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Mercury(II) Halide Complexes of Tertiary Phosphines. Part VI.* The Crystal Structure of $HgCl_2(PPh_3)_2$ and a Comparison with Related Compounds

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Dichlorobis(triphenylphosphine)mercury(II) has been confirmed as having a discrete monomeric structure by a full single-crystal X-ray diffraction study. However, the structure is distorted, with angles about mercury ranging from 134.1(1)° (P–Hg–P) to 98.6(1)° (Cl–Hg–P). The extent of the angular distortion, and the bond length data, have been compared with values for $HgI_2(PPh_3)_2$ and $HgCl_2(PEt_3)_2$, and with initial data obtained in the present work for $HgBr_2(PPh_3)_2$. It is thus confirmed that: (a) the greater the donor strength of the phosphine (e.g. PEt_3), the more the P–Hg bonding dominates over X–Hg, with larger P–Hg–P angles and longer Hg–X bond lengths, and (b) the greater the mercury–halogen interaction (i.e. in iodides), the less significant is the Hg–P bonding, with smaller P–Hg–P angles and longer Hg–P bonds.

Introduction

Compounds of formula $HgX_2(PR_3)_2$ [X = halide] have been studied for many years [2], but for only two members have the full crystal structures been determined, *viz.* $HgI_2(PPh_3)_2$ [3] and $HgCl_2(PEt_3)_2$ [4], although data are available [5, 6] also for $HgX_2(PPh_3)_2$ [X = CF_3, CN, SCN, or ONO_2]. We have recently shown [4] that distortions from regular tetrahedral geometry arise from competition between the phosphine and anionic ligands for σ-bonding about mercury, the more effective σ-donor tending towards linear coordination. Since the only two definitive structures known had both different phosphine and halide ligands, we have determined the crystal structure of a third compound, one which enables the full comparisons to be made, *viz.* $HgCl_2(PPh_3)_2$. Initial results are also reported for $HgBr_2(PPh_3)_2$.

Experimental

The complexes $HgX_2(PPh_3)_2$ [X = Cl or Br] were prepared as previously described [7] and were recrystallised from ethanol.

Crystal Data

$HgCl_2(PPh_3)_2$

$C_{36}H_{30}Cl_2HgP_2$, M_r = 796.08. Monoclinic, $P2_1/n$, a = 9.907(5), b = 17.525(9), c = 19.664(12) Å, β = 90.15(6)°, U = 3414.1 Å^3, D_m (by flotation) = 1.53, D_c = 1.55 g cm^{-3}. Z = 4, Mo-K$_\alpha$, λ = 0.7107 Å, μ(Mo-K$_\alpha$) = 45.82 cm^{-1}, $F(000)$ = 1560.

$HgBr_2(PPh_3)_2$

$C_{36}H_{30}Br_2HgP_2$, M_r = 884.95. Orthorhombic, $Pna2_1$ (confirmed by X-ray analysis), a = 17.874(17), b = 10.156(12), c = 18.551(20) Å; U = 3367.4 Å^3, D_m (by flotation) = 1.77, D_c = 1.75 g cm^{-3}. Z = 4, Mo-K$_\alpha$, λ = 0.7107 Å, μ(Mo-K$_\alpha$) = 68.27 cm^{-1}, $F(000)$ = 1704.

Although intensity data were collected for both the chloride and the bromide complexes, the poor quality of available crystals has prevented a full X-ray analysis of $HgBr_2(PPh_3)_2$. The following sections dealing with collection of intensity data and structure analysis are consequently limited to $HgCl_2(PPh_3)_2$.

X-Ray Intensity Measurements

A crystal of approximate dimensions 0.21 × 0.24 × 0.35 mm was mounted with its a-axis coincident with the ω-axis of a Stöe Stadi-2 two-circle diffractometer. Data were collected using the background-ω scan-background technique and with graphite monochromated Mo-K$_\alpha$ radiation. 5431 unique reflections were measured of which 3591 had $I/\sigma(I) \geqslant 3.0$ and were used for subsequent analysis. Data were corrected for Lorentz, polarisation and absorption effects.

