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# Synthesis and characterization of binuclear mercury(II) complexes of phosphorus ylides, X-ray analysis and multinuclear NMR measurements

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### ABSTRACT

The reactions of phosphorus ylide  $(p-tolyl)_3PCHC(O)CH_3$  ( $\mathbf{Y}_1$ ) with HgX<sub>2</sub> (X = Cl and Br) and  $(p-tolyl)_3PCHC(O)C_6H_4NO_2$  ( $\mathbf{Y}_2$ ) with HgX<sub>2</sub> (X = Cl, Br and I) in equimolar ratios using methanol as a solvent are reported. These reactions led to binuclear complexes. C-Coordination of ylides and *trans*-like structure of complexes  $[(\mathbf{Y}_1) \cdot \text{HgBr}_2]_2$  and  $[(\mathbf{Y}_2) \cdot \text{HgBr}_2]_2 \cdot 2DMSO$  are demonstrated by single crystal X-ray analyses. The IR, <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR data for the other synthesized compounds are similar to the latter complexes, indicating similar structures. Elemental analyses indicate a 1:1 stoichiometry between the ylide and Hg(II) halide in all the products. The ab initio studies indicated that for all dimeric compounds, the observed *trans*-like structures are 7–10 kcal/mol more stable than the alternative possible *cis*-like isomers. Although the calculated bond lengths are slightly longer than the measured ones, the similarity of calculated and measured bond angles reflects the similar geometrical structures for these compounds in both the solid state and the gas phase.

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### 1. Introduction

The utility of metalated phosphorus ylides in the synthetic chemistry has been well documented [1]. The synthesis of complexes derived from phosphorus ylides and Hg(II) halides was started in 1965 by Nesmeyanov et al. [2]. In 1975, Weleski et al. [3] proposed a halide-bridged dimeric structure for Hg(II) halide complexes of phosphorus ylides with equal bridged bonds, whereas Kalyanasundari et al. in 1995 [4] reported centrosymmetric halide-bridged dimeric structures with unequal bridged bonds. We have recently focused on the binuclear [5] and polynuclear [6] complexes derived from mercury(II) salts and phosphorus ylides. The α-keto-stabilized phosphorus ylides  $R_3P=C(R')COR''$  show interesting properties such as their high stability and their ambidentate character as ligands (C- versus O-coordination) [7]. This ambidentate character can be rationalized in terms of the resonance forms A-C, together with the isomeric form D (Chart 1).

Form B can be considered as leading to coordination by the carbon atom to give a complex of form E, whereas isomers C and D would both lead to coordination by the oxygen atom, affording structures F (transoid) and G (cisoid), respectively. Although many coordination modes are possible for keto ylides [8], coordination

\* Corresponding author. *E-mail address:* Jsabounchei@yahoo.co.uk (S.J. Sabounchei). through carbon is more predominant and observed with soft metal ions, *e.g.*, Pd(II), Pt(II), Ag(I), Hg(II), Au(I) and Au(III) [4,9], whereas O-coordination dominates when the metals involved are hard, *e.g.*, Ti(IV), Zr(IV), and Hf(IV) [10]. However, some instances of O-coordination to the soft metal ions are: Pd(II) complexes of the type [Pd(C<sub>6</sub>F<sub>5</sub>)(L<sub>2</sub>)(APPY)](ClO<sub>4</sub>) [9a] [APPY = Ph<sub>3</sub>PCHCOMe; L = PPh<sub>3</sub> and PBu<sub>3</sub>; L<sub>2</sub> = bipy], W(0) complexes of the type W(CO)<sub>5</sub>L(L = ylide) [11] and Hg(II) complexes of doubly keto-stabilized phosphorus ylide [PPh<sub>3</sub>CC(O)CH<sub>3</sub>C(O)Ph] with Hg(II) halides [12]. In this study, we describe the synthesis, spectroscopic characterization (IR and NMR), theoretical and X-ray structural study of some new Hg(II) complexes, in which the C-coordination by the carbon atom of the ylide ligands is demonstrated by the single crystal X-ray analyses of [(Y<sub>1</sub>) · HgBr<sub>2</sub>]<sub>2</sub> and [(Y<sub>2</sub>) · HgBr<sub>2</sub>]<sub>2</sub> · 2DMSO.

## 2. Experimental

#### 2.1. Materials

All the reactions were performed in air. The starting materials were purchased from commercial sources and used without further purification. The ligands were synthesized by the reaction of the related phosphine with bromoacetone or 2-bromo-4'-nitro-acetophenone and by concomitant elimination of HBr by NaOH [13].





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#### 2.2. Physical measurements

Melting points were measured on a SMPI apparatus. Elemental analyses for C, H and N atoms were performed using a Perkin–Elmer 2400 series analyzer. IR spectra were recorded on a Shimadzu 435-U-04 FT spectrophotometer from KBr pellets. <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectra were recorded on a 300 MHz Bruker spectrometer in CDCl<sub>3</sub> or DMSO- $d_6$  as a solvent at 25 °C. Chemical shifts (ppm) are reported according to internal TMS and external 85% phosphoric acid.

