Formation of a Trinuclear Mercury(II) Complex Mediated by a Phosphorane: Molecular Structure of $[Hg\{Hg(I)(Ph_3PCHCOPh)(\mu\text{-}I)_2\}_2]$

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Phenacylidenetriphenylphosphorane reacts with HgI_2 in 2 : 3 molar ratio to form a novel trinuclear iodobridged symmetrical complex whose structure has been elucidated by IR, multinuclear NMR, and X-ray crystallography. The Hg···Hg distance [3.648(1) Å] indicates a negligible bonding interaction between the mercury atoms.

The resonance-stabilized keto ylides of phosphorus are amphidentate ligands, and can coordinate either through carbon or oxygen.[1] The reaction of the above mentioned ylide with mercury(II) halides in 1 : 1 molar ratio led to the formation of a dinuclear complex, $[Hg_2(I)_2(Ph_3PCHCOPh)_2(\mu\text{-}I)_2]$.[2] The present investigation was undertaken to determine whether HgI_2 would form a polynuclear or C,C-dimercurated complex, since phosphoylides can be metallated at the ylidic carbon.[3]

Experimental

$(C_6H_5)_3PCHCOPh$ was prepared and characterized by the published procedure.[4] Methanol was dried by the reported methods.[5]

Instrumentation. The IR spectrum was recorded on a Perkin–Elmer 1600 FTIR spectrophotometer as a KBr pellet. The NMR spectrum was recorded on a JEOL 400 MHz instrument at the Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Chennai, India. The elemental analysis was carried out at the Central Drug Research Institute, Lucknow.

Preparation of $[Hg\{Hg(I)(Ph_3PCHCOPh)(\mu\text{-}I)_2\}_2]$. A solution of 0.29 mmol of the ylide in methanol was added to a methanolic solution of 0.58 mmol of mercury(II) iodide. Slow evaporation of the solvent in a dark room resulted in yellow-green crystals, which was washed with cold methanol and dried under a high vacuum. Yield: 0.56 g (91%), mp 184—185 °C. Anal. Calcd for $Hg_3I_6P_2O_2C_{52}H_{42}$: C, 29.41; H, 1.99%. Found: C, 29.38; H, 2.01%. IR 1624, 1434, 1288, 1187, 1105, 1010, 885, 821, 779, 747, 724, 670, 535, 509 cm^{-1}. ^1H NMR (dmso-d_6) δ = 5.34 (d, $^2J_{PH}$ = 6.8 Hz, 1H), 7.44—8.24 (m, 20H). ^{31}P NMR (dmso-d_6) δ = 21.53 (s). ^{13}C NMR (dmso-d_6) δ = 48.18 (d, $^1J_{PC}$ = 77.7 Hz, CH), 122.89 (s, COPh-*o*), 123.79 (s, COPh-*m*), 128.12 (d, $^4J_{PC}$ = 12.3 Hz, Ph_3P-*p*), 129.42 (d, $^3J_{PC}$ = 12.2 Hz, Ph_3P-*m*), 132.15 (s, COPH-*p*), 133.17 (d, $^1J_{PC}$ = 27.4 Hz, Ph_3P-*i*), 133.48 (d, $^2J_{PC}$ = 13.7 Hz, Ph_3P-*o*), 137.45 (s, COPh-*i*), 190.68 (s, CO).

Results and Discussion

Synthesis and Spectroscopic Studies. The formation of **1** from the resonance-stabilized ylide can be represented by the following equation:

$$2Ph_3PCHCOPh + 3HgI_2 \longrightarrow [Hg\{Hg(I)(Ph_3PCHCOPh)(\mu\text{-}I)_2\}_2] \quad (1)$$

The dinuclear complex, $[Hg_2I_2(Ph_3PCHCOPh)_2(\mu\text{-}I)_2]$, was formed when the reaction was carried out with the same reactants in 1 : 1 molar ratio in the same solvent.[2] The isolation of **1** shows that the ylide and HgI_2 can react to give a different product in the same solvent by changing the molar ratio of the reactants. Initially, compound **1** was characterized by elemental analysis, IR, ^1H, ^{31}P, and ^{13}C NMR spectra. The increase in ν_{CO} (1624 cm^{-1}) from that of the free ylide (1525 cm^{-1}) in the IR spectrum is diagnostic of coordination of the ylide through carbon, as observed for similar ketostabilized phosphorus ylide complexes.[6] Coordination of the ligand through oxygen is ruled out, since it is expected to cause a decrease in this frequency.[7]

