ELSEVIER

Journal of Organometallic Chemistry 491 (1995) 103–109

Journal of Organo metallic Chemistry

Reactions of benzoylmethylenetriphenylphosphorane with mercury(II) halides: spectral and structural characterization of $[(C_6H_5)_3PCHCOC_6H_5 \cdot HgCl_2]_2 \cdot 2CH_3OH$ and $[(C_6H_5)_3PCHCOC_6H_5 \cdot HgI_2]_2$

Meenakshisundaram Kalyanasundari [a], Krishnaswamy Panchanatheswaran [a,*], Ward T. Robinson [b], Huo Wen [b]

[a] Department of Chemistry, Bharathidasan University, Tiruchirappalli 620 024, India
[b] Department of Chemistry, University of Canterbury, Christchurch, New Zealand

Received 3 August 1994; in revised form 21 September 1994

Abstract

The reactions of the title ylide with mercury(II) chloride and mercury(II) iodide in equimolar ratios using methanol as solvent have yielded crystals of $[(C_6H_5)_3PCHCOC_6H_5\ HgCl_2]_2 \cdot 2CH_3OH$ (**1**) and $[(C_6H_5)_3PCHCOC_6H_5\ HgI_2]_2$ (**2**) respectively. Single crystal X-ray analyses reveal the presence of centrosymmetric dimeric structures containing the ylide and HgX_2 (X = Cl or I) in both cases. The IR and ^1H NMR data of the product **3** formed by the reaction of mercury (II) bromide with the same ylide are similar to those of **1** and **2**. Analytical data indicate a 1:1 stoichiometry between the ylide and Hg^{II} halide in each of the three products.

Keywords: Mercury; Ylide; Crystal structure

1. Introduction

The coordination chemistry of the phosphoranes of the type, $R_3P^+–C^-H_2$ is well known [1–4]. Resonance stabilized phosphorus ylides, particularly the keto ylides are also successfully used as ligands in organometallic and coordination chemistry owing to their accessibility and stability towards air and moisture [5,6]. Although many bonding modes are possible for the keto ylides [7], the coordination through carbon is more predominant and observed with Pd^{II}, Pt^{II} and Ag^I [8–10]. We are currently interested in the synthesis and reactivity of metal derivatives of such ylides.

The reaction of the above ylide with mercury(II) chloride has already been reported along with the analytical and IR data of the product. The product was formulated by Nesmeyanov et al. [11] to be a mercurated phosphonium salt, $[(C_6H_5)_3PCHCOC_6H_5\ HgCl]Cl$. Weleski et al. [12] proposed a symmetrical chloro-bridged dimeric structure for the analogous complex formed by the reaction of $CH_3COCHP(C_6H_5)_3$ and mercury(II) chloride to account for its molecular weight data and negligible electrical conductivity in nitrobenzene solution. However, the details of the structure and its NMR data are not available. The aims of our present work are (i) to correctly determine and compare the molecular structures of the products formed by the title ylide with mercury(II) halides, and (ii) to characterize all the products by IR, ^1H, ^{13}C and ^{31}P NMR spectra.

2. Experimental details

Benzoylmethylenetriphenylphosphorane was prepared and characterized by the published procedure [13]. All the solvents were dried by the reported methods [14].

---

[*] Corresponding author.

SSDI 0022-328X(94)05217-4

2.1. Instrumentation

UV spectra were measured on a Hitachi U-3410 spectrophotometer using methanol as solvent. Solid state IR spectra in the region of 4000–200 cm^{-1} using KBr pellets were obtained on a BIO-RAD SPC 3200 spectrophotometer. ^1H NMR spectra were obtained using a Jeol 400 MHz instrument at Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Madras, India. ^{31}P and ^{13}C NMR spectra were recorded on an AMX 400 MHz Bruker instrument at the Sophisticated Instruments Facility, Indian Institute of Science, Bangalore, India. Elemental analyses were carried out at Central Drug Research Institute, Lucknow, India.

2.2. Preparation of ylide–Hg^{II} complexes

2.2.1. $(C_6H_5)_3PCHCOC_6H_5 \cdot HgCl_2$ complex (1)

A solution of 0.16 g of mercury(II) chloride (0.59 mmol) in methanol was added to a methanolic solution of 0.22 g (0.58 mmol) of benzoylmethylenetriphenylphosphorane in dry methanol. The white crystals formed by the slow evaporation of the solvent were dried in vacuo. Yield 0.34 g (90.2%), m.p. 210–212°C. Anal. Found: C, 47.46; H, 3.03. $C_{26}H_{21}OPHgCl_2$ Calc.: C, 47.90; H, 3.25%. $\lambda_{max}^{CH_3OH}$ 315, 274, 268 nm.

2.2.2. $(C_6H_5)_3PCHCOC_6H_5 \cdot HgI_2$ complex (2)

A solution of 0.19 g of the ylide (0.51 mmol) in methanol was added to a solution of 0.23 g of mercury(II) iodide (0.51 mmol). On concentration by removing the solvent in vacuum, a pale yellow, light sensitive crystalline solid was obtained. The crystals were washed with benzene and dried in vacuo. Yield 0.36 g (86.3%), m.p. 188–190°C. Anal. Found: C, 36.30; H, 2.24. $C_{26}H_{21}OPHgI_2$ Calc.: C, 37.41; H, 2.54%. $\lambda_{max}^{CH_3OH}$ 315, 271, 265 nm.