Suitable crystals were obtained from dimethylsulfoxide solution by slow evaporation of the solvent. The single crystal X-ray diffraction analyses were performed on a Bruker SMART 4000 APEX II CCD diffractometer. Structural solution and refinement were performed using SHELXT [14]. The structure was solved by direct methods. Refinement of  $F^2$  was against all reflections. All the non-hydrogen atoms were refined anisotropically. All the hydrogens were included in calculated positions.

#### 2.3. Computational methods

The geometries of compounds were fully optimized at the Hartree–Fock (HF) level of theory using the GAUSSIAN 98 program [15] on a Pentium-PC computer with 3600 MHz processor. The standard LanL2mb basis set was used for all complexes [16]. This basis set includes effective core potentials (ECP) for both the mercury and phosphorus atoms as well as halide (Cl, Br, I) ions. Vibrational frequency analyses, calculated at the same level of theory, indicate that the optimized structures are at the stationary points corresponding to local minima, without any imaginary frequency. Atomic coordinates for ab initio calculations were obtained from the data of the X-ray crystal structure analyses.

## 2.4. Data for ligands

#### 2.4.1. Preparation of $(p-tolyl)_3PCHC(0)CH_3(Y_1)$

To a solution of chloroacetone (0.092 g, 1 mmol) in chloroform (20 ml) was added dropwise a solution of triparatolylphosphine (0.304 g, 1 mmol) in the same solvent (5 ml). The pale yellow solution was refluxed for 24 h. The solution was concentrated under reduced pressure to 10 ml and diethyl ether (20 ml) was added. The white precipitate was filtered off, washed with light petroleum ether (20 ml) and dried under reduced pressure. In order to get the final product, the whole of the crude solid (0.344 g, 87%) was transferred to an aqueous solution of NaOH (5%) and stirred at 40 °C for 3 h. The pale white precipitate of acetylmethylenetripara-

tolylphosphorane was obtained, washed with distilled water and air dried. Yield 0.316 g (92%), mp 100–102 °C. IR (KBr disk): v (cm<sup>-1</sup>) 1711, 1599 (C=O), 1502, 1448, 1425, 1402, 1363, 1313, 1193, 1156, 1111, 1038, 1002, 848 (P–C), 808 and 777. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 2.04 (3H, s, COCH<sub>3</sub>), 2.36 (9H, s, 3CH<sub>3</sub>), 3.65 (1H, d, <sup>2</sup>J<sub>PH</sub> = 24.8 Hz, CH); 7.24–7.52 (12H, m, Ph). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 10.59. <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 21.49 (s, 3CH<sub>3</sub>); 28.43 (d, <sup>3</sup>J<sub>PC</sub> = 15.1 Hz, COCH<sub>3</sub>); 52.53 (d, <sup>1</sup>J<sub>PC</sub> = 107.7 Hz, CH); 124.29 (d, <sup>1</sup>J<sub>PC</sub> = 92.7 Hz, *p*-tolyl (*i*)); 133.05 (d, <sup>2</sup>J<sub>PC</sub> = 10.5 Hz, *p*-tolyl (*o*)); 129.51 (d, <sup>3</sup>J<sub>PC</sub> = 12.3 Hz, *p*-tolyl (*m*)); 142.32 (*p*-tolyl (*p*)); 190.38 (CO).

## 2.4.2. Data for (p-tolyl)<sub>3</sub>PCHCOC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub> (Y<sub>2</sub>) [17]

IR (KBr disk): v (cm<sup>-1</sup>) 1600 (C=O), 1530, 1407, 1339, 1187, 1179, 1112, 886 (P–C) and 807. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 4.47 (1H, d, <sup>2</sup>J<sub>PH</sub> = 22.7 Hz, CH) 2.41 (s, 9H, 3CH<sub>3</sub>), 7.26–8.14 (12H, m, Ph). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 13.13. <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 21.33 (s, 3CH<sub>3</sub>); 54.13 (d, <sup>1</sup>J<sub>PC</sub> = 113.5 Hz, CH); 122.98 (d, <sup>1</sup>J<sub>PC</sub> = 93.6 Hz, 3*p*-tolyl (*i*)); 122.72 (COPh (*m*)); 127.55 (*p*-tolyl (*p*)); 129.52 (d, <sup>3</sup>J<sub>PC</sub> = 12.6 Hz, *p*-tolyl (*m*)); 132.84 (d, <sup>2</sup>J<sub>PC</sub> = 10.5 Hz, *p*-tolyl (*o*)); 147.87 (COPh (*p*)); 147.21 (d, <sup>3</sup>J<sub>PC</sub> = 1.6 Hz, COPh (*i*)); 142.66 (d, <sup>4</sup>J<sub>PC</sub> = 2.6 Hz, COPh (*o*)); 181.15 (CO).