The ^{31}P NMR of the complex in dmso-d_6 displayed a singlet resonance shifted downfield with respect to the corresponding signals of the ligand (δ = 15.59) and the dinuclear complex[2] mentioned above (δ = 17.38). The downfield shift of the ylidic proton in ^1H NMR and the upfield shift of the ylidic carbon in ^{13}C NMR with a lower coupling constant with respect to the corresponding values observed in the parent ylide, ([4.4(d), $^2J_{P-H}$ = 24.5 Hz] and [50.2(d), $^1J_{P-C}$ = 111.9 Hz]), again reveal the C-coordination, as noted for the dinuclear complex [5.39(d), $^2J_{P-H}$ = 7.8 Hz and 48.35(d), $^1J_{P-C}$ = 78.4 Hz].[2] The NMR spectrum in

dmso-d_6 does not indicate the presence of free ylide and points out the stability of the complex in this solvent. The presence of only one isomer in solution has been confirmed by the appearance of a single signal in the ^{31}P NMR of the complex. This is in contrast to *O*-coordinated complexes for which two ^{31}P signals were obtained corresponding to the cisoid and transoid forms.[8]

X-Ray Crystallography. In order to confirm the structure of **1**, a single-crystal X-ray diffraction study was carried out. The structure was solved using SHELXS-86[9] and SHELXL-93[10] programs. Details concerning the data collection and refinement are given in Table 1. The molecular structure of **1** (Fig. 1), as obtained from the ZORTEP[11] package, reveals that it is a trinuclear complex in which the two ylidic groups are attached to the terminal Hg atoms through carbon. The molecule has a two-fold axis passing through Hg(1), which has an occupancy factor of 0.5. The coordination of ylidic carbon introduces a chiral centre, and the configuration of the ylidic carbon atoms can be described as RR or SS. The three mercury atoms form an almost linear array

Table 1. Crystal Structure Determination and Refinement of [Hg{Hg(I)($Ph_3PCHCOPh$)(μ-I)$_2$}$_2$]

Molecular formula	$Hg_3I_6P_2O_2C_{52}H_{42}$
Formula weight	2124
Crystal size/mm	$0.88\times0.22\times0.36$
Color	Yellow-green
Crystal system	Monoclinic
Space group	$C2/c$
a/Å	28.020(6)
b/Å	10.010(2)
c/Å	20.174(3)
β/°	101.97(2)
V/Å^3	5535(2)
Z	4
D_{calcd}/g cm^{-3}	2.549
Diffractometer	Nicolet R3m four-circle
Radiation used	Mo $K\alpha$
Wavelength (λ/Å)	0.71073
μ/mm^{-1}	11.74
Temperature/K	130(2)
Scan mode	ω
Scan range/°	$3.5<2\theta<50.0$
Total no. of unique data	4874
Criteria for observation	$I > 2.5\sigma(I)$
No. unique observed data	3100
Weighting scheme	$1/[\sigma^2(F_o)^2+(0.0318P)^2+130.81P]$ where $P=(F_o^2+2F_c^2)/3$
$R1$[a] for $I > 2.5\sigma(I)$	0.0479
$wR2$[a]	0.0889
Goodness of fit	1.116
F(000)	3832
T_{max}	0.791
T_{min}	0.265

a) $R1=\sum F_o-F_c/\sum F_o$; $wR2=[\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. The carbon atoms of the phenyl groups were refined isotropically using a rigid model with fixed C–C (1.39 Å) and C–H (0.95 Å) bond lengths. An empirical absorption correction was applied via psi scans.

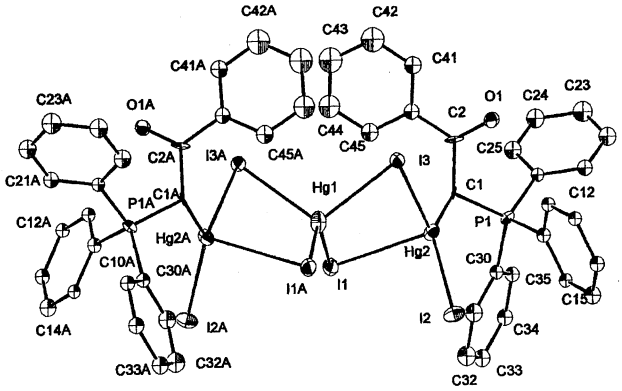

Fig. 1. Thermal ellipsoidal plot of **1** with 30% probability of the thermal ellipsoids.