2.2.3. $(C_6H_5)_3PCHCOC_6H_5 \cdot HgBr_2$ complex (3)

A solution of 0.15 g (0.39 mmol) of the above ylide in methanol was added to 0.14 g (0.39 mmol) of mercury(II) bromide in methanol and the mixture was stirred for 4 h. The solvent was then removed in vacuo. The white product obtained was washed with ice-cold methanol and dried in vacuum. Yield 0.22 g (80.7%), m.p. 194–195°C. Anal. Found: C, 42.49; H, 2.67; $C_{26}H_{21}OPHgBr_2$ Calc.: C, 42.15; H, 2.86%. $\lambda_{max}^{CH_3OH}$ 316, 274, 267 nm.

3. Results and discussion

The $\nu(CO)$ which is sensitive to complexation occurs at 1525 cm^{-1} in the parent ylide, as in the case of other resonance stabilized ylides [15]. Coordination of ylide through carbon causes an increase in $\nu(CO)$ while for O-coordination a lowering of $\nu(CO)$ is expected (Table 1). The IR absorption bands observed for the three complexes at 1635, 1622 and 1630 cm^{-1} indicate coordination of the ylide through carbon. The $\nu(P^+–C^-)$ which is also diagnostic of the coordination occurs at 899 cm^{-1} in $(C_6H_5)_3P^+–C^-H_2$ and at 887 cm^{-1} in $(C_6H_5)_3PCHCOC_6H_5$ [17]. These assignments were confirmed by comparing the IR spectra of the corresponding ^{13}C substituted ylides. In the present study, the $\nu(P^+–C^-)$ values for all three complexes were shifted to lower frequencies and observed at 831, 821 and 827 cm^{-1} for **1**, **2** and **3**, respectively, suggesting some removal of electron density in the P–C bond.

Table 1
$\nu(CO)$ of selected phosphoranes and their metal derivatives

Complex	$\nu(CO)$ (cm^{-1})	Ref.
$Ph_3PCHCON(CH_3)_2$	1530	15
$Ph_3PCHCOCH_3$ (APPY)	1530	16
$Ph_3PCHCOCH_3$ (BPPY)	1525	13
C-coordination		
$BPPY \cdot HgCl_2$	1635	This work
$BPPY \cdot HgI_2$	1622	This work
$BPPY \cdot HgBr_2$	1630	This work
$AuCl\{CH(PPh_3)CON(CH_3)_2\}$	1605	15
$[Pd(\eta^5\text{-}C_5H_5)(PPh_3)\{APPY\}ClO_4$	1640	16
O-coordination		
$[(Sn(CH_3)_3 \cdot BPPY]Cl$	1480	6
$[(SnPh_3) \cdot BPPY]Cl$	1470	6
$[Pd(C_6F_5)(PPh_3)_2(APPY)]ClO_4$	1513	8

Ph = C_6H_5, APPY = acetylmethylenetriphenylphosphorane, BPPY = benzoylmethylenephenylphosphorane.

The ^1H NMR data of the mercury(II) ylide complexes along with those of the parent ylide are listed in Table 2. The signals due to methine protons, when recorded in $CDCl_3$ was either broad or unobserved probably due to very low solubility of all the complexes in $CDCl_3$. Similar behaviour was observed earlier in the case of ylide complexes of platinum(II) chloride [18]. However, a sharp doublet for the above proton was obtained in DMSO-d_6 for each of the three complexes in the same region. This indicates that the complexes do not react with DMSO-d_6. The expected

Table 2
^1H and ^{31}P NMR data of BPPY and its complexes with Hg^{II} halides (T = 298 K; J in Hz; TMS δ = 0.00 ppm)

Complex	δ(CH)	^2J(PH)	$\delta(PPh_3)$	$\delta(^{31}P)$ [b]
$Ph_3PCHCOPh$ (BPPY) [a]	4.44(d)	24.5	7.33–7.99(m)	15.59(s)
$HgCl_2 \cdot BPPY$ [c]	5.24(d)	10.4	7.39–8.02(m)	23.41(s)
$HgBr_2 \cdot BPPY$ [c]	5.34(d)	8.2	7.40–8.02(m)	18.51(s)
$HgI_2 \cdot BPPY$ [c]	5.39(d)	7.8	7.40–8.04(m)	17.38(s)

BPPY = benzoylmethylenetriphenylphosphorane. [a] In $CDCl_3$, 270 MHz, values (ppm) relative to internal TMS. [b] In $CDCl_3$, 400 MHz, values (ppm) relative to external 85% phosphoric acid. [c] In DMSO-d_6, values (ppm) relative to internal TMS. d, doublet; s, singlet; m, multiplet.

Table 3
13C NMR data of BPPY and its complexes with mercury(II) halides (SF = 100.61; $T = 298$ K; J in Hz; TMS $\delta = 0.00$ ppm)

Possible assignments	$Ph_3PCHCOPh$ (BPPY) [a]	BPPY · $HgCl_2$ [b]	BPPY · $HgBr_2$ [b]	BPPY · HgI_2 [b]
(CH)	50.21(d)	46.98(d)	48.13(d)	48.35(d)
^1J(PC)	111.9	80.9	75.0	78.4
(CO–Ph)(o)	126.18(s)	123.22(s)	123.9(s)	123.44(s)
(PPh_3)(i)	126.88(d)	127.70(s)	127.84(d)	128.02(s)
^1J(PC)	79.0 [d]			
(CO–Ph)(m)	127.09(s)	124.11(s)	124.8(s)	124.34(s)
(PPh_3)(m)	128.42(d)	129.04(d)	129.3(d)	129.40(d)
^3J(PC)	12.0	8.8	12.0	11.8
(CO–Ph)(p)	128.87(s)	126.81(s)	128.2(s)	131.9(s)
(PPh_3)(p)	131.63(s)	131.40(s)	131.32(s)	131.77(s)
(PPh_3)(o)	132.66(d)	133.12(d)	133.27(d)	133.31(d)
^2J(PC)	10.1	9.8	10.0	10.1
(CO–Ph)(i)	140.91(d)	137.62(s)	138.5	137.93(s)
^3J(PC)	14.7			
(CO)	184.37(s)	189.69(s)	189.0(s)	189.51(s)

s, singlet; d, doublet; (o), *ortho*; (m), *meta*; (p), *para*; (i), *ipso* carbon. [a] Recorded in $CDCl_3$.

[b] Recorded in DMSO-d_6.

[c] Based upon the previous assignments given in Ref. [19].

[d] Reported as 90.02 Hz in C_6D_6 (Ref. [19]). The difference in ^1J(PC) may be due to the solvent used.

Table 4
Crystal data and refinement parameters for **1** and **2**

Complex	$[(C_6H_5)_3PCHCOC_6H_5 \cdot HgCl_2]_2 \cdot 2CH_3OH$	$[(C_6H_5)_3PCHCOC_6H_5 \cdot HgI_2]_2$
Molecular formula	$C_{54}H_{50}O_4P_2Cl_4Hg_2$	$C_{26}H_{21}OPI_2Hg$
Formula weight	1367	834
Crystal size (mm)	0.06 × 0.09 × 0.30	0.10 × 0.18 × 0.42
Crystal system	Triclinic	Hexagonal
Space group	$P\bar{1}$	$R\bar{3}$
a (Å)	10.485(5)	36.664(9)
b (Å)	10.142(3)	36.664(9)
c (Å)	14.115(4)	10.589(3)
α (°)	76.60(2)	90
β (°)	64.11(3)	90
Γ (°)	68.08(3)	120
V (Å^3)	1248(1)	12328(7)
Z	1	18
D_{calc} (g cm^{-3})	1.80	2.02
Temperature (K)	153	153
F(000)	664	6948
Linear absorption coefficient (cm^{-1})	64.62	79.20
Transmission factors min	0.734	0.571
max	0.986	0.953
Merge	0.023	0.016
Scan mode	ω	ω
Octants	$h, \pm k, \pm l$	$h, k, \pm l$
$2\theta_{max}$	50	52
Reflections measured	4407	5391
Reflection used	3734	3136
Parameters refined	202	102
Weighting (g × 10^3)	7.2	2.6
GOOF	1.32	1.06
R	3.67	4.12
R_w	3.74	3.75

Ph = C_6H_5, $R = [\Sigma(\|F_o| - |F_c\|/\Sigma|F_o|]$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

downfield shifts of ^{31}p and ^{1}H signals for PCH group upon complexation were observed in their corresponding spectra. The appearance of single signals for PCH group in each of ^{31}P and ^{1}H NMR indicates the presence of only one molecule for all the three complexes, as expected for C-coordination. It must be noted that O-coordination of the ylide generally leads to the formation of *cis* and *trans* isomers giving rise to two different signals in ^{31}P and ^{1}H NMR [8].

The ^{13}C NMR data of the complexes and the title ylide are listed in Table 3 along with possible assignments. The most interesting aspect of the ^{13}C spectra of the complexes is the upfield shift of the signals due to ylidic carbon. Such upfield shift observed in PdCl (η^3-2-XC$_3$H$_4$) (C$_6$H$_5$)$_3$PCHCOR (X = H, CH$_3$; R = CH$_3$, C$_6$H$_5$) was attributed to change in hybridization of the ylidic carbon [20]. Similar upfield shifts of 2-3 ppm with reference to the parent ylide were also observed [21] in the case of [(C$_6$H$_5$)$_3$PC$_5$H$_4$HgI$_2$]$_2$. The ^{13}C shifts of CO group in the complexes are around 189 ppm, lower than 184 ppm noted for the same carbon in the parent ylide, indicating much lower shielding of carbon of the CO group in the complexes. No coupling to Hg was observed at room temperature in ^{1}H, ^{13}C and ^{31}P NMR spectra of all these complexes. Failure to observe satellites in the above spectra was previously noted in the ylide complexes of Hg$^{\mathrm{II}}$ [21] and Ag$^{\mathrm{I}}$ [10] which had been assigned to fast exchange of the ylide with the metal.

Table 5
Fractional atomic coordinates and equivalent isotropic displacement coefficients U_{eq} ($\times 10^3$) for non-hydrogen atoms of **1**, with their e.s.d.s in parentheses. $U_{\mathrm{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$

ATOM	x	y	z	U_{eq}
Hg(1)	−0.1743(1)	0.0250(1)	(0).1273(1)	23(1)
Cl(1)	−0.0957(2)	0.1584(2)	−0.0699(1)	22(1)
Cl(2)	−0.2962(2)	−0.1237(3)	0.1105(2)	36(1)
O(1)	−0.4653(5)	0.2218(5)	0.3378(4)	23(2)
C(11)	0.1425(5)	0.0956(5)	0.1851(3)	22(2)
C(12)	0.2839(5)	0.1084(5)	0.1521(3)	23(2)
C(13)	0.3191(5)	0.1564(5)	0.2199(3)	23(2)
C(14)	0.2128(5)	0.1915(5)	0.3206(3)	24(2)
C(15)	0.0714(5)	0.1787(5)	0.3536(3)	21(2)
C(16)	0.0362(5)	0.1307(5)	0.2858(3)	15(1)
C(21)	0.0033(4)	−0.1764(4)	0.3650(4)	18(1)
C(22)	0.0149(4)	−0.3207(4)	0.3890(4)	25(2)
C(23)	−0.1049(4)	−0.3657(4)	0.4071(4)	28(2)
C(24)	−0.2364(4)	−0.2663(4)	0.4013(4)	27(2)
C(25)	−0.2480(4)	−0.1220(4)	0.3773(4)	22(2)
C(26)	−0.1282(4)	−0.0770(4)	0.3592(4)	15(1)
C(31)	−0.3272(5)	0.1186(3)	0.5426(3)	20(1)
C(32)	−0.4125(5)	0.1839(3)	0.6372(3)	24(2)
C(33)	−0.4353(5)	0.3281(3)	0.6388(3)	23(2)
C(34)	−0.3728(5)	0.4070(3)	0.5458(3)	24(2)
C(35)	−0.2875(5)	0.3417(3)	0.4512(3)	21(2)
C(36)	−0.2647(5)	0.1975(3)	0.4496(3)	18(1)
C(41)	−0.3318(3)	0.4569(5)	0.1043(3)	23(2)
C(42)	−0.3883(3)	0.5808(5)	0.0484(3)	26(2)
C(43)	−0.5420(3)	0.6416(5)	0.0772(3)	26(2)
C(44)	−0.6393(3)	0.5785(5)	0.1618(3)	25(2)
C(45)	−0.5827(3)	0.4545(5)	0.2177(3)	20(2)
C(46)	−0.4290(3)	0.3937(5)	0.1889(3)	17(1)
C(1)	−0.2108(7)	0.1893(7)	0.2233(5)	17(3)
C(2)	−0.3757(7)	0.2649(7)	0.2571(5)	16(3)
P(1)	−0.1463(2)	0.1109(2)	0.3288(1)	14(1)
O(2)	−0.1598(7)	0.5352(8)	0.2145(5)	51(4)
C(3)	−0.0065(11)	0.5026(10)	0.1532(8)	50(5)

Table 6
Fractional atomic coordinates and equivalent isotropic displacement coefficients U_{eq}($\times 10^3$) for non-hydrogen atoms of **2**, with their e.s.d.s in parentheses. $U_{\mathrm{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$

Atom	x	y	z	U_{eq} (Å)^2
Hg(1)	0.5531(1)	0.0552(1)	0.5277(1)	26(1)
I(1)	0.4630(1)	0.0161(1)	0.6144(1)	24(1)
I(2)	0.6097(1)	0.0699(1)	0.7125(1)	45(1)
P(1)	0.5384(1)	0.4190(1)	0.2707(2)	20(1)
O(1)	0.6186(2)	0.1687(2)	0.5026(7)	29(3)
C(1)	0.5560(3)	0.1119(3)	0.4230(9)	19(2)
C(2)	0.5804(4)	0.1458(4)	0.5115(10)	24(3)
C(11)	0.5507(3)	0.4508(2)	0.0294(6)	31(3)
C(12)	0.5561(3)	0.4802(2)	−0.0629(6)	36(3)
C(13)	0.5583(3)	0.5179(2)	−0.0284(6)	35(3)
C(14)	0.5551(3)	0.5263(2)	0.0984(6)	34(3)
C(15)	0.5497(3)	0.4969(2)	0.1908(6)	27(3)
C(16)	0.5476(3)	0.4591(2)	0.1563(6)	22(2)
C(21)	0.6477(2)	0.2006(2)	0.2238(6)	26(3)
C(22)	0.6650(2)	0.2428(2)	0.1902(6)	37(3)
C(23)	0.6387(2)	0.2585(2)	0.1553(6)	33(3)
C(24)	0.5951(1)	0.2318(2)	0.1539(6)	35(3)
C(25)	0.5778(1)	0.1896(2)	0.1875(6)	29(3)
C(26)	0.6041(2)	0.1740(2)	0.2224(6)	23(3)
C(41)	0.5136(2)	0.1334(2)	0.6270(5)	28(3)
C(42)	0.4948(2)	0.1410(2)	0.7306(5)	31(3)
C(43)	0.5198(2)	0.1672(2)	0.8282(5)	32(3)
C(44)	0.5635(2)	0.1857(2)	0.8223(5)	35(3)
C(45)	0.5823(2)	0.1781(2)	0.7187(5)	33(3)
C(46)	0.5574(2)	0.1520(2)	0.6211(5)	22(2)
C(31)	0.6212(2)	0.0800(3)	0.1642(6)	37(3)
C(32)	0.6501(2)	0.0659(3)	0.1610(6)	45(3)
C(33)	0.6778(2)	0.0746(3)	0.2617(6)	50(4)
C(34)	0.6765(2)	0.0973(3)	0.3655(6)	44(3)
C(35)	0.6475(2)	0.1114(3)	0.3687(6)	31(3)
C(36)	0.6199(2)	0.1027(3)	0.2680(6)	29(3)

3.1. X-Ray crystallography

Crystals suitable for X-ray diffraction were obtained by the slow evaporation of the methanolic solution of the mixture of ylide and HgX$_2$ (X = Cl or I). Crystal data and refinement details for the two complexes, **1** and **2**, are listed in Table 4. Intensity data were collected with a Nicolet R3m four-circle diffractometer at 153 K. Graphite monochromatised Mo Kα radiation (λ = 0.71069 Å) was used with fixed omega scans for both complexes. The structures were solved by conventional Patterson and Fourier methods using the SHELXTL [22] programs. Refinements were carried out by blocked cascade least-squares procedures, using

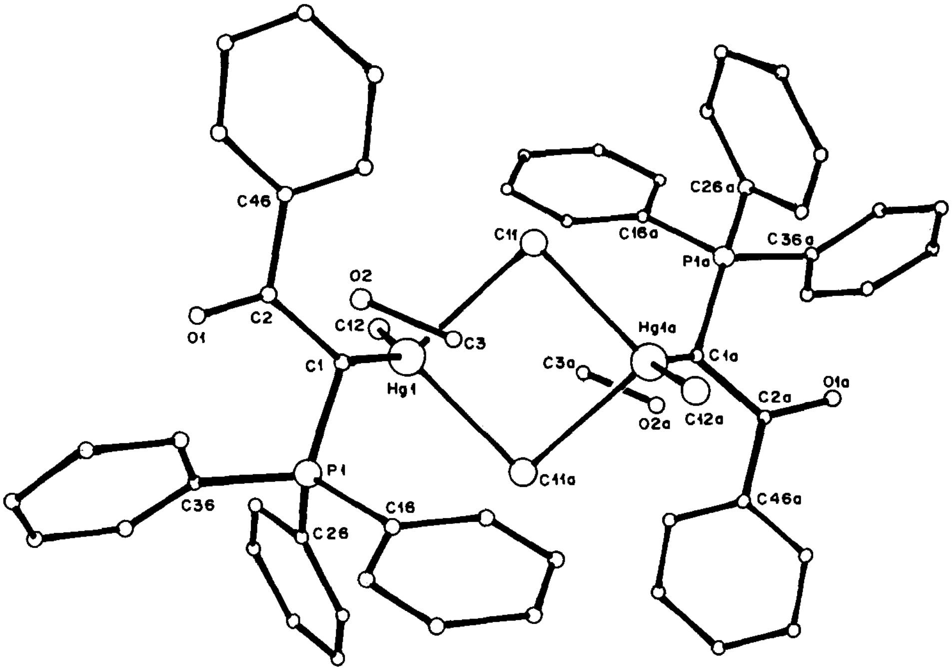

Fig. 1. Molecular structure and atom numbering scheme for $[(C_6H_5)_3PCHCOC_6H_5 \cdot HgCl_2]_2 \cdot 2CH_3OH$.

anisotropic thermal parameters for Hg, C(1) and P atoms. The carbon atoms of the phenyl groups were refined using a rigid model with fixed C–C (1.395 Å) and C–H (0.960 Å) bond lengths. Hydrogen atoms were inserted at calculated positions using a riding mode with fixed thermal parameters. No significant peaks were seen in the final Fourier maps, for both structures. Fractional atomic coordinates and equivalent isotropic displacement coefficients U_{eq} for the non-hydrogen atoms of complexes **1** and **2** are listed in Tables 5 and 6, respectively. The molecular structures of **1** and **2** are given along with atom numbering scheme in Figs. 1 and 2. Bond parameters and equations to the plane were obtained by the use of the PARST program [23]. Selected bond distances, bond angles and torsion angles are listed in Table 7.

X-ray crystal structure analysis shows that the 1:1 complex, $[(C_6H_5)_3PCHCOC_6H_5 \cdot HgCl_2 \cdot CH_3OH]$

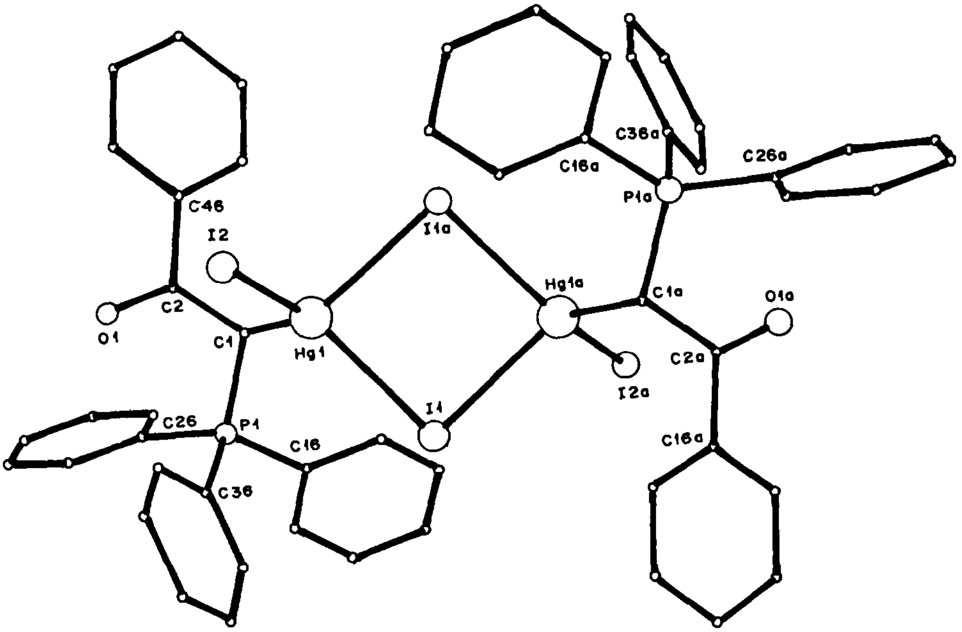

Fig. 2. Molecular structure and atom numbering scheme for $[(C_6H_5)_3PCHCOC_6H_5 \cdot HgI_2]_2$.

Table 7
Selected bond lengths (Å), bond angles (°) and torsion angles (°) with e.s.d.s in parentheses (involving non-hydrogen atoms)

HgX_2	X = Cl	X = I
Hg(1)–X(1)	2.710(2)	3.010(1)
Hg(1)–X(2)	2.417(3)	2.705(1)
Hg(1)–C(1)	2.208(8)	2.312(13)
Hg(1)–X(1a)	2.624(2)	2.812(1)
Hg(1a)–X(1)	2.624(2)	2.812(1)
O(1)–C(2)	1.229(8)	1.224(13)
C(16)–P(1)	1.814(6)	1.803(8)
C(26)–P(1)	1.809(5)	1.812(8)
C(36)–P(1)	1.803(4)	1.810(1)
C(46)–C(2)	1.512(8)	1.518(15)
C(1)–C(2)	1.504(9)	1.453(14)
C(1)–P(1)	1.798(8)	1.806(10)
O(2)–C(3)	1.401(11)	–
X(1)–Hg(1)–X(1a)	88.8(1)	92.9(1)
C(1)–Hg(1)–X(1a)	113.8(2)	118.3(2)
X(2)–Hg(1)–X(1a)	97.1(1)	110.8(1)
Hg(1)–X(1)–Hg(1a)	91.2(1)	87.1(1)
X(2)–Hg(1)–C(1)	142.1(2)	118.8(3)
X(1)–Hg(1)–C(1)	101.7(2)	97.0(3)
X(1)–Hg(1)–X(2)	100.3(1)	115.1(0)
Hg(1)–C(1)–P(1)	111.4(3)	110.9(6)
Hg(1)–C(1)–C(2)	102.5(5)	101.1(7)
C(2)–C(1)–P(1)	115.5(5)	113.4(8)
C(46)–C(2)–C(1)	118.6(5)	118(1)
O(1)–C(2)–C(1)	128.7(6)	122.7(11)
O(1)–C(2)–C(46)	120.7(7)	119(1)
C(36)–P(1)–C(1)	113.2(3)	112.8(5)
C(26)–P(1)–C(1)	112.8(3)	110.0(4)
C(26)–P(1)–C(36)	107.6(2)	110.8(5)
C(16)–P(1)–C(1)	107.1(3)	108.2(5)
C(16)–P(1)–C(36)	107.6(2)	108.0(4)
C(16)–P(1)–C(26)	108.4(3)	106.8(4)
X(2)–Hg(1)–C(1)–C(2)	−30.7(7)	−19.1(9)
X(1)–Hg(1)–C(1)–C(2)	93.6(5)	104.7(7)
X(2)–Hg(1)–C(1)–P(1)	93.5(4)	101.5(6)
X(1)–Hg(1)–C(1)–P(1)	−142.2(3)	−134.8(5)
C(25)–C(26)–P(1)–C(1)	−51.2(5)	−70.8
C(21)–C(26)–P(1)–C(1)	129.1(5)	107.2(8)
C(35)–C(36)–P(1)–C(1)	−60.3(5)	−41.3(10)
C(31)–C(36)–P(1)–C(1)	123.0(5)	137.2(8)
C(41)–C(46)–C(2)–O(1)	171.9(6)	167(1)
C(45)–C(46)–C(2)–O(1)	−4.2(9)	−12(1)
C(45)–C(46)–C(2)–C(1)	175.0(6)	166(1)
C(41)–C(46)–C(2)–C(1)	−8.9(9)	−14.4(15)
Hg(1)–C(1)–C(2)–C(46)	−91.5(6)	−83(1)
Hg(1)–C(1)–C(2)–O(1)	87.7(7)	95(1)
Hg(1)–C(1)–P(1)–C(36)	−142.2(3)	−30.2(7)
Hg(1)–C(1)–P(1)–C(26)	−19.7(5)	−154.5(5)
Hg(1)–C(1)–P(1)–C(16)	99.4(4)	89.2(6)
C(2)–C(1)–P(1)–C(16)	−144.2(5)	−157.9(8)
C(2)–C(1)–P(1)–C(26)	96.7(6)	−41.5(10)
C(2)–C(1)–P(1)–C(36)	−25.8(6)	82.7(10)
P(1)–C(1)–C(2)–C(46)	147.2(5)	158.0(8)
P(1)–C(1)–C(2)–O(1)	−33.6(9)	−24(16)
X(1)–Hg(1)–X(1a)–Hg(1a)	0.0(1)	0.0(1)
X(2a)–Hg(1a)–X(1a)–Hg(1)	97.0(1)	114.6(2)
C(1a)–Hg(1a)–X(1a)–Hg(1)	−114.1(2)	119.0(3)

adopts the centrosymmetric dimeric structure in the solid state which is in contrast to the iodo bridged unsymmetrical structure reported [24] for $[Pr_3PHgI_2]_2$ (Pr = n-propyl) in which two phosphines are coordinated to one mercury atom and two iodine atoms to the other mercury atom.

The Hg^{II} in the molecule **1** is sp^3 hybridized and has a tetrahedral coordination environment with one short Hg–Cl bond, one Hg–C bond, and two asymmetric bridging Hg–Cl bonds at the distances of 2.625(2) Å and 2.710(2) Å.

The significant shortening of the Hg–C bond of length, 2.208(8) Å compared to analogous distances in **2** and in $(C_5H_4P(C_6H_5)_3HgI_2)_2$ [21] (2.312(13) and 2.292(8) Å, respectively) must be attributed to the use of Hg^{II} orbitals with high s character for bonding to ylidic carbon. The use of non-equivalent hybrid orbitals with high s character to bond to low electronegative atoms was proposed by Bent in the concept of isovalent hybridization [25] to account for the variation in bond lengths and bond angles around a central atom. As expected on the basis of the same concept, the Hg–C bond in **2** is much longer than in **1**, because of very low difference in electronegativity between carbon and iodine.

The terminal Hg–Cl bond length, 2.417(3) Å is comparable to 2.40(1) Å observed [26] in the case of $Hg_2Cl_5N_2C_{11}H_{17}$ which has a tetrahedral coordination environment around mercury with a bridging structure. The two bridged Hg–Cl bonds fall within the range, 2.62–3.08 Å reported for other structures [27–29] containing chloro bridged mercury.

The ClHgC angle, 142.1(2)° deviates from the tetrahedral angle. Such deviation has been explained by assuming an sp hybrid state for Hg^{II} [30] in similar structures. However, the Hg–C and Hg–Cl bond lengths in compounds cotaining sp hybridized Hg are shorter than the corresponding bond lengths observed in mercury ylide complexes **1** and **2**. Thus the Hg–C and Hg–Cl bond lengths in $ClHgCH_2CHO$ are only 2.11(2) Å and 2.326(6) Å, respectively [31]. We believe that the widening of the ClHgC angle by about 33° from the tetrahedral angle must be due to the higher s character of the sp^3 hybrid mercury orbitals involved in the above bonds (vide supra) and the formation of a strong chloro bridge between Hg atoms which requires the internal ClHgCl angle (88.8(1)°) to be considerably smaller.

The C(1)–C(2) bond length, 1.504(9) Å is significantly longer than the corresponding bond found in the uncomplexed phosphorane (1.407(8) Å) [32]. Plane calculations show that the delocalization in P(1)–C(1)–C(2)–O(1) unit in the phosphorane is destroyed so that the partial double bond character of C(2)–O(1) shows very strongly in the complexes. Also the P(1)–C(1) bond is cosiderably elongated from 1.72 Å, observed in the parent ylide, [1.716(5) and 1.723(5) Å] [32] to 1.800(4) Å in complex **1**.

The molecular structure of $[(C_6H_5)_3PCHCOC_6H_5 \cdot$

$HgI_2]_2$ is very similar to that of the complex of the ylide with mercuric chloride. The plane defined by the two Hg atoms and two bridging halogens is perfectly planar in both the structures. However, the bridge in the former case is more unsymmetrical, as revealed by the bond lengths within the bridge. The maximum absolute deviations for the plane containing P(1)–C(1)–C(2)–O(1) unit in **1** and **2** are 0.183(7) Å and 0.452(11) Å, respectively observed for C(2) in both the structures.

The internuclear distances between mercury atoms were found to be 3.810(2) Å and 4.014(1) Å in structures **1** and **2**, respectively. These distances are much longer than the sum of Van der Waals radii (1.5 Å) of the two mercury atoms [33] indicating the absence of significant bonding interactions between the mercury atoms in the molecular structures. The adaptation of dimeric structures in Hg^{II} ylide complexes may be explained by both the preference of Hg^{II} to four coordination and the stability of 18 electron configuration around Hg^{II}.

Tables of structure factors, hydrogen atom coordinates, complete list of bond parameters etc. for structures **1** and **2** have been deposited with the Cambridge Crystallographic Centre.

Acknowledgement

One of the authors, KP thanks the UGC, New Delhi for financial assistance under Special Assistance Programme, sanctioned to the Department of Chemistry, Bharathidasan University, Tiruchirappalli. MK thanks the same organization for a grant under Minor Research Project.

References

[1] H. Schmidbaur, *Acc. Chem. Res., 8* (1975) 62.
[2] H. Schmidbaur, *Pure Appl. Chem., 50* (1978) 19; *52* (1980) 1057.
[3] H. Schmidbaur, *Angew. Chem., Int. Ed. Engl., 22* (1983) 907.
[4] W.C. Kaska, *Coord. Chem. Rev., 48* (1983) 1.
[5] J. Vicente, M.T. Chicote, J.A. Cayuelas, J. Fernandez-Baeza, P.G. Jones, G.M. Sheldrick and P. Espinet, *J. Chem. Soc. Dalton Trans.,* (1985) 1163.
[6] S. Kato, T. Kato, M. Mizuta, K. Itoh and Y. Ishii, *J. Organomet. Chem., 51* (1973) 167.
[7] J.A. Albanese, A.L. Rheingold and J.L. Burmeister, *Inorg. Chim. Acta, 150* (1988), 213.
[8] R. Uson, J. Fornies, R. Navarro, P. Espinet and C. Mendivil, *J. Organomet. Chem., 290* (1985) 125.
[9] H. Koezuka, G. Matsubayashi and T. Tanaka, *Inorg. Chem., 15* (1976) 417.
[10] J. Vicente, M.T. Chicote, J. Fernandez-Baeza, J. Martin, I. Saura-Llamas, J. Turpin and P.G. Jones, *J. Organomet. Chem., 331* (1987) 409.
[11] N.A. Nesmeyanov, V.M. Novikov and O.A. Reutov, *J. Organomet. Chem., 4* (1965) 202.
[12] E.T. Weleski, Jr., (The Late) J.L. Silver, M.D. Jansson and J.L. Burmeister, *J. Organomet. Chem., 102* (1975) 365.
[13] F. Ramirez and S. Dershowitz, *J. Org. Chem., 22* (1957) 41.
[14] A.J. Gordon and R.A. Ford, *The Chemist's Companion – A Handbook of Practical Data, Techniques and References*, Wiley interscience, New York, 1972, p. 438.
[15] J. Vicente, M.T. Chicote, M.C. Lagunas and P.G. Jones, *J. Chem. Soc. Dalton Trans.,* (1991) 2579.
[16] M. Onishi, Y. Ohama, K. Hiraki and H. Shintan, *Polyhedron, 1* (1982) 539.
[17] W. Lüttke and K. Wilhelm, *Angew. Chem., Int. Ed. Engl., 4* (1965) 875.
[18] J.A. Teagle and J.L. Burmeister, *Inorg. Chim. Acta, 118* (1986) 65.
[19] T.A. Albright, M.D. Gardon and W.J. Freeman, *J. Am. Chem. Soc., 98* (1976) 6249.
[20] G. Facchin, R. Bertani, M. Calligaris, G. Nardin and M. Mari, *J. Chem. Soc., Dalton Trans.,* (1987) 1381.
[21] N.L. Holy, N.C. Baenziger, R.M. Flynn and D.C. Swenson, *J. Am. Chem. Soc., 98* (1976) 7823.
[22] G.M. Sheldrick, SHELXTL *Users's Manual*, Revision 4.1, Nicolet XRD Corporation, Madison, Wisconsin, USA, 1984.
[23] M. Nardelli, *Comput. Chem., 7* (1983) 95.
[24] G.A. Bowmaker, H.J. Clase, N.W. Alcock, J.M. Kessler, J.H. Nelson and J.S. Frye, *Inorg. Chim. Acta, 210* (1993) 107.
[25] K.F. Purcell and J.C. Kotz, *Inorganic Chemistry*, 1st edition, W.B. Saunders, Philadelphia, 1977, p. 109.
[26] A. Albinati, S.V. Meille, F. Cariati, G. Marcotrigiano, L. Menabue and G.C. Pellacani, *Inorg. Chim. Acta, 38* (1980) 221.
[27] L. Book and T.C.W. Mak, *Inorg. Chim. Acta, 92* (1984) 265.
[28] P. Biscarini, L. Fusina, G.D. Nivellini, A. Mangia and G. Pelizzi, *J. Chem. Soc. Dalton Trans.,* (1974) 1846.
[29] M. Authier-Martin, J. Hubert, R. Rivest and A.L. Beauchamp, *Acta Crystallogr. Sect. B, 34* (1978) 273.
[30] P. Biscarini and G. Pelizzi, *J. Chem. Soc. Dalton Trans.,* (1988) 2915.
[31] J. Halfpenny and R.W.H. Small, *Acta Crystallogr. Sect. B 35* (1979) 1239.
[32] M. Kalyanasundari, K. Panchanatheswaran, V. Parthasarathi, W.T. Robinson and Huo Wen, *Acta Crystallogr.*, *(50)* (1994) 1738.
[33] J.E. Huheey, *Inorganic Chemistry – Principles of Structure and Reactivity*, 2nd. edition, Harper Int. Ed., New York, 1978, p. 233.