#### 2.5. Synthesis of the complexes

#### 2.5.1. $[(Y_1) \cdot HgCl_2]_2$ (1), General procedure for complexes

To a methanolic solution (15 ml) of HgCl<sub>2</sub> (0.082 g, 0.3 mmol) was added a methanolic solution (10 ml) of Y<sub>1</sub> (0.108 g, 0.3 mmol). The mixture was stirred for 1 h. The separated solid was filtered and washed with diethyl ether. Yield 0.161 g, 85%. mp 235–238 °C. *Anal.* Calc. for C<sub>48</sub>H<sub>50</sub>Cl<sub>4</sub>Hg<sub>2</sub>O<sub>2</sub>P<sub>2</sub>: C, 45.62; H, 3.99. Found: C, 44.99; H, 4.28%. IR (KBr disk): v (cm<sup>-1</sup>) 1663 (C=O), 1597, 1499, 1448, 1400, 1271, 1192, 1143, 1107, 871 and 806. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  (ppm) 2.26 (3H, s, COCH<sub>3</sub>); 2.41 (9H, s, CH<sub>3</sub>); 4.85 (1H, br, CH); 7.48–7.62 (12H, m, Ph). <sup>31</sup>P NMR (DMSO-*d*<sub>6</sub>):  $\delta$  (ppm) 22.92 (s). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>):  $\delta$  (ppm) 20.98 (3CH<sub>3</sub>); 30.21 (d, <sup>3</sup>J<sub>PC</sub> = 7.2 Hz, COCH<sub>3</sub>); 49.16 (d, <sup>1</sup>J<sub>PC</sub> = 68.6 Hz, CH); 119.46 (d, <sup>1</sup>J<sub>PC</sub> = 91.3 Hz, *p*-tolyl (*i*)); 129.95 (d, <sup>3</sup>J<sub>PC</sub> = 13.0 Hz, *p*-tolyl (*m*)); 133.18 (d, <sup>2</sup>J<sub>PC</sub> = 10.6 Hz, *p*-tolyl (*o*)); 144.12 (*p*-tolyl (*p*)); 199.98 (CO).

#### 2.5.2. Data for $[(Y_1) \cdot HgBr_2]_2$ (2)

Yield 0.169 g, 78%. mp 229–231 °C. *Anal.* Calc. for  $C_{48}H_{50}Br_4Hg_2O_2P_2$ : C, 39.99; H, 3.50. Found: C, 39.64; H, 3.85%. IR (KBr disk):  $\nu$  (cm<sup>-1</sup>) 1663 (C=O), 1597, 1498, 1399, 1353, 1288, 1191, 1149, 1109, 964, 855 and 807. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$ 

(ppm) 2.22 (3H, s, COCH<sub>3</sub>); 2.41 (9H, s, CH<sub>3</sub>); 4.76 (1H, br, CH); 7.47–7.61 (12H, m, Ph). <sup>31</sup>P NMR (DMSO-*d*<sub>6</sub>):  $\delta$  (ppm) 22.19 (s). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>):  $\delta$  (ppm) 20.84 (3CH<sub>3</sub>); 30.11 (d, <sup>3</sup>*J*<sub>PC</sub> = 11.2 Hz, COCH<sub>3</sub>); 49.51 (d, <sup>1</sup>*J*<sub>PC</sub> = 41.2 Hz, CH); 119.64 (d, <sup>1</sup>*J*<sub>PC</sub> = 91.2 Hz, *p*tolyl (*i*)); 130.42 (d, <sup>3</sup>*J*<sub>PC</sub> = 13.0 Hz, *p*-tolyl (*m*)); 133.41 (d, <sup>2</sup>*J*<sub>PC</sub> = 10.3 Hz, *p*-tolyl (*o*)); 143.87 (*p*-tolyl (*p*)); 198.00 (CO).

## 2.5.3. Data for $[(Y_2) \cdot HgCl_2]_2$ (3)

Yield 0.173 g, 78%. mp 210–212 °C. *Anal.* Calc. for  $C_{58}H_{52}Cl_4Hg_2N_2O_6P_2$ : C, 47.13; H, 3.55; N, 1.90. Found: C, 47.24; H, 3.52; N, 2.06%. IR (KBr disk): v (cm<sup>-1</sup>) 1650 (C=O), 1599, 1523, 1345, 1304, 1285, 1184, 1111, 1029, 1006, 858, 822 (P-C) and 804. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  (ppm) 5.13 (1H, br, CH); 7.46–8.22 (16H, m, Ph). <sup>31</sup>P NMR (DMSO-*d*<sub>6</sub>):  $\delta$  (ppm) 22.05 (s). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>):  $\delta$  (ppm) 22.05 (s). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>):  $\delta$  (ppm) 20.77 (3CH<sub>3</sub>); 49.11 (d, <sup>1</sup>*J*<sub>PC</sub> = 84.8 Hz, CH); 122.76 (COPh (*m*)); 120.68 (d, <sup>1</sup>*J*<sub>PC</sub> = 93.6 Hz, *p*-tolyl (*i*)); 128.73 (*p*-tolyl (*p*)); 129.69 (d, <sup>3</sup>*J*<sub>PC</sub> = 12.80 Hz, *p*-tolyl (*m*)); 143.52 (COPh (*o*)); 132.87 (d, <sup>2</sup>*J*<sub>PC</sub> = 10.4 Hz, *p*-tolyl (*o*)); 143.41 (COPh (*i*)); 148.69 (COPh (*p*)); 186.01 (CO).