with an angle of 168.9(2)° around the central mercury. The molecular structure of **1** offers an interesting comparison with the dinuclear complex, [$Hg_2(I)_2(Ph_3PCHCOPh)_2(\mu$-I)$_2$]. In both the structures within the ylide moieties the phosphorus and oxygen are *cis* oriented, probably due to the interaction between the P^+ and O^- centres. The intramolecular interaction between phosphorus and oxygen is reflected in the short contact at 2.93(1) Å (sum of the van der Waals radii = 3.32 Å). There is no intermolecular short contact involving the above mentioned atoms. However, the two PPh_3 groups are oriented almost in the same direction in **1** in contrast to their opposite orientations in the dinuclear complex. This may be attributed to the planarity of the Hg_2I_2 plane in the dinuclear complex and the non-planarity of the Hg_3I_4 core, reducing the steric hindrance between the two bulky PPh_3 groups in **1**. The atomic coordinates and equivalent isotropic displacement parameters for the non-hydrogen atoms which were refined anisotropically are listed in Table 2. Selected bond lengths and angles of **1** are listed in Table 3. The Hg–I(terminal) bond distance (2.664(1) Å) is comparable to 2.681(1) Å in the iodo-bridged dimer, {$Hg_2(I)_2[Ph_3P(C_5H_4)]_2(\mu$-I)$_2$].[12,13] The different Hg–I(bridging) bond lengths show the asymmetric bridging nature of the iodo ligands. The Hg2–I1(bridging) distance (3.223(1) Å) is rather long, indicating a weak Hg–I-(bridging) interaction. The bond angles around the Hg atoms reveal the tetrahedral geometry of groups around them (Table 3). However, the terminal Hg atoms exhibit large distortions from a tetrahedral arrangement (Table 3). The Hg–C distances, (2.31(1) and 2.25(1) Å), in the dinuclear and trinuclear mercury complexes, respectively, clearly show stronger Hg–C bonding in the latter. The Hg···Hg internuclear distance (3.648(1) Å) is shorter than the 4.014(1) Å observed for the same distance in the dinuclear mercury complex, [$Hg_2I_2(Ph_3PCHCOPh)_2(\mu$-I)$_2$}$_2$][2] (Table 3). However, it is longer than the distance of 2.797(1) Å observed for the Hg(II)–Hg(II) bond in the dinuclear mercury cluster, [Hg-($C_{10}H_6$)]$_2$,[14] and also longer than the sum of the radii (1.44 Å) of the Hg atoms.[15] The rather long distance proves the absence of any significant bonding interaction between Hg atoms in **1**. The Hg–C bond distance in **1** is comparable to other Hg–C bond distances observed in the iodobridged

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Coefficents of Non-Hydrogen Atoms of [Hg{Hg(I)(Ph$_3$PCHCOPh)(μ-I)$_2$}$_2$]

Atom	X/a	Y/b	Z/c	$U_{eq} \times 10^n$ Å^2 a)
Hg1	0.00000(0)	0.89135(11)	0.25000(0)	308(4)
Hg2	0.10589(2)	0.85646(7)	0.17232(3)	214(2)
I1	−0.00683(4)	0.76884(12)	0.12640(5)	268(4)
I2	0.13758(4)	0.63432(12)	0.24002(5)	261(3)
I3	0.08572(3)	1.05364(11)	0.26807(5)	178(3)
P1	0.1671(1)	0.8913(4)	0.0512(2)	13(1)
C1	0.1153(5)	0.961(2)	0.0774(6)	9(4)
C2	0.1195(5)	1.107(2)	0.0948(6)	14(5)
O1	0.1607(3)	1.1576(11)	0.1084(5)	22(4)
C10	0.2147(3)	0.8422(9)	0.1221(4)	17(3)
C11	0.2285(3)	0.9254(8)	0.1780(4)	16(3)
C12	0.2641(3)	0.8839(9)	0.2329(4)	16(3)
C13	0.2858(3)	0.7593(9)	0.2319(4)	18(3)
C14	0.2720(3)	0.6761(8)	0.1760(4)	24(4)
C15	0.2365(3)	0.7175(9)	0.1212(4)	14(3)
C20	0.1910(3)	1.0067(10)	−0.0021(4)	14(3)
C21	0.2409(3)	1.0219(10)	0.0028(4)	20(4)
C22	0.2581(2)	1.1055(11)	−0.0420(5)	27(4)
C23	0.2255(3)	1.1740(10)	−0.0917(5)	33(4)
C24	0.1755(3)	1.1588(10)	−0.0966(4)	28(4)
C25	0.1583(2)	1.0751(11)	−0.0518(5)	25(4)
C30	0.1470(3)	0.7442(8)	0.0016(4)	15(3)
C31	0.1269(4)	0.6369(10)	0.0300(3)	26(4)
C32	0.1130(4)	0.5225(9)	−0.0083(5)	31(4)
C33	0.1191(4)	0.5156(8)	−0.0748(4)	24(4)
C34	0.1392(3)	0.6229(10)	−0.1031(3)	21(4)
C35	0.1532(3)	0.7373(8)	−0.0649(4)	17(3)
C40	0.0757(3)	1.1851(10)	0.0962(5)	19(4)
C41	0.0825(3)	1.3114(10)	0.1253(5)	24(4)
C42	0.0426(4)	1.3839(9)	0.1365(6)	47(5)
C43	−0.0041(3)	1.3302(11)	0.1187(6)	48(5)
C44	−0.0108(3)	1.2040(12)	0.0896(6)	40(5)
C45	0.0290(4)	1.1314(9)	0.0784(5)	25(4)

a) The esd's are given in parantheses. $U_{eq} = (1/3)\sum_i\sum_j a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j$.

$n = 4$ for Hg1, Hg2, I1, I2, and I3; 3 for the remaining atoms.

mercury(II) complexes.[2,12,13] The increase in P1–C1 and C1–C2 bond distances, and the decrease in C2–O1 bond distances in **1** (Table 3) with respect to the corresponding distances (Å) observed in Ph$_3$PCHCOPh [1.716(5), 1.407(8), 1.265(7); 1.723(5), 1.399(8), 1.247(7)], respectively, for two molecules] are due to the coordination of the ylide through carbon. The formation of this trinuclear complex can be explained by the initial formation of the dinuclear complex, followed by the insertion of HgI_2 into the HgIHg bridge along with the reorientations of the PPh_3 groups. This is supported by the formation of the title complex by the action of HgI_2 on [Hg$_2$(I)$_2$(Ph$_3$PCHCOPh)$_2$(μ-I)$_2$] which was confirmed, based on the cell parameters obtained from the initial X-ray data.

The formation of the title trinuclear mercury complex is ascribed to the stability of the Hg–C bond as well as the tendency of mercury(II) to form extended bridges.

Tables of structure factors and the hydrogen atom coordinates as well as the complete list of the bond parameters

Table 3. Selected Bond Lengths (Å) and Angles (°) of [Hg{Hg(I)(Ph$_3$PCHCOPh)(μ-I)$_2$}$_2$]

Bond lengths		Bond angles	
Hg1–I1	2.750(1)	I1–Hg1–I3	105.52(3)
Hg1–I3	2.860(1)	I1–Hg1–I3A	103.84(3)
Hg2–I3	2.898(1)	I3–Hg1–I1A	103.84(3)
Hg2–I2	2.664(1)	I3–Hg1–I3A	110.77(6)
Hg2–I1	3.223(1)	I1A–Hg1–I3A	105.52(3)
Hg2–C1	2.25(1)	I1A–Hg1–I1	127.03(7)
P1–C1	1.79(1)	I2–Hg2–I1	97.05(4)
C1–C2	1.50(2)	I3–Hg2–I2	108.49(4)
C2–O1	1.24(2)	I1–Hg2–C1	99.4(3)
		I3–Hg2–C1	108.9(4)
		I2–Hg2–C1	137.9(4)
		I1–Hg2–I3	93.55(3)
		Hg1–I1–Hg2	74.83(3)
		Hg1–I3–Hg2	78.63(3)
		Hg2–C1–P1	108.3(7)
		Hg2–C1–C2	105.9(9)
		P1–C1–C2	115(1)
		C1–C2–O1	118(1)

have been deposited as Document No. 71064 at the Office of the Editor of Bull. Chem. Soc. Jpn. and available from the Cambridge Crystallographic Data Centre.

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