and iodide analogues are isostructural [7]. In order to shed further light on the effect of halogen on the structure adopted we have determined the structure of the iodide analogue which is reported herein.

Experimental

Triphenylphosphine mercury(II) iodide was prepared as described previously [13] and recrystallised from DMF/H_2O as white needles. A crystal of approximate dimensions 0.125 × 0.45 × 0.037 mm was mounted with its b axis coincident with the ω axis of a Stöe Stadi 2 two circle diffractometer. Fourteen layers ($h0l \rightarrow h013$) were collected using the background-ω scan-background technique and with graphite monochromated Mo Kα radiation. 4444 unique reflections were measured of which 2984 had $I/\sigma(I) \geqslant 3.0$ and were used for subsequent analysis. Data were corrected for Lorentz and polarisation effects but absorption corrections were not applied.

Crystal Data

$C_{36}H_{30}P_2Hg_2I_4$, $M = 1432.8$, monoclinic, $a = 19.299(4)$, $b = 11.130(3)$, $c = 19.102(2)$ Å, $\beta = 90.50(1)°$, $U = 4103.1$ Å^3, $F(000) = 2592$, space group $P2_1/c$, $Z = 4$, D_m (by flotation) = 2.41 $D_c = 2.32$ g cm^{-3}, Mo Kα radiation, $\lambda = 0.71069$ Å, μ(Mo Kα) = 101.06 cm^{-1}.

The structure was solved by the heavy atom method and refined by full matrix least-squares

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*For part XII see ref. 4.

**Author to whom correspondence should be addressed.

†Present address: School of Chemistry, Robert Gordon's Institute of Technology, St. Andrew Street, Aberdeen AB1 1HG, U.K.

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TABLE 1. Final Fractional Coordinates of $[Ph_3PHgI_2]_2$ $(\times 10^4)^a$ (non-hydrogen atoms)

	x	y	z
Hg1	6775(1)	1399(1)	8340(1)
Hg2	8118(1)	923(1)	6831(1)
I1	6949(1)	36(2)	9479(1)
I2	6766(1)	−187(2)	7162(1)
I3	8141(1)	2511(2)	7999(1)
I4	7928(1)	2166(2)	5641(1)
P1	6002(3)	3138(8)	8177(3)
C11	5204(13)	2975(36)	8698(13)
C12	4907(16)	2050(42)	8774(18)
C13	4307(16)	1887(51)	9184(20)
C14	4029(12)	2803(45)	9463(16)
C15	4347(16)	3951(41)	9400(15)
C16	4943(13)	4029(38)	9070(14)
C21	6466(13)	4491(35)	8392(15)
C22	6836(17)	4474(36)	9013(17)
C23	7145(22)	5395(64)	9264(26)
C24	7151(27)	6484(57)	8828(27)
C25	6741(27)	6493(62)	8106(29)
C26	6405(19)	5316(41)	8010(20)
C31	5712(11)	3213(30)	7302(12)
C32	5022(12)	3384(35)	7114(15)
C33	4825(17)	3439(31)	6414(17)
C34	5308(17)	3250(30)	5878(14)
C35	6033(15)	3227(28)	6043(14)
C36	6208(12)	3200(29)	6776(14)
P2	8949(3)	−749(8)	7026(4)
C41	9278(12)	−812(31)	7938(13)
C42	8826(16)	−672(36)	8416(16)
C43	9020(21)	−863(33)	9186(15)
C44	9738(24)	−1033(51)	9279(18)
C45	10196(21)	−1197(34)	8773(21)
C46	9968(13)	1016(35)	8028(17)
C51	9673(12)	−559(30)	6445(11)
C52	9974(16)	530(47)	6339(18)
C53	10505(19)	675(38)	5874(21)
C54	10821(18)	−317(43)	5588(17)
C55	10563(14)	−1457(45)	5668(14)
C56	9930(15)	−1573(43)	6058(19)
C61	8553(14)	−2130(30)	6834(13)
C62	8595(18)	−3050(40)	7240(18)
C63	8261(26)	−4251(55)	7115(29)
C64	7978(29)	−4247(63)	6475(28)
C65	7881(21)	−3545(78)	6038(26)
C66	8154(26)	−2254(38)	6196(18)

[a] e.s.d.s given in parentheses.

techniques. Mercury, iodine and phosphorus atoms and all carbon atoms except C24, C25, C26, C61, C62, C63 and C64 were assigned anisotropic thermal parameters. These seven carbon atoms were assigned isotropic thermal parameters. Hydrogen atoms were included in ideal positions (C–H = 1.08 Å) and were given a common isotropic temperature factor. Complex neutral atom scattering factors [14] were employed throughout the refinement and in the final cycles the weighting scheme $w = 1.000/[\sigma^2(F_o) + 0.0175(F_o)^2]$ was adopted. Refinement converged

TABLE 2. Selected Bond Lengths (Å) and Bond Angles (°) for $[Ph_3PHgI_2]_2{}^a$

Bond lengths (Å)			
Hg(1)–I(1)	2.671(2)	Hg(2)–I(4)	2.684(2)
Hg(1)–I(2)	2.860(2)	Hg(2)–I(2)	2.960(2)
Hg(1)–I(3)	2.990(2)	Hg(2)–I(3)	2.846(2)
Hg(1)–P(1)	2.461(8)	Hg(2)–P(2)	2.483(8)
P(1)–C(11)	1.85(3)	P(2)–C(41)	1.85(3)
P(1)–C(21)	1.80(4)	P(2)–C(51)	1.80(2)
P(1)–C(31)	1.76(2)	P(2)–C(61)	1.75(3)
Bond angles (°)			
I1–Hg1–I2	106.9(1)	I3–Hg2–I4	110.2(1)
I1–Hg1–I3	107.9(1)	I2–Hg2–I4	106.4(1)
I1–Hg1–P1	128.4(2)	I4–Hg2–P2	126.6(2)
I2–Hg1–I3	94.8(1)	I2–Hg2–I3	95.8(1)
I2–Hg1–P1	112.8(2)	I3–Hg2–P2	110.0(2)
I3–Hg1–P1	100.5(2)	I2–Hg2–P2	103.0(2)
C(11)–P1–C(21)	112.0(15)	C(41)–P(1)–C(51)	108.8(11)
C(11)–P(1)–C(31)	104.9(11)	C(41)–P(2)–C(61)	108.0(14)
C(11)–P(1)–Hg(1)	111.2(12)	C(41)–P(2)–Hg(2)	112.7(10)
C(21)–P(1)–C(31)	109.3(14)	C(51)–P(2)–C(61)	108.0(14)
C(21)–P(1)–Hg(1)	109.3(10)	C(51)–P(2)–Hg(2)	108.8(10)
C(31)–P(1)–Hg(1)	110.1(10)	C(61)–P(2)–Hg(2)	110.3(10)
Hg1–I3–Hg2	84.6(1)	Hg2–I2–Hg1	84.9(1)

[a] e.s.d.s given in parentheses.

at $R = 0.094$ and $R' = 0.091$. Final positional parameters are given in Table 1, bond distances and angles in Table 2. See also 'Supplementary Material'. All calculations were performed on an IBM 4341 computer using SHELX [15].

Results and Discussion

The complex is found to be a halogen-bridged dimer in which the phosphine ligands are mutually *trans* (Fig. 1). Each mercury atom is four-coordinate with significant distortion from tetrahedral, angles about the metal ranging from 94.8(1) to 128.4(2)°. In contrast to the chloride analogue which is a centrosymmetric dimer [7], in $(Ph_3PHgI_2)_2$ a non-centrosymmetric arrangement is adopted with four differing $Hg-I_{br}$ distances. Salient parameters for the chloride and iodide complexes are given in Table 3. While the larger $X_{br}-Hg-X_{br}$ angles and Hg–X distances in the iodide complex may be readily attributed to the increasing size of the halogen, no ready explanation is available for the greater asymmetry of the $Hg-X_{br}$ distances found in the iodide complex. In contrast to the $(R_3P)_2HgX_2$ complexes in which the $R_3P-Hg-PR_3$ angle is an effective indicator of the σ-donating ability of both the phosphine and also of the halogen [3, 4] the $Ph_3P-Hg-X_t$ angles in the present complex which might (on the basis of the stronger σ-donor properties of iodide compared to chloride) have been anticipated to be larger than in the chloride, are in fact very similar. The relative σ-donating ability of the two halides is however reflected in the Hg–P distances. Thus the significantly larger distances found in the iodide complex may be attributed to the greater σ-donor ability of iodide compared to chloride. The geometry of the Ph_3P groupings are as expected with the phenyl rings being planar and the interplanar angles between them being very similar to those found in the corresponding chloride complex, *viz.* iodide complex: 76.8, 81.4, 83.7°; chloride complex: 75.4, 80.1, 84.4° [7].

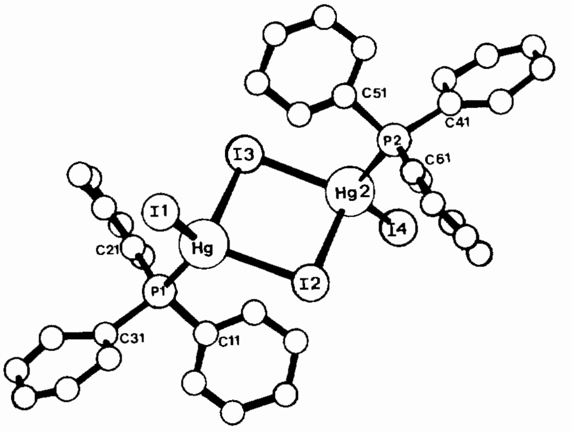

Fig. 1. Molecular structure of $[Ph_3PHgI_2]_2$.

The stronger donor capacity of iodide to mercury(II) as compared to chloride is further supported by NMR data. Stronger σ-donor phosphine ligands have higher coupling constants $^1J(Hg-P)$ with mercury(II) halides than weaker donors and the coupling constants in complexes decrease for a given phosphine from chloride to iodide as exemplified by the series $(Ph_3PHgX_2)_2$ ($J(^{199}Hg-^{31}P)$ X = Cl, 7431; X = Br, 6464; X = I, 4700 Hz) [16] showing that the donor ability of the halogen increases from chloride to iodide at the expense of the phosphine.

Supplementary Material

Hydrogen positions, thermal parameters, observed and calculated structure factors have been deposited and are available from authors on request.

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TABLE 3. Comparison of Selected Bond Lengths and Angles for $(Ph_3PHgX_2)_2$ (X = Cl, I)[a]

X	Hg–P (Å)	$Hg-X_t$ (Å)	$Hg-X_{br}$ (Å)	$P-Hg-X_t$ (°)	$X_{br}-Hg-X_{br}$ (°)
Cl [7]	2.406(7)	2.370(10)	2.658(8) 2.623(8)	128.7(4)	85.4(3)
I	2.461(8)	2.671(2)	2.860(2) 2.990(2)	128.4(2)	94.8(1)
	2.483(8)	2.684(2)	2.846(2) 2.960(2)	126.6(2)	95.8(1)

[a] t = terminal, br = bridging.

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