#### 2.5.4. Data for $[(Y_2) \cdot HgBr_2]_2 \cdot 2DMSO(4)$

Yield 0.206 g, 83%. mp 213–214 °C. *Anal.* Calc. for C<sub>58</sub>H<sub>52</sub>Br<sub>4</sub>Hg<sub>2</sub>N<sub>2</sub>O<sub>6</sub>P<sub>2</sub>: C, 42.07; H, 3.17; N, 1.69. Found: C, 42.52; H, 3.12; N, 1.75%. IR (KBr disk):  $\nu$  (cm<sup>-1</sup>) 1636 (C=O), 1598, 1520, 1499, 1400, 1342, 1316, 1287, 1184, 1108, 1024, 1006, 855, 828 (P–C) and 803. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  (ppm) 5.40 (1H, d, <sup>2</sup>J<sub>PH</sub> = 7.7 Hz, CH); 7.46–8.24 (16H, m, Ph). <sup>31</sup>P NMR (DMSO-*d*<sub>6</sub>):  $\delta$  (ppm) 22.00 (s). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>):  $\delta$  (ppm) 21.01 (3CH<sub>3</sub>); 49.85 (d, <sup>1</sup>J<sub>PC</sub> = 60.3 Hz, CH); 122.98 (COPh (*m*)); 120.42 (d, <sup>1</sup>J<sub>PC</sub> = 92.2 Hz, *p*-tolyl (*i*)); 129.18 (*p*-tolyl (*p*)); 129.93 (d, <sup>3</sup>J<sub>PC</sub> = 12.8 Hz, *p*-tolyl (*m*)); 143.77 (COPh (*o*)); 133.11 (d, <sup>2</sup>J<sub>PC</sub> = 10.5 Hz, *p*-tolyl (*o*)); 143.17 (COPh (*i*)); 148.97 (COPh (*p*)); 187.27 (CO).

#### 2.5.5. Data for $[(Y_2) \cdot HgI_2]_2$ (5)

Yield 0.210 g, 76%. mp 215–216 °C. *Anal.* Calc. for  $C_{58}H_{52}H_{52}H_{52}H_{2}I_{4-}$ N<sub>2</sub>O<sub>6</sub>P<sub>2</sub>: C, 37.78; H, 2.84; N, 1.52. Found: C, 37.87; H, 2.81; N, 1.55%. IR (KBr disk):  $\nu$  (cm<sup>-1</sup>) 1635 (C=O), 1598, 1521, 1400, 1343, 1286, 1182, 1108, 1023, 1007, 856, 826 (P-C) and 801. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  (ppm) 5.21 (1H, d, <sup>2</sup>*J*<sub>PH</sub> = 9.5 Hz, *CH*); 7.43–8.17 (16H, m, Ph). <sup>31</sup>P NMR (DMSO-*d*<sub>6</sub>):  $\delta$  (ppm) 20.78 (s). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>):  $\delta$  (ppm) 21.67 (3*C*H<sub>3</sub>); 51.06 (d, <sup>1</sup>*J*<sub>PC</sub> = 83.2 Hz, *CH*); 123.60 (COPh (*m*)); 121.3 (d, <sup>1</sup>*J*<sub>PC</sub> = 93.1 Hz, *p*-tolyl (*i*)); 129.63 (*p*-tolyl (*p*)); 130.48 (d, <sup>3</sup>*J*<sub>PC</sub> = 12.7 Hz, *p*-tolyl (*m*)); 144.28 (d, <sup>3</sup>*J*<sub>PC</sub> = 2.4 Hz, COPh (*i*)); 149.32 (COPh (*p*)); 186.91 (CO).

### 3. Results and discussion

The reaction of mercury halides with ylides in a 1:1 stoichiometry afforded halide-bridged dimeric structures **1–5** (Scheme 1) containing C-coordinated ylide ligands.

#### 3.1. Spectroscopy

The v (CO) band, which is sensitive to complexation, is observed for complexes at higher frequencies compared to the parent ylides, indicating the coordination of the ylide through carbon atom in each case [18]. The v (P<sup>+</sup>–C<sup>-</sup>) band, which is also diagnostic of the coordination modes, occurs at lower frequencies for complexes in comparison to the parent ylides, consistent with some removal of electron density in the P–C bonds [5]. C-Coordination causes an increase in v (CO) and a decrease in v (P<sup>+</sup>–C<sup>-</sup>), while for O-coordination a lowering for both frequencies is expected [9d]. The P–C bands for complexes **1** and **2** overlapped with other intense bands present at the same regions and thus were not seen.

In the <sup>1</sup>H NMR spectra, the signals due to the methinic protons for complexes are doublet or broad. A similar behavior was observed earlier in the case of vlide complexes of platinum(II) chloride [19]. The expected downfield shifts of <sup>31</sup>P and <sup>1</sup>H signals for the PCH group upon complexation in the case of C-coordination were observed in their corresponding spectra. The proton decoupled <sup>31</sup>P NMR spectra show only one sharp singlet between 20.77 and 22.92 ppm in the complexes. The appearance of single signals for PCH group in each of the <sup>31</sup>P and <sup>1</sup>H NMR spectra indicates the presence of only one molecule for all the complexes, as expected for C-coordination [4]. It must be noted that the O-coordination of the ylide generally leads to the formation of a mixture of cisoid and transoid isomers, giving rise to two different signals in the <sup>31</sup>P and <sup>1</sup>H NMR spectra (Chart 1) [9a]. The <sup>31</sup>P chemical shift values for the complexes appear to be shifted downfield by about 7.6-11.5 ppm with respect to the parent ylide, also indicating that coordination of the ylide has occurred [4,5,20]. Satellites due to coupling to <sup>199</sup>Hg for ylidic complexes of Hg(II) halides are only observed at low temperature [5a,20] or by solid-state <sup>31</sup>P NMR [20] and also in the case of  $Hg(NO_3)_2 \cdot H_2O$  as metal source [6]. Failure to observe satellites in the above spectra was previously noted in the ylide complexes of Hg(II) [21] and Ag(I) [9c], and was assigned to a fast exchange of the ylide with the metal which caused exchange decoupling [21].

The most interesting aspect of the <sup>13</sup>C NMR spectra of the complexes is the upfield shift of the signals due to the ylidic carbon atoms. Such an upfield shift was observed in [PdCl( $\eta^3$ -2-XC<sub>3</sub>H<sub>4</sub>)(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PCHCOR] (X = H, CH<sub>3</sub>; R = CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>), and is due to the change in the hybridization of the ylidic carbon atom on coordination [22]. The downfield shifts of the carbonyl C atom in the complexes are 5–10 ppm compared to the same C atom in the parent ylides, indicating a much lower shielding of carbon of the CO group in these complexes.

#### 3.2. X-ray crystallography

Table 1 provides the crystallographic results and refinement information for complexes **2** and **4** (Scheme 1). The molecular



Table 1			
Crystallographic data	summary for	complexes	<b>2</b> and

Compound	$[(Y_1) \cdot HgBr_2]_2$ (2)	$[(Y_2) \cdot HgBr_2]_2 \cdot 2DMSO$
		( <b>4</b> )
Empirical formula	$C_{48}H_{50}Br_4Hg_2O_2P_2$	$C_{62}H_{64}Br_4Hg_2N_2O_8P_2S_2$
Formula weight	1442	1812
Temperature (K)	150(2)	150(2)
Wavelength (A)	0.71	0.71
Crystal system	triclinic	triclinic
Space group	PĨ	PĪ
a (Å)	11.4586(14)	10.946(4)
b (Å)	11.5310(13)	11.190(4)
c (Å)	11.594(2)	15.104(6)
α (°)	105.235(6)	103.917(7)
β(°)	115.254(6)	95.612(8)
γ (°)	106.269(4)	114.259(7)
$V(Å^3)$	1194.1(3)	1596.3(11)
Ζ	1	1
$D_{\text{calc.}}$ (Mg/m <sup>3</sup> )	2.01	1.89
Absorption coefficient (mm <sup>-1</sup> )	9.87	7.48
F(000)	684	876
Crystal size (mm)	$0.21\times0.19\times0.12$	$0.21\times0.18\times0.16$
$\theta$ Range for data collection (°)	2.05-26.00	1.42-25.00
Reflections collected	13935	15466
Index ranges	$-14 \leq h \leq 8$ ,	$-13 \leq h \leq 13$ ,
0	$-13 \leq k \leq 14$ ,	$-13 \leq k \leq 13$ ,
	$-13 \leq l \leq 14$	$-17 \leq l \leq 17$
Independent reflections	$4673 [R_{int} = 0.0267]$	$5605 [R_{int} = 0.0841]$
Completeness to $\theta = 25.00^{\circ}$	99.7%	99.8%
Absorption correction	semi-empirical from	semi-empirical from
I I I I I I I I I I I I I I I I I I I	equivalents	equivalents
Maximum and minimum	0.3838 and 0.2310	0.3809 and 0.3028
transmission		
Refinement method	full-matrix least-	full-matrix least-
	squares on $F^2$	squares on $F^2$
Data/restraints/parameters	4673/0/266	5605/236/375
$Goodness-of-fit on F^2$	1 07	0.953
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0313$	$R_1 = 0.0479$
	$wR_{\rm a} = 0.0826$	$wR_{\rm p} = 0.0996$
R indices (all data)	$R_1 = 0.0377$	$R_1 = 0.0760$
(in data)	$wR_{0} = 0.0858$	$wR_{\rm o} = 0.1100$
Largest difference peak and	2.118  and  0.0050	1 722 and 1 858
hole (e Å <sup>-3</sup> )	2.110 dilu -0.330	1.722 dilu = 1.030

4

structures are shown in Fig. 1. Pertinent bond distances and angles are given in Tables 2 and 3. Packing diagrams, fractional atomic coordinates and equivalent isotropic displacement coefficients  $(U_{eq})$  for the non-hydrogen atoms of complexes **2** and **4** are shown in the Supplementary material.

