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# New mononuclear mercury(II) complexes of a bifunctionalized ylide containing five-membered chelate ring: Spectral and structural characterization

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## ABSTRACT

The reaction of a new bifunctionalized ylide,  $Ph_2PCH_2PPh_2=C(H)C(O)(C_6H_4CI)$  (2) with mercury(II) halides in equimolar ratios using dry methanol as solvent yielded the P, C-chelated complexes, {HgX<sub>2</sub> [Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>C(H)C(O)(C<sub>6</sub>H<sub>4</sub>CI)]} where X = Cl (3), Br (4), I (5). The structures of complexes 4 and 5 have been characterized crystallographically. Single crystal X-ray analyses reveal the presence of mononuclear complexes containing Hg atom in a distorted tetrahedral environment. Characterization of the obtained compounds was also performed by elemental analysis, IR, <sup>1</sup>H, <sup>31</sup>P, and <sup>13</sup>C NMR. A theoretical study at DFT (B3LYP) level using standard CEP-31G basis set showed that the experimentally determined structure of the complex 5 is about 0.6–15.75 kcal mol<sup>-1</sup> more stable than its other bonding modes.

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## 1. Introduction

The coordination and organometallic chemistry of  $\alpha$ -keto stabilized phosphorus ylides has been investigated extensively and their ambidenticity explained in terms of a delicate balance between electronic and steric factors [1–6]. The  $\alpha$ -keto stabilized ylides derived from bisphosphines, viz., Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>n</sub>PPh<sub>2</sub>=C(H)C(O)R (*n* = 1, 2) (R = Me, Ph or OMe) [7] and PhC(O)C(H)=PPh<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub> PPh<sub>2</sub>=C(H)C(O)Ph [8] form an important class of such ligands which can exist in ylidic and enolate forms. These ligands can therefore engage in different types of bonding as illustrated in Chart 1 for Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>=C(H)C(O)C<sub>6</sub>H<sub>4</sub>Cl.

The bonding mode (f) had been previously observed for Rh(I), Pd(II), Pt(II), Hg(II) [7–17]. In addition, Rh(I) and Hg(II) were shown to exhibit the P-bonding mode (a) [14,17]. Hg(II) forms C-coordinated complexes with Ph<sub>3</sub>P=C(H)C(O)Ph [18,19] and Ph<sub>3</sub>P=C(H)CO(OEt) [20], whereas, regiospecific O-coordination of the acetyl oxygen observed with Ph<sub>3</sub>P=C(COPh)(COMe) [21]. The remarkable change in reactivity arises from a subtle variation in the molecular electronic structures of the ylide due to the presence of additional keto stabilization. Although HgBr<sub>2</sub> and HgI<sub>2</sub> form 1:1 dimeric halobridged complexes with the above ylide, HgCl<sub>2</sub> forms a 1:2 monomeric square planar complex [21]. The reactivity and coordination chemistry of carbonyl stabilized phosphorus ylides is an important research field of our group [22–24]. As part of this

ongoing study we have chosen to investigate the bonding modes adopted by bifunctionalized ylide when ligated to Hg(II). Herein, we report the reactivity of the ligand  $Ph_2PCH_2PPh_2=C(H)C(O)$  (C<sub>6</sub>H<sub>4</sub>Cl), towards mercury(II) halides.

# 2. Experimental

## 2.1. Physical measurements and materials

All reactions were carried out under an atmosphere of dry nitrogen. Methanol was distilled over magnesium powder and diethyl ether (Et<sub>2</sub>O) over a mixture of sodium and benzophenone just before use. All other solvents were reagent grade and used without further purifications. Melting points were measured on a SMP3 apparatus. 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 300 MHz Bruker and 90 MHz Jeol spectrometer in DMSO- $d_6$  or CDCl<sub>3</sub> as solvent at 25 °C. Chemical shifts (ppm) are reported according to internal TMS and external 85% phosphoric acid. Coupling constants are given in Hz. Elemental analysis for C, H and N atoms were performed using a Perkin–Elmer 2400 series analyzer.