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*Part V: Ref. [1].

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TABLE I. Final Fractional Coordinates (Hg × 10^5; other atoms × 10^4) with Estimated Standard Deviations in Parentheses.

	x	*y*	*z*
Hg	56941(3)	24261(1)	87488(1)
Cl(1)	4977(2)	3591(1)	8052(1)
Cl(2)	3898(3)	2086(1)	9621(1)
P1	7614(2)	2862(1)	9445(1)
P2	5341(2)	1348(1)	7953(1)
C11	8149(10)	2096(4)	10011(4)
C12	8161(17)	1365(5)	9774(7)
C13	8522(19)	769(7)	10201(9)
C14	8913(17)	901(8)	10844(7)
C15	8944(18)	1633(8)	11091(6)
C16	8545(15)	2244(6)	10674(5)
C21	9043(10)	3123(4)	8930(4)
C22	8815(10)	3530(5)	8326(4)
C23	9910(12)	3766(5)	7933(6)
C24	11207(12)	3609(5)	8128(6)
C25	11466(12)	3214(5)	8714(5)
C26	10385(11)	2961(5)	9129(5)
C31	7242(10)	3685(4)	9959(4)
C32	8212(14)	4219(6)	10120(6)
C33	7922(15)	4839(6)	10530(6)
C34	6683(16)	4934(6)	10779(5)
C35	5701(17)	4413(9)	10629(8)
C36	5991(14)	3785(7)	10228(7)
C41	3553(10)	1192(4)	7771(4)
C42	2966(12)	475(5)	7757(6)
C43	1607(15)	409(6)	7578(7)
C44	881(16)	1036(8)	7421(8)
C45	1462(17)	1735(8)	7418(10)
C46	2807(14)	1815(5)	7604(7)
C51	6008(10)	470(4)	8315(4)
C52	7146(11)	108(4)	8045(5)
C53	7656(12)	−533(5)	8352(5)
C54	7045(14)	−814(6)	8945(6)
C55	5923(16)	−465(5)	9203(5)
C56	5385(13)	182(5)	8893(5)
C61	6174(10)	1468(4)	7138(4)
C62	7137(13)	2021(5)	7061(6)
C63	7779(15)	2095(7)	6409(7)
C64	7418(17)	1633(9)	5883(6)
C65	6488(19)	1100(10)	5978(6)
C66	5828(16)	1004(8)	6603(5)
H12	7889	1250	9251
H13	8487	190	10014
H14	9204	431	11168
H15	9276	1740	11606
H16	8547	2821	10867
H22	7797	3659	8166
H23	9730	4079	7468
H24	12037	3798	7815
H25	12495	3095	8862
H26	10585	2648	9591
H32	9221	4153	9922
H33	8704	5247	10650
H34	6457	5420	11097
H35	4693	4491	10825
H36	5212	3368	10127
H42	3552	−26	7881
H43	1135	−146	7565
H44	−176	980	7297
H45	880	2230	7272
H46	3263	2375	7615
H52	7621	333	7593
H53	8523	−819	8140
H54	7462	−1308	9198
H55	5448	−694	9652
H56	4498	456	9099
H62	7408	2391	7479
H63	8553	2521	6336
H64	7886	1701	5391
H65	6228	728	5560
H66	5060	572	6662

Structure Determination and Refinement

The position of the mercury atom was located from the three-dimensional Patterson function and remaining atoms were located from successive difference electron-density maps. Hydrogen atoms were included in positions calculated from the geometry of the molecule (C–H, 1.08 Å). A common isotropic temperature factor was applied to the phenyl hydrogen atoms and refined to a final value of $U = 0.136(23)$ Å^2. Scattering factors were calculated using an analytical approximation [8] and the weighting scheme adopted was $w = 0.4218/[\sigma^2(F_o) + 0.0027(F_o)^2]$. Full matrix refinement with anisotropic temperature factors applied to all non-hydrogen atoms gave the final $R = 0.035$ and $R' = 0.038$. Final atomic parameters are given in Table I, bond distances and angles in Table II. Observed and calculated structure factors, thermal parameters and least-squares planes data have been deposited and are available from the Editor.

Structure Calculations

All calculations, apart from preliminary data processing, were carried out on a IBM 370/165 computer at the SERC Computing Centre, Daresbury, using the SHELX computing package [9].

Results

The present X-ray study shows $HgCl_2(PPh_3)_2$ to be a distorted tetrahedral monomer (Fig. 1). While the gross structure is thus similar to that found in $HgI_2(PPh_3)_2$ [3], there are a number of significant differences between the two complexes. Most noteworthy is the extent of the tetrahedral distortion, for while angles about mercury range from

TABLE II. Bond Lengths (Å) and Angles (°) with Estimated Standard Deviations in Parentheses.

Distances (Å)			
Hg–Cl(1)	2.559(2)	Hg–Cl(2)	2.545(3)
Hg–P1	2.462(2)	Hg–P2	2.478(2)
P1–C11	1.823(8)	P2–C41	1.826(10)
P1–C21	1.802(9)	P2–C51	1.820(7)
P1–C31	1.800(8)	P2–C61	1.816(8)
C11–C12	1.362(13)	C41–C42	1.385(12)
C11–C16	1.384(14)	C41–C46	1.359(13)
C12–C13	1.387(19)	C42–C43	1.396(19)
C13–C14	1.342(22)	C43–C44	1.348(19)
C14–C15	1.372(19)	C44–C45	1.354(20)
C15–C16	1.405(18)	C45–C46	1.388(22)
C21–C22	1.402(12)	C51–C52	1.400(13)
C21–C26	1.413(15)	C51–C56	1.390(13)
C22–C23	1.396(15)	C52–C53	1.371(13)
C23–C24	1.369(16)	C53–C54	1.405(16)
C24–C25	1.368(15)	C54–C55	1.367(19)
C25–C26	1.419(15)	C55–C56	1.392(14)
C31–C32	1.377(15)	C61–C62	1.368(14)
C31–C36	1.361(17)	C61–C66	1.372(14)
C32–C33	1.383(15)	C62–C63	1.439(19)
C33–C34	1.334(21)	C63–C64	1.360(20)
C34–C35	1.366(21)	C64–C65	1.326(24)
C35–C36	1.384(20)	C65–C66	1.405(17)
Angles (°)			
P1–Hg–Cl(1)	105.3(1)	P2–Hg–Cl(1)	103.4(1)
P1–Hg–Cl(2)	103.8(1)	P2–Hg–Cl(2)	98.6(1)
P1–Hg–P2	134.1(1)	Cl(1)–Hg–Cl(2)	110.7(1)
Hg–P1–C11	109.5(3)	Hg–P2–C41	111.9(3)
Hg–P1–C21	111.9(3)	Hg–P2–C51	110.3(2)
Hg–P1–C31	113.7(3)	Hg–P2–C61	113.9(2)
C11–P1–C21	107.6(4)	C41–P2–C51	107.5(4)
C11–P1–C31	107.9(4)	C41–P2–C61	106.7(4)
C21–P1–C31	105.9(4)	C51–P2–C61	106.1(4)
P1–C11–C12	119.0(8)	P2–C41–C42	123.2(7)
P1–C11–C16	121.2(7)	P2–C41–C46	117.0(7)
C12–C11–C16	119.8(9)	C42–C41–C46	119.7(10)
C11–C12–C13	120.1(12)	C41–C42–C43	119.0(9)
C12–C13–C14	121.0(12)	C42–C43–C44	120.3(11)
C13–C14–C15	120.0(12)	C43–C44–C45	120.8(15)
C14–C15–C16	120.0(11)	C44–C45–C46	119.9(13)
C11–C16–C15	119.1(10)	C41–C46–C45	120.3(10)
P1–C21–C22	118.7(7)	P2–C51–C52	121.8(6)
P1–C21–C26	122.2(6)	P2–C51–C56	117.7(7)
C22–C21–C26	119.1(8)	C52–C51–C56	120.4(8)
C21–C22–C23	119.7(9)	C51–C52–C53	120.0(8)
C22–C23–C24	121.0(10)	C52–C53–C54	119.6(10)
C23–C24–C25	120.8(11)	C53–C54–C55	120.2(10)
C24–C25–C26	120.1(10)	C54–C55–C56	120.9(10)
C21–C26–C25	119.3(8)	C51–C56–C55	118.8(10)
P1–C31–C32	122.0(8)	P2–C61–C62	119.9(7)
P1–C31–C36	120.6(8)	P2–C61–C66	119.6(8)
C32–C31–C36	117.3(9)	C62–C61–C66	120.5(9)
C31–C32–C33	121.4(12)	C61–C62–C63	118.2(10)
C32–C33–C34	120.4(12)	C62–C63–C64	120.6(12)
C33–C34–C35	119.4(11)	C63–C64–C65	119.6(12)
C34–C35–C36	120.5(15)	C64–C65–C66	122.2(13)
C31–C36–C35	120.9(12)	C61–C66–C65	119.0(13)

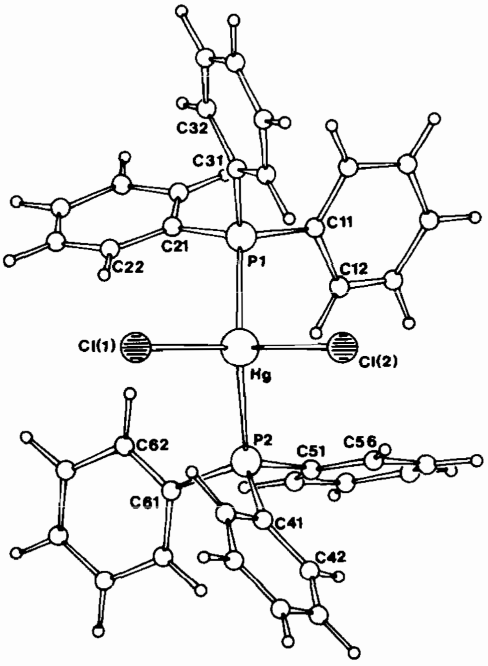

Fig. 1. Molecular Structure of $HgCl_2(PPh_3)_2$.

98.6(1) to 134.1(1)° in $HgCl_2(PPh_3)_2$, a much more regular arrangement is found in the iodide complex with angles varying from 104.7(1) to 113.1(1)°. In addition, projection down the Hg–P bonds and examination of selected dihedral and torsion angles reveals differences in the relative orientation of the phenyl rings in the two complexes (Table III; Figs. 2, 3). While all six carbon atoms attached to the phosphorus atoms occupy almost ideal gauche positions in the chloride complex, projection down the P1–Hg bond in $HgI_2(PPh_3)_2$ reveals a highly eclipsed arrangement.

Discussion

Important parameters are given in Table IV in comparison with those for closely related compounds. In comparing the differing degrees of tetrahedral distortion between $HgCl_2(PPh_3)_2$ and $HgI_2(PPh_3)_2$, the most striking feature is the much larger P–Hg–P angle found in the chloride complex. In considering the origin of this difference, the steric and electronic properties of the two types of halogen have both to be examined. The closest intra and intermolecular hydrogen-halogen distances are given in Table V. If steric factors were of major importance one might expect intramolecular interactions to dominate the short contacts, but in neither complex does this occur. Thus the differing electronic properties of the two types of halogen appear

TABLE III. Selected Dihedral Angles and Torsion Angles in $HgX_2(PPh_3)_2$ (X = Cl, I).[a]

Torsion Angles (°); X = Cl, I	$HgCl_2(PPh_3)_2$	$HgI_2(PPh_3)_2$
C11–P1–Hg–X(2)	59.7	15.0
C11–P1–Hg–P2	–57.1	–99.1
C21–P1–Hg–X(1)	64.5	–105.0
C21–P1–Hg–P2	62.2	19.3
C31–P1–Hg–X(1)	55.4	14.7
C31–P1–Hg–X(2)	–61.0	–106.9
C41–P2–Hg–X(1)	–67.9	–70.7
C41–P2–Hg–X(2)	45.9	49.6
C51–P2–Hg–X(2)	–73.7	–67.0
C51–P2–Hg–P1	45.1	50.5
C61–P2–Hg–X(1)	53.3	51.4
C61–P2–Hg–P1	–74.1	–70.9

Dihedral Angles (°)	$HgCl_2(PPh_3)_2$	$HgI_2(PPh_3)_2$
A/B	88.1	77.3
A/C	86.8	86.1
B/C	88.1	79.9
D/E	63.1	63.1
D/F	89.3	72.3
E/F	78.8	45.0
G/H	88.7	86.9

Plane A	C11–C16	Plane E	C51–C56
Plane B	C21–C26	Plane F	C61–C66
Plane C	C31–C36	Plane G	P1, Hg, P2
Plane D	C41–C46	Plane H	X(1), Hg, X(2); [X = Cl, I]

[a] For comparison with present work, atomic labelling for $HgI_2(PPh_3)_2$ given in ref. 3 has been changed.

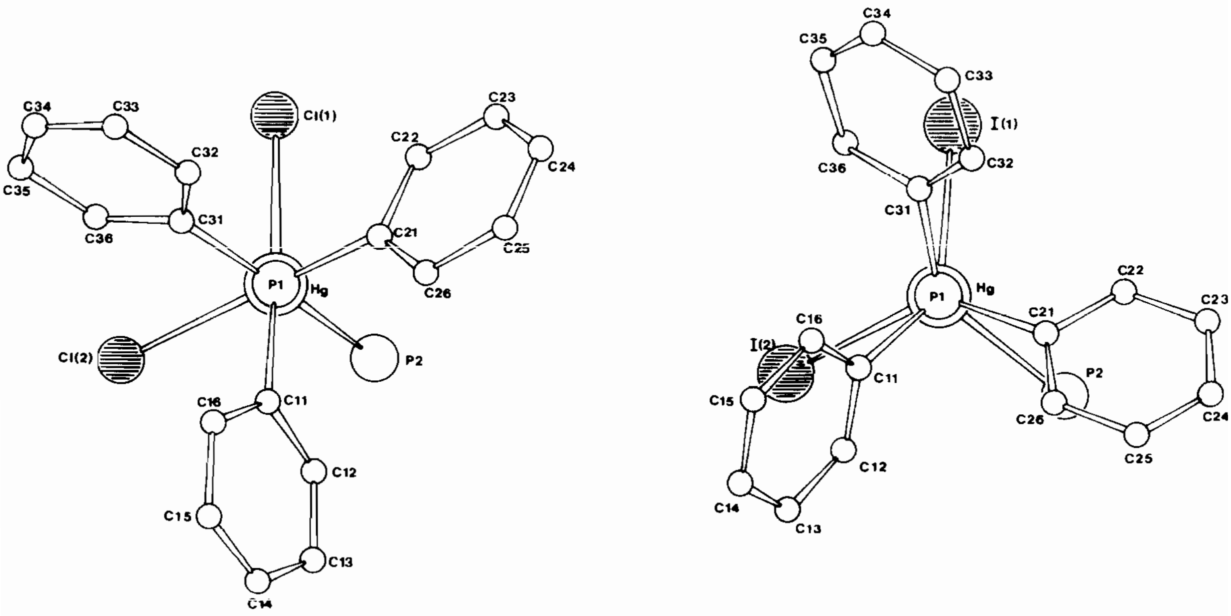

Fig. 2. Projection down the P1–Hg bond for (a), $HgCl_2(PPh_3)_2$; (b), $HgI_2(PPh_3)_2$.

TABLE IV. Important Molecular Parameters in $HgX_2(PR_3)_2$ Complexes.

	$HgI_2(PPh_3)_2$	$HgBr_2(PPh_3)_2$	$HgCl_2(PPh_3)_2$	$HgCl_2(PEt_3)_2$
Reference	[3]	Present Work	Present Work	[4]
d(Hg–X)/Å	2.733(1) 2.763(1)	2.633(6) 2.626(8)	2.559(2) 2.545(3)	2.68(1) 2.68(1)
d(Hg–P)/Å	2.574(3) 2.557(3)	2.540(16) 2.535(15)	2.478(2) 2.462(2)	2.39(1) 2.39(1)
X–Hg–X/°	110.43(4)	106.9(3)	110.7(1)	105.5(5)
P–Hg–P/°	108.95(9)	113.0(5)	134.1(1)	158.5(5)

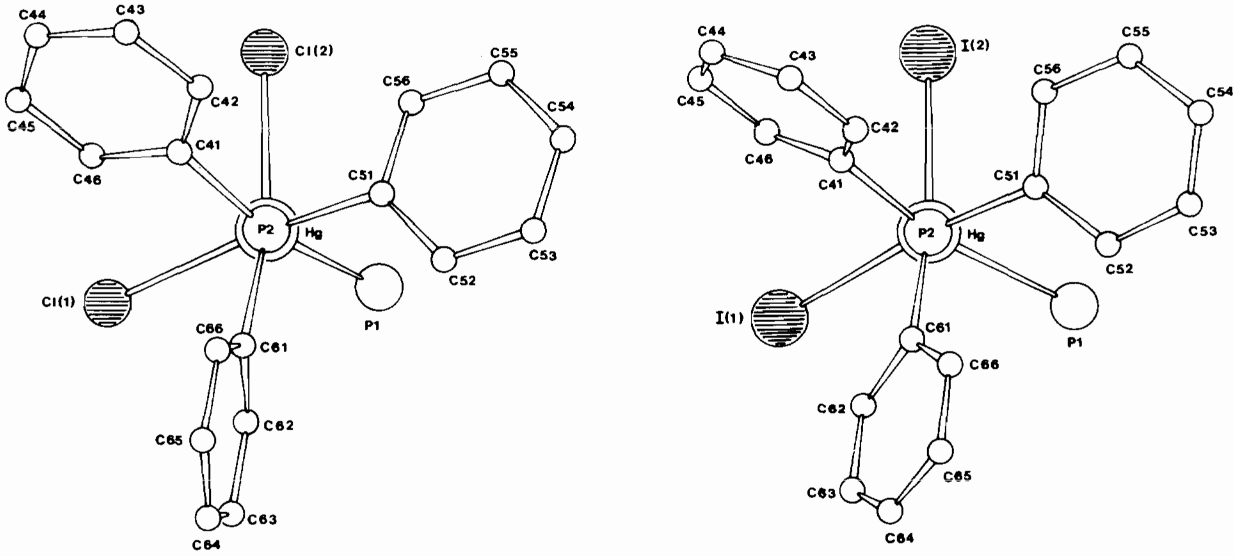

Fig. 3. Projection down the P2–Hg bond for (a), $HgCl_2(PPh_3)_2$; (b), $HgI_2(PPh_3)_2$.

TABLE V. Shortest Intra and Intermolecular Hydrogen-Halogen Distances (Å) in $HgX_2(PPh_3)_2$, (X = Cl, I).[a,b]

$HgCl_2(PPh_3)_2$

Intramolecular		Intermolecular	
Cl(1)–H22	2.805	Cl(1)–H34^{i}	2.799
Cl(1)–H46	2.856	Cl(1)–H43^{ii}	2.752
Cl(2)–H36	2.780	Cl(2)–H25^{iii}	2.697
		Cl(2)–H64^{iv}	2.797

Symmetry Code

none	x, y, z
i	$1 - x, 1 - y, 2 - z$
ii	$0.5 - x, 0.5 + y, 1.5 - z$
iii	$-1 + x, y, z$
iv	$-0.5 + x, 0.5 - y, 0.5 + z$

TABLE V. *(continued)*

$HgI_2(PPh_3)_2$

Intramolecular		Intermolecular	
I(1)–H62	3.023	I(1)–H24^{i}	3.207
I(2)–H12	3.459	I(2)–H13^{ii}	3.254
		I(2)–H14^{ii}	3.250
		I(2)–H44^{iii}	3.113
		I(2)–H53^{i}	3.381
		I(2)–H55^{iv}	3.420

Symmetry Code

none	x, y, z
i	$x, 1 + y, z$

(continued overleaf)

TABLE V. *(continued)*

ii	$-x, -y, 1 - z$
iii	$x, 0.5 - y, 0.5 + z$
iv	$-x, 0.5 + y, 0.5 - z$

[a]See footnote for Table III. [b]Hydrogen atoms are labelled according to the carbon atoms to which they are bonded. Hydrogen atoms for $HgI_2(PPh_3)_2$ have been located in idealised positions (C–H 1.08 Å), based on positional parameters for carbon atoms given in ref. 3.

to be more significant and in terms of the previous formulated rationale [4, 6] the implication is that chlorine forms weaker bonding with mercury than iodine – the expected relationship. This weaker Hg–Cl interaction allows the $Hg–PPh_3$ bonding to dominate, thereby tending towards linear P–Hg–P coordination. In accord with this it should be noted that the Hg–P bond lengths are much shorter in $HgCl_2(PPh_3)_2$ compared with $HgI_2(PPh_3)_2$.

The smaller P–Hg–P angle in $HgCl_2(PPh_3)_2$ compared with $HgCl_2(PEt_3)_2$ is the order predicted on the basis of NMR and ν(HgCl) data [4], and reflects the stronger donor strength towards mercury of PEt_3 compared with PPh_3. The fact that the Hg–Cl distances are longer in the PEt_3 adduct confirms that the bonding to chlorine is weakened when the phosphine coordinates more strongly.

Our initial data on $HgBr_2(PPh_3)_2$ are fully in accord with these conclusions (Table IV).

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References

1 N. A. Bell, M. Goldstein, T. Jones and I.W. Nowell, *Inorg. Chim. Acta, 69,* 155 (1982).
2 D. G. Tuck, *Rev. Inorg. Chem.*, 209 (1979).
3 L Fälth, *Chem. Scripta, 9,* 71 (1976).
4 N. A. Bell, T. D. Dee, P. L. Goggin, M. Goldstein, R. J. Goodfellow, T. Jones, K. Kessler, D. M. McEwan and I. W. Nowell, *J. Chem. Res. (S)*, 2; (*M*), 0201 (1981).
5 D. J. Brauer, Abstracts of Papers, *IXth Int. Conf. on Organomet. Chem.*, Dijon, 359 (1979).
6 H. B. Buergi, R. W. Kunz and P. S. Pregosin, *Inorg. Chem., 19,* 3707 (1980).
7 T. Allman, R. G. Goel and P. Pilon, *Spectrochim. Acta, 35A,* 923 (1979).
8 'International Tables for X-Ray Crystallography', Vol. IV, Kynoch Press, Birmingham (1974).
9 G. M.Sheldrick, 'SHELX, Programs for Crystal Structure Determination', University of Cambridge, U. K.