The Hg(II) centre in each of complexes **2** and **4** is sp<sup>3</sup> hybridized and has a tetrahedral coordination environment with one short terminal Hg-Br bond, one Hg-C bond and two asymmetric bridging Hg-Br bonds. The Hg-C bond lengths in 2 (2.228(6) Å) and 4 (2.223(8)Å) are comparable to the analogous distances in  $[Ph_3PCHCOC_6H_4OCH_3 \cdot HgBr_2]_2$  (2.218(11)Å) [5b] and [{(ptolyl)<sub>3</sub>PCHCOOCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>}HgBr<sub>2</sub>]<sub>2</sub> (2.226(4) Å) [5a]. These distances are shorter than the Hg–C distance for  $[Ph_3PCHCOPh \cdot HgI_2]_2$ (2.312(13) Å) [4]. The shortening of the Hg–C bond lengths in 2 and 4 (bromide complexes) compared to the analogous distances in  $[Ph_3PCHCOPh \cdot HgI_2]_2$  [4] (iodide complex) must be attributed to the use of mercury orbitals with a high s character for bonding to the ylidic carbon. The use of non-equivalent hybrid orbitals with a high s character to bond to low electronegative atoms was proposed by Bent in the concept of isovalent hybridization to account for the variation in bond lengths and bond angles around a central atom [23]. The terminal Hg-Br bond lengths in 2 (2.5389(7) Å) and **4** (2.5362(12)Å) are comparable to the analogous distances in  $[Ph_3PCHCOC_6H_4OCH_3 \cdot HgBr_2]_2$  (2.559(2)Å) [5b] and [{(p $tolyl_{3}PCHCOOCH_{2}C_{6}H_{5}HgBr_{2}l_{2}$  (2.5255(6)Å) [5a].

The angles subtended by the ligands at the Hg(II) centre in **2** and **4** vary from 92.99(2) to 124.04(18) (**2**) and from 87.67(4) to

132.4(2) (**4**), indicating a much distorted tetrahedral environment in each case. The widening of the BrHgC angles by about  $12-23^{\circ}$ from the tetrahedral angle must be due to the higher s character of the sp<sup>3</sup> hybrid mercury orbitals involved in the above bonds and the formation of a strong halide-bridge between Hg atoms which requires the internal BrHgBr angles (92.99(2) (**2**) and 87.67(4) (**4**)) to be considerably smaller. The internuclear distances between the mercury atoms in these complexes were found to be 3.797 (**2**) and 4.039 (**4**), that are much longer than the sum of Van der Waals radii (1.5 Å) of the two mercury atoms [24], indicating the absence of significant bonding interactions between the mercury atoms in the molecular structures.

The stabilized resonance structure for the title ylides is destroyed by the complex formation; thus, the C(1)–C(2) bond lengths (1.422(10) (**2**) and 1.486(11) (**4**)) are significantly longer than the corresponding distances found in the uncomplexed phosphoranes (1.407(8) Å [25] and 1.401(2) Å [26]). On the other hand, the bond length of P(1)–C(1) in the similar ylide is 1.7194(17) Å [26] which shows that the above bonds are considerably elongated to 1.791(7) Å (**2**) and 1.786(8) Å (**4**).

The C-coordination of the title ylides is in contrast to the Ocoordination of the phosphorus ylide Ph<sub>3</sub>PC(COMe)(COPh) (ABPPY) in a different Hg(II) complex [12]. The difference in the coordination mode between ABPPY and the present ylides to Hg(II) can be rationalized in terms of the electronic properties, steric requirements, and size and shape of the ligand in the final bonding mode. This may also be explained by the electronic nature of the metals (Pd, Pt, Ru, Au, etc.) and even by the position of the coordination site (trans to a C atom, trans to a N atom, trans to an O atom, and so on). The nucleophilicity of the carbanion in ABPPY is less than that in our ylides; this is due to the additional delocalization of the ylide electron density in ABPPY which is facilitated by the second carbonyl group. This will reduce the ability of ABPPY to bind via the ylidic carbon. Belluco et al. have studied steric influences on the coordination modes of ylide molecules to Pt(II) systems [27]. These authors concluded that the preferred coordination mode is via the vlidic carbon, but that steric hindrance around the metal centre or the vlidic carbon will necessitate O-coordination. Indeed, this trend is reflected here, these ylides are slightly less sterically demanding than ABPPY and are C-coordinated to Hg(II).

## 3.3. Theoretical studies

We were interested to (i) study the gas phase structure of all the complexes, (ii) determine the energy difference between the observed *trans*-like structures and the alternative possible *cis*-like isomers.

The observed geometries of compounds **2** and **4** were used as a basis for ab initio calculations. A comparison made between the calculated bond lengths (Å) and bond angles (°) with the corresponding experimental values for compounds **2** and **4** is presented in Tables 4 and 5, respectively. The calculated structures in the gas phase agree well with the structures observed by X-ray crystallography, although the calculated bond lengths are slightly longer than the measured ones.

We then changed the geometrical structure of compounds **2** and **4** by the replacement of the positions of one terminal halide atom with one coordinated ylide group to obtain *cis*-like isomers which were used as the basis for additional calculations. The minimization of these isomers at the same level of theory gave the desired *cis*-like isomers. The optimized *cis* and *trans* structures of compounds  $[(Y_1) \cdot HgBr_2]_2$  and  $[(Y_2) \cdot HgBr_2]_2$  are shown in Figs. 2 and 3, respectively. A list of selected key bond lengths and angles for *trans*-like molecular structures of  $[(Y_1) \cdot HgX_2]_2$  and  $[(Y_2) \cdot HgX_2]_2$  (X = Cl, Br and I) together with the optimized



**Fig. 1.** ORTEP view of X-ray crystal structure of complexes: (a)  $[(Y_1) + HgBr_2]_2$  (2) and (b)  $[(Y_2) + HgBr_2]_2$  · 2DMSO (4).

*cis*- and *trans*-like structures are given in the Supplementary material.

As can be seen in Table 6, the latter *cis*-like isomers are about 7–10 kcal/mol less stable than the *trans*-like structures. The latter energy differences between the *cis*- and *trans*-like isomers of the present compounds are more than the corresponding calculated values for similar complexes [5a].

It is interesting to note that when the ylide is bulky such as  $Y_2$ , the relative energy of *cis*- and *trans*-like isomers significantly depends on the size of the bridging halide. Note that the *cis*-like isomer in the case of compound **6** (Table 6) is only about 7 kcal/mol less stable than the *trans*-like isomer, but in the case of compounds **1–3**, the *cis*-like isomers are more than 10 kcal less stable than the *trans*-like isomers.

In the *trans*-like structures of compounds **1–6**, the internuclear distances between the mercury atoms were calculated to be more than 4.1 Å (Table S1) indicating the absence of significant bonding interactions between the mercury atoms. These distances are also increased by increasing the size of the bridging anions (Cl, Br and I). The Hg–C bond lengths in the above structures decrease with an increase in the electronegativity of the coordinated halide ligands (Tables S7 and S13), indicating a slight increase in the s character of the Hg(II) orbitals when bonding to the ylidic carbon [5a,23].

On the other hand, we were interested to compare the relative stability of two possible C- and O-coordinated isomers. Thus we made an O-coordinated structural isomer for compound **1**. This isomer was optimized, similar to compound **1**, at HF level of theory using LanL2MB basis set (Fig. 4). The results showed that this

Table 5

for the compound **4** with corresponding ov

#### Table 2

Selected key	bond	lengths	(Å)	and	angles	(°)	for	[(Y <sub>1</sub> )	· HgBr	2]2	(2)	
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#### $[(Y_1) \cdot HgBr_2]_2 (\mathbf{2})$ Bond lengths Hg(1)-C(1)2.228(6) Hg(1)-Br(1)2.5389(7) 2.8968(8) Hg(1)-Br(2)Hg(1)-Br(2A)2.6097(7) C(1) - C(2)1.422(10) O(1) - C(2)1.231(9)P(1)-C(1)1.791(7) Bond angles C(1)-Hg(1)-Br(1)121.46(19) C(1)-Hg(1)-Br(2A)124.04(18) Br(1)-Hg(1)-Br(2A)109.34(3) 95.67(19) C(1)-Hg(1)-Br(2)104.35(2) Br(1)-Hg(1)-Br(2)Br(2A)-Hg(1)-Br(2)92.99(2) Hg(1A)-Br(2)-Hg(1)87.01(2) Hg(1)-C(1)-H(1A)109.2 C(2)-C(1)-Hg(1)101.6(5) P(1)-C(1)-Hg(1)110.0(3)

for the compound 4 with corresponding experimental values				
$[(Y_2) \cdot HgBr_2]_2 \cdot 2DMSO(4)$	X-ray	HF/Lanl2mb		
Bond lengths				
Hg(1)-C(1)	2.223(8)	2.259		
Hg(1)-Br(1A)	2.6513(14)	2.977		
Hg(1)-Br(1)	2.9411(12)	2.964		
Hg(1)-Br(2)	2.5362(12)	2.768		
P(1)-C(1)	1.786(8)	1.927		
C(1)-C(2)	1.486(11)	1.543		
O(1)-C(2)	1.228(9)	1.223		
Bond angles				
C(1)-Hg(1)-Br(1A)	117.4(2)	107.778		
C(1)-Hg(1)-Br(2)	132.4(2)	129.017		
Br(1A)-Hg(1)-Br(1)	87.67(4)	87.502		
Br(2)-Hg(1)-Br(1A)	106.79(4)	107.955		
C(1)-Hg(1)-Br(1)	99.7(2)	111.039		
Br(2)-Hg(1)-Br(1)	98.65(4)	105.672		
Hg(1A)-Br(1)-Hg(1)	92.33(4)	92.502		
C(2)-C(1)-Hg(1)	112.5(5)	111.858		
P(1)-C(1)-Hg(1)	110.2(4)	111.087		

A comparison between the selected calculated bond lengths (Å) and bond angles (°)

arimontal value

Table	3
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Selected key bond lengths (Å) and angles (°) for  $[(Y_2) \cdot HgBr_2]_2 \cdot 2DMSO$  (4)

$[(Y_2) \cdot HgBr_2]_2 \cdot 2DMSO(4)$	
Bond lengths	
Hg(1)-C(1)	2.223(8)
Hg(1)–Br(2)	2.5362(12)
Hg(1)–Br(1A)	2.6513(14)
Hg(1)-Br(1)	2.9411(12)
P(1)-C(1)	1.786(8)
C(1)-C(2)	1.486(11)
O(1)-C(2)	1.228(9)
Bond angles	
C(1)-Hg(1)-Br(2)	132.4(2)
C(1)-Hg(1)-Br(1A)	117.4(2)
Br(2)-Hg(1)-Br(1A)	106.79(4)
C(1)-Hg(1)-Br(1)	99.7(2)
Br(2)-Hg(1)-Br(1)	98.65(4)
Br(1A)-Hg(1)-Br(1)	87.67(4)
Hg(1A)-Br(1)-Hg(1)	92.33(4)
C(2)-C(1)-Hg(1)	112.5(5)
P(1)-C(1)-Hg(1)	110.2(4)
Hg(1)-C(1)-H(1A)	106.8