# 2.2. X-ray crystallography

Suitable crystals were obtained from dimethylsulfoxide solution by the slow evaporation of the solvent over several days. All



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(g) P, O-bonding, chelate

Chart 1. The possible bonding modes of Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>C(H)C(O)C<sub>6</sub>H<sub>4</sub>Cl to metal M.

measurements were made on an Oxford Diffraction Xcalibur S Sapphire system at 150(2) K, using graphite monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.7107 Å). Structure solution and refinement were carried out using SHELXS-97 and SHELXL-97, respectively [25,26] The structure was solved by direct methods and refined by full matrix least-squares methods on  $F^2$ . All non-hydrogen atoms were refined anisotropically. All hydrogen were included in calculated positions.

# 2.3. Computational method

The geometry of the metal complexes **4** and **5** as determined by X-ray crystal structure analysis (Figs. 1 and 2) were fully optimized at DFT (B3LYP) [27,28] level of theory using the GAUSSIAN 03 set of programs [29]. The observed geometry of compounds **4** and **5** was used as a basis of DFT calculations for compound **3**. The geometries of other available coordinated isomers for complex **5** (Fig. 3, isomers **I–V**) were also optimized at the B3LYP level of theory. The atomic coordinates of **4** and **5** in their crystal structures were used for corresponding DFT calculations on isomer **I** using the CEP-31G basis set. This basis set includes effective core potentials (ECP) for both the mercury and phosphorus atoms as well as halide (Cl, Br and I) ions. A starting molecular-mechanics for isomers **II–V** for the *ab* initio calculations was obtained using the HYPERCHEM 5.02 program [30]. Calculations were performed on a Pentium-PC computer with a 4400 MHz processor.

# 2.4. Preparation of compounds

# 2.4.1. Preparation of $[Ph_2PCH_2PPh_2CH_2C(O)(C_6H_4Cl)]Br(1)$

Bis(diphenylphosphino)methane (dppm) (0.2 g, 0.52 mmol) was dissolved in 5 ml of chloroform and then a solution of 4-chlorophenacyl bromide (0.12 g, 0.52 mmol) in the same solvent (5 ml) was added dropwise to the above solution. The resulting yellow solution was stirred for 2 h. The solution was concentrated under reduced pressure to 2 ml, and diethyl ether (20 ml) was added. The yellow solid formed was filtered off, washed with diethyl ether (2 × 10 ml) and dried under reduced pressure. Yield: 0.28 g, 87%. M.p. 170–172 °C. Anal. Calc. for  $C_{33}H_{28}BrOP_2Cl$ : C, 64.15; H, 4.57.



Fig. 1. ORTEP view of the X-ray crystal structure of [HgBr<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>C(H)C(O)C<sub>6</sub>H<sub>4</sub>Cl)] (4).



Fig. 2. ORTEP view of the X-ray crystal structure of  $[HgI_2(Ph_2PCH_2PPh_2C(H)-C(O)C_6H_4CI)]$  (5).

Found: C, 63.89; H, 4.71%. IR (KBr, cm<sup>-1</sup>): 3337, 3045, 2836, 1674 (C=O), 1587, 1486, 1436, 1365, 1209, 1160, 1113, 997, 806, 740, 691. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta_{\rm H}$  = 4.28 (d, 2H, PCH<sub>2</sub>P, <sup>2</sup>*J*<sub>P-H</sub> = 14.96); 5.95 (d, 2H, PCH<sub>2</sub>CO, <sup>2</sup>*J*<sub>P-H</sub> = 12.81); 7.27–8.52 (m, 24H, Ph). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta_{\rm P}$  = -29.42 (d, PPh<sub>2</sub>, <sup>2</sup>*J*<sub>P-P</sub> = 65.15); 20.93 (d, PCH<sub>2</sub>CO, <sup>2</sup>*J*<sub>P-P</sub> = 64.40). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta_{\rm C}$  = 21.54 (dd, PCH<sub>2</sub>P, <sup>1</sup>*J*<sub>P-C</sub> = 52.22, 51.85); 36.11 (d, PCH<sub>2</sub>, <sup>1</sup>*J*<sub>P-C</sub> = 61.43); 117.64–140.95 (Ph); 191.17 (d, CO, <sup>2</sup>*J*<sub>P-C</sub> = 69.5).

#### 2.4.2. Preparation of $[Ph_2PCH_2PPh_2=C(H)C(O)(C_6H_4Cl)]$ (2)

The resulting phosphonium salts (1) (0.52 mmol) were treated with triethyl amine (0.52 ml) in toluene (16 ml). The triethyl amine hydrobromide was filtered off. Concentration of the toluene layer to 3 ml and subsequent addition of petroleum ether (25 ml) results in the precipitation of ligands as free-flowing white solids. They were further purified by crystallization from toluene/petroleum ether. Yield: 0.24 g, 85%. M.p. 150–152 °C. Anal. Calc. for  $C_{33}H_{27}OP_2Cl$ : C, 73.81; H, 5.07. Found: C, 74.02; H, 5.14%. IR (KBr,

cm<sup>-1</sup>): 3450, 3051, 2926, 1581, 1503 (C=O), 1436, 1403, 1383, 1174, 1102, 1012, 902, 846, 740, 695. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta_{\rm H}$  = 3.65 (d, 2H, CH<sub>2</sub>, <sup>2</sup>*J*<sub>P-H</sub> = 14.33); 4.32 (br, 1H, CH); 7.24–7.69 (m, 24H, Ph). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta_{\rm P}$  = –29.90 (d, PPh<sub>2</sub>, <sup>2</sup>*J*<sub>P-P</sub> = 64.00); 11.35 (d, PCH, <sup>2</sup>*J*<sub>P-P</sub> = 63.82). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta_{\rm C}$  = 24.99 (dd, CH<sub>2</sub>, <sup>1</sup>*J*<sub>P-C</sub> = 57.60, 57.72); 50.73 (d, CH, <sup>1</sup>*J*<sub>P-C</sub> = 110.55); 128.15–137.82 (Ph); 184.05 (s, CO).

# 2.4.3. Preparation of $\{HgCl_2[Ph_2PCH_2PPh_2C(H)C(O)(C_6H_4Cl)]\}$ (3)

*General procedure for complexes:* To a solution of HgCl<sub>2</sub> (0.1 g 0.37 mmol) in dry methanol (10 ml), a solution of 2 (0.2 g, 0.37 mmol) also in dry methanol (10 ml) was added dropwise at 0 °C and stirred for 2 h. The separated solid was filtered, and recrystallised in dichloromethane. Yield: 0.17 g, 56%. M.p. 205–208 °C. *Anal.* Calc. for C<sub>33</sub>H<sub>27</sub>Cl<sub>3</sub>HgOP<sub>2</sub>: C, 49.03; H, 3.37. Found: C, 48.66; H, 3.87%. IR (KBr, cm<sup>-1</sup>): 3439, 2887, 1710, 1603 (C=O), 1438, 1327, 1182, 1107, 779, 748, 691. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta_{\rm H}$  = 4.63 (br, 2H, CH<sub>2</sub>); 5.16 (br, 1H, CH); 7.40–7.91 (m, 24H, Ph). <sup>31</sup>P NMR (DMSO-*d*<sub>6</sub>):  $\delta_{\rm P}$  = 6.66 (br, PPh<sub>2</sub>); 25.12 (d, PCH, <sup>2</sup>*J*<sub>P-P</sub> = 40.14). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>):  $\delta_{\rm C}$  = 24.99 (br, CH<sub>2</sub>); 34.24 (br, CH); 119.14–140.31 (Ph); 191.96 (s, CO).