Table	4
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A comparison between the selected calculated bond lengths (Å) and bond angles (°)
for the compound <b>2</b> with corresponding experimental values

$[(Y_1) \cdot HgBr_2]_2 (2)$	X-ray	HF/Lanl2mb
Bond lengths		
Hg(1)-Br(2A)	2.610	2.930
Hg(1)-Br(2)	2.897	3.052
Hg(1)-Br(1)	2.539	2.763
Hg(1)-C(1)	2.230	2.252
C(1)-C(2)	1.422	1.542
O(1)-C(2)	1.231	1.219
P(1)-C(1)	1.791	1.966
Bond angles		
C(1) - Hg(1) - Br(1)	121.46	127.774
C(1)-Hg(1)-Br(2)	95.67	101.017
C(1)-Hg(1)-Br(2A)	124.04	116.747
Br(1)-Hg(1)-Br(2)	104.35(2)	107.958
Br(1)-Hg(1)-Br(2A)	109.34(3)	107.226
Br(2A)-Hg(1)-Br(2)	92.99(2)	87.390
P(1)-C(1)-Hg(1)	110.0(3)	110.969
Hg(1A)-Br(2)-Hg(1)	87.01(2)	92.606
C(2)-C(1)-Hg(1)	101.6(5)	111.450
P(1)-C(1)-Hg(1)	110.0(3)	110.966



Fig. 2. Calculated molecular structure of  $[(Y_1) \cdot HgBr_2]_2;$  (a) trans-like and (b) cislike.

structure is 49.63 kcal/mol less stable than its observed C-coordinated isomer. Note that the energy difference between *cis*- and *trans*-like isomers for compound **1** was only 10.10 kcal/mol. Thus, a difference value of 49.63 clearly shows that C-coordination is significantly preferred with all ligands in the present complexes.

A comparison between the most important characteristic bond lengths for the observed  $[(Y_1-C) \cdot HgCl_2]_2$  and its  $[(Y_1-O) \cdot HgCl_2]_2$ 





**Fig. 3.** Calculated molecular structures of  $[(Y_2) \cdot HgBr_2]_2$ ; (a) *trans*-like and (b) *cis*-like.

#### Table 6

A comparison between energies of trans-like and cis-like isomers

	Compound	Cis (Hartree)	Trans (Hartree)	$\Delta E$ (kcal/mol) <sup>a</sup>
1	$[(Y_1) \cdot HgCl_2]_2$	-2126.3497989	-2126.3659036	10.10
2	$[(Y_1) \cdot HgBr_2]_2$	-2119.2653984	-2119.2820837	10.47
3	$[(Y_1) \cdot HgI_2]_2$	-2112.1858169	-2112.2029602	10.76
4	$[(Y_2) \cdot HgCl_2]_2$	-2904.1062182	-2904.1213403	9.49
5	$[(Y_2) \cdot HgBr_2]_2$	-2897.0211901	-2897.0336097	7.79
6	$[(Y_2)\cdot Hgl_2]_2$	-2889.9391804	-2889.9501725	6.90

<sup>a</sup> The energy of *cis*-like isomer relative to *trans*-like isomer.

isomer is made in Table 7. As can be seen, the results show that the C(H)–C bond length in the case of C-coordination is longer, and the C–O bond length is shorter than the corresponding bond lengths in the O-coordinated isomer. This clearly shows the displacement of  $\pi$ -bonding electrons to the C(H)–C bond upon O-coordination, as it has been shown in Chart 1. On the other hand, as expected for a sp<sup>2</sup> carbon atom, the C(H)–P bond length in [(Y<sub>1</sub>–O) · HgCl<sub>2</sub>]<sub>2</sub> is shorter than the corresponding bond length in [(Y<sub>1</sub>–C) · HgCl<sub>2</sub>]<sub>2</sub>.

## 4. Conclusion

The present study describes the synthesis and characterization of a series of dimeric mercury(II) complexes derived from mercuric halides and phosphorus ylides. On the basis of the physico-chemical and spectroscopic data, we propose that the ligands herein exhibit monodentate C-coordination to the metal centre, which is further confirmed by the X-ray crystal structure of the complexes. Theoretical studies in the gas phase indicate that the observed *trans*-like structures for the present complexes are always more stable than the possible *cis*-like structures.



Fig. 4. Calculated molecular structures of  $[(Y_1)\cdot HgCl_2]_2;$  (a) C-coordinated and (b) O-coordinated isomer.

Table 7

Comparison of important characteristic calculated bond lengths for observed  $[(Y_1-C)\cdot HgCl_2]_2$  and its unobserved  $[(Y_1-O)\cdot HgCl_2]_2$  isomers

Bond lengths (Å)	$[(Y_1-C) \cdot HgCl_2]_2$	$[(Y_1-0)\cdot HgCl_2]_2$
C(H)-P	1.967	1.883
C(H)–Hg	2.249	
O-Hg		2.099
С(Н)-С	1.540	1.349
C-0	1.219	1.323

## Appendix A. Supplementary material

CCDC 648219 and 648220 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2008.03.015.

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