# 2.4.4. Preparation of $\{HgBr_2(Ph_2PCH_2PPh_2C(H)C(O)(C_6H_4Cl))\}$ (4)

Yield: 0.21 g, 62%. M.p. 200–202 °C. *Anal.* Calc. for  $C_{33}H_{27}Br_2HgOP_2CI$ : C, 44.17; H, 3.03. Found: C, 43.94; H, 3.04%. IR (KBr, cm<sup>-1</sup>): 3475, 2888, 1709, 1605 (C=O), 1562, 1485, 1438, 1357, 1326, 1181, 1105, 1052, 1015, 845, 779, 749, 722, 691. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta_{\rm H}$  = 4.65 (t, br, 2H, CH<sub>2</sub>); 5.26 (br, 1H, CH); 7.45–7.73 (m, 24H, Ph). <sup>31</sup>P NMR (DMSO-*d*<sub>6</sub>):  $\delta_{\rm P}$  = 1.35 (br, PPh<sub>2</sub>); 24.47 (d, PCH, <sup>2</sup>*J*<sub>P-P</sub> = 42.24). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>):  $\delta_{\rm C}$  = 23.51 (br, CH<sub>2</sub>); 34.24 (br, CH); 120.62–140.33 (Ph); 190.52 (s, CO).

# 2.4.5. Preparation of $\{HgI_2(Ph_2PCH_2PPh_2C(H)C(O)(C_6H_4Cl))\}$ (5)

Yield: 0.29 g, 78%. M.p. 197–199 °C. Anal. Calc. for  $C_{33}H_{27}I_2$ HgOP<sub>2</sub>Cl: C, 39.98; H, 2.75. Found: C, 40.45; H, 3.06%. IR (KBr, cm<sup>-1</sup>): 3420, 3052, 2889, 1711, 1606 (C=O), 1581, 1561, 1484, 1437, 1324, 1180, 1103, 1015, 874, 844, 777, 748, 690. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta_{\rm H}$  = 4.68 (t, 2H, CH<sub>2</sub>, <sup>2</sup>*J*<sub>P-H</sub> = 11.91), 5.34 (br, 1H, CH), 7.45–7.962 (m, 24H, Ph). <sup>31</sup>P NMR (DMSO-*d*<sub>6</sub>):  $\delta_{\rm P}$  = -7.07 (br, PPh<sub>2</sub>), 26.67 (d, PCH, <sup>2</sup>*J*<sub>P-P</sub> = 48.95). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>):  $\delta_{\rm C}$  = 23.52 (d, CH<sub>2</sub>, <sup>1</sup>*J*<sub>P-C</sub> = 51.62); 123.14–136.95 (Ph); 191.50 (s, CO); (CH, was not seen).



Fig. 3. Illustration of the five possible isomers for complex 5.

# 3. Results and discussion

# 3.1. Synthesis

The ligand (2) was synthesized by treating 4-chlorophenacyl bromide (prepared by reacting 4-chloroacetophenone with bromide in glacial acetic acid) with dppm and removal of the proton from the phosphonium salt (Scheme 1). Reactions of  $HgX_2$  with the ylide in a 1:1 stoichiometry afforded the P, C-chelated complexes (Scheme 2).

# 3.2. Spectroscopy

The <sup>31</sup>P NMR spectrum of **1** exhibits two doublets at 20.98 and -29.39 ppm that indicate the PCH<sub>2</sub>CO and PPh<sub>2</sub> groups, respectively. The <sup>1</sup>H NMR spectrum exhibits a doublet at 5.95 ppm, with a coupling constant <sup>2</sup>*J*<sub>P-H</sub> of 12.81 Hz, relative to a CH<sub>2</sub> group of a 4-chlorophenacyl bromide system bonded to a phosphonium moiety.

The <sup>31</sup>P NMR spectrum of **2** shows two doublets at 11.35 and -29.90 ppm, which are assigned to the PCH and PPh<sub>2</sub> groups, respectively. The <sup>1</sup>H NMR spectrum shows a broad at 4.32 ppm

attributable to the ylidic proton [16]. This compound shows upfield shifts compared to that of phosphonium of the phosphonium salt (1), suggesting some increasing of electron density in the P–C bond.

The <sup>31</sup>P chemical shift values for the complexes appear to be shifted downfield with respect to the parent ylide, also indicating that coordination of the ylide has occurred. In the <sup>31</sup>P NMR spectra the signal due to phosphonium group appears as a doublet at 25.12, 24.47 and 26.67 ppm for 3, 4 and 5, respectively. The coordination of phosphine is clearly evident from the strong downfield shifts of the signal due to PPh<sub>2</sub> group at 6.66, 1.35 and -7.07 ppm for **3**, **4** and **5**, respectively, when compared to that of same signal in the free ylide ( $\delta$  –29.90). In the <sup>1</sup>H NMR spectra, the signals due to the methinic protons for complexes are broad. Similar behavior was observed earlier in the case of vlide complexes of platinum(II) chloride [31]. The expected lower shielding of <sup>31</sup>P and <sup>1</sup>H nuclei for the PCH group upon complexation in the case of C-coordination were observed in their corresponding spectra. The most interesting aspect of the <sup>13</sup>C spectra of the complexes is the upfield shift of the signals due to the ylidic carbon. Such an upfield shift observed in  $[PdCl (\eta^{3}-2-XC_{3}H_{4}) (C_{6}H_{5})_{3}PCHCOR] (X = H, CH_{3}; R = CH_{3}, C_{6}H_{5})$ was attributed to the change in hybridization of the ylidic carbon



Scheme 1. The synthesis route for preparation of bifunctionalized ylide (2).



Scheme 2. Reaction of bifunctionalized ylide (2) with Hg(II) halides.

[32]. Similar upfield shifts of 2–3 ppm with reference to the parent ylide were also observed in the case of  $[(C_6H_5)_3PC_5H_4HgI_2]_2$  [33]. The <sup>13</sup>C shifts of the CO group in the complexes are around 190 ppm, relative to 184.05 ppm noted for the same carbon in the parent ylide, indicating much lower shielding of the carbon of the CO group in these complexes. No coupling to Hg was observed at room temperature in the <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectra for all these complexes. Failure to observe satellites in the above spectra was previously noted in the ylide complexes of Hg(II) [33] and Ag(I) [34], which had been explained by fast exchange of the ylide with the metal.

The IR data confirm the complete formation of the carbonylic ylide with the disappearance of the phosphonium CO band at 1674 cm<sup>-1</sup> and the presence of a new strong CO band relative to a carbonyl stabilized ylide at 1503 cm<sup>-1</sup> [16]. The *v*(CO), which is sensitive to complexation, occurs at 1503 cm<sup>-1</sup> in the parent ylide, as in the case of other resonance stabilized ylides [35]. Coordination of the ylide through C-coordination causes an increase in *v*(CO) [22–24] while for O-coordination a lowering of *v*(CO) is expected [36]. The infrared absorption bands observed for the three complexes around 1600 cm<sup>-1</sup> indicate coordination of the ylide through carbon. Thus, the spectral data indicate the bidentate coordination of the ligand (**2**) through both phosphine group and ylidic carbon atom.

# 3.3. X-ray crystallography

Table 1 provides the crystallographic results and refinement information for complexes **4** and **5**. The molecular structures are shown in Figs. 1 and 2. Selected bond lengths (Å) and angles (°) are given in Table 2. Fractional atomic coordinates and equivalent isotropic displacement coefficients ( $U_{eq}$ ) for the non-hydrogen atoms of the complexes are shown in Supplementary material.

The X-ray analysis reveals the P, C-chelate mode of coordination of the ligand,  $Ph_2PCH_2PPh_2=C(H)C(O)C_6H_4Cl$  to Hg(II) atom in complexes **4** and **5**. The Hg(II) centre in complexes **4** and **5** is four-coordinate with sp<sup>3</sup> hybridization. The Hg atom is bonded to one vlidic C atom, one P atom of the PPh<sub>2</sub> unit and two terminal halogen atoms. The angles subtended by the ligand at the Hg(II) centre in **4** and **5** vary from 90.30(8) to 117.89(3)(**4**) and 89.43(10) to 116.26(3)(5) indicating a distorted tetrahedral environment. The stabilized resonance structures for the parent ylide are destroyed by the complex formation, thus, the C(26)-C(27)bond lengths 1.439(5)Å (4) and 1.460(6)Å (5) are longer than the corresponding distances found in the similar uncomplexed phosphorane [Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>C(H)C(O)Ph] (1.404(3) Å) [15]. On the other hand, the bond length of P-C(H) in the similar ylide [Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>C(H)C(O)Ph] is 1.705(2) Å [15] which shows that the corresponding bonds are considerably elongated to 1.761(4) Å (**4**) and 1.754(4) Å (**5**).

The two terminal Hg–Br distances in **4** (2.5675(4) and 2.6009(4) Å) are shorter than the corresponding distances in [HgBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (2.559(2) and 2.545(3) Å) [37]. The Hg–I distances in **5** (2.7270(14) and 2.7483(3) Å) are in agreement with the values reported in [HgI<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (2.733(1) and 2.763(1) Å) [38].

The Hg–P distances in **4** (2.4984(9) Å) and **5** (2.5429(12) Å) are less than those of found in [HgBr<sub>2</sub>(PPh<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>C(H)C(O)Ph)] (2.546(3) Å) and [HgI<sub>2</sub>(PPh<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>C(H)C(O)Ph)] (2.5688(19) Å) [15]. The Hg–P bond lengths in **4** and **5** are consistent with the values reported for the majority of Hg(II)–phosphine complexes [39]. However, this distance is longer when compared to those in the polymeric complex {HgI<sub>2</sub>[PPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CPh<sub>2</sub>C(H)C(O)Ph]}<sub>n</sub> (2.472(2) Å) [17], and P, P-coordinated monomeric complexes HgCl<sub>2</sub>(dppeO)<sub>2</sub> (2.453(2) Å) and HgBr<sub>2</sub>(dppeO)<sub>2</sub> (2.456(2) Å) [40].

The Hg–C distances in 4 (2.412(3)Å) and 5 (2.424(5)Å) are comparable to analogous distances in  $[HgBr_2(PPh_2CH_2PPh_2C(H)$ 

## Table 1

Crystal	data	and	refinement	details	for	comp	lexes 4	1 and	5

Compound	4	5
Empirical formula	C33H27Br2ClHgOP2	C33H27ClHgI2OP2
Formula weight	897.35	991.33
T (K)	150(2)	150(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	13.0756(3)	13.1440(2)
b (Å)	16.1069(3)	16.2491(3)
<i>c</i> (Å)	15.6853(3)	15.9487(3)
α(°)	90	90
β (°)	106.478(2).	106.7339(19)
γ (°)	90	90
$V(Å^3)$	3167.77(11)	3262.05(10)
Ζ	4	4
Absorption coefficient (mm <sup>-1</sup> )	7.592	6.816
<ul> <li>θ Range for data collection</li> <li>(°)</li> </ul>	2.99-25.00	2.95-25.00
Index ranges	$-11 \leqslant h \leqslant 15$	$-15 \leqslant h \leqslant 15$
	$-19 \leqslant k \leqslant 19$	$-18 \leqslant k \leqslant 19$
	$-18 \leqslant l \leqslant 18$	$-18 \leqslant l \leqslant 18$
Reflections collected	14 034	14 806
Independent reflections $[R_{(int)}]$	5564 [0.0241]	5724 [0.0328]
Absorption correction	semi-empirical from	semi-empirical from
	equivalents	equivalents
Maximum and minimum transmission	0.5482 and 0.2091	0.5210 and 0.4487
Refinement method	Full-matrix least- squares on F <sup>2</sup>	Full-matrix least- squares on F <sup>2</sup>
Data/restraints/	5564/0/361	5724/0/361
parameters		
Goodness-of-fit on $F^2$	0.958	0.948
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0237$ ,	$R_1 = 0.0295$ ,
	$wR_2 = 0.0417$	$wR_2 = 0.0452$
R indices (all data)	$R_1 = 0.0377$ ,	$R_1 = 0.0452,$
	$wR_2 = 0.0432$	$wR_2 = 0.0474$
Largest diff. peak and hole $(e \text{ Å}^{-3})$	0.734 and -0.807	0.821 and -0.973

#### Table 2

Selected bond lengths (Å) and bond angles (°) for 4 and 5.

	4	5
Bond lengths		
Hg(1)-C(26)	2.412(3)	2.424(5)
Hg(1)-P(1)	2.4984(9)	2.5429(12)
$Hg(1)-X(1)^{a}$	2.5675(4)	2.7270(14)
$Hg(1)-X(2)^{a}$	2.6009(4)	2.7483(3)
O(1)-C(27)	1.242(4)	1.234(5)
P(2)-C(26)	1.761(4)	1.754(4)
C(26)-C(27)	1.439(5)	1.460(6)
Bond angles		
C(26)-Hg(1)-P(1)	90.30(8)	89.43(10)
$C(26)-Hg(1)-X(1)^{a}$	112.59(10)	111.54(10)
$C(26)-Hg(1)-X(2)^{a}$	108.92(8)	113.79(9)
$P(1)-Hg(1)-X(1)^{a}$	116.59(2)	113.18(3)
$P(1)^{a}-Hg(1)-X(2)^{a}$	117.89(3)	116.26(3)
$X(1)-Hg(1)-X(2)^{a}$	109.059(14)	111.04(12)
C(1)-P(1)-Hg(1)	100.92(11)	100.89(14)
C(2) - P(1) - Hg(1)	116.79(12)	117.30(16)
C(8) - P(1) - Hg(1)	116.44(12)	117.31(15)
C(26)-P(2)-C(1)	111.17(16)	111.8(2)

<sup>a</sup> X in the compounds **4** and **5** is Br and I, respectively.

C(O)Ph)] (2.415(12) Å) and  $[HgI_2(PPh_2CH_2PPh_2C(H)C(O)Ph)]$ (2.418(8) Å) [15]. The Hg–C bond distances in **4** and **5** are longer than those of found in mononuclear or dinuclear Hg(II)–phosphoylide compounds (2.223(8)–2.310(6) Å) [22–24], indicating relatively weak Hg–C bonds in these complexes. The P–C(H) distance is found to be shorter than the corresponding distances in

#### Table 3

A comparison between the calculated energies for the five possible isomers of compound  ${\bf 5}.$ 

	E (Hartree)	$\Delta E$ (kcal mol <sup>-1</sup> )
P, C-coordinated (I)	-422.897069	0
P, O-coordinated (II)	-422.8961062	0.604
C-coordinated (III)	-422.8950892	1.242
P-coordinated (IV)	-422.8828843	8.901
O-coordinated (V)	-422.8719609	15.755

C-coordinated Hg(II)–phosphorus ylide complexes which lie in the range, 1.786(10)–1.806(10) Å [18–20]. Furthermore, the C=O distances of 1.248(9) and 1.244(16) Å in **4** and **5**, respectively, are found to be close to that of the same distance in the similar ylide [Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>C(H)C(O)Ph] (1.249(2) Å). All these data perhaps indicate that the interaction of carbon atom in present P, C-chelated ligand is not as strong as that in similar C-coordinated ligands.

# 3.4. Theoretical studies

For complex **5** we can consider five different isomers (see Fig. 3, **I–V**). In two cases, corresponding ylide acts as a bidentate ligand



Fig. 4. Calculated molecular structures of complexes (a) 3 and (b) 4.

coordinated through P and C atoms or P and O atoms, Fig. 3, isomers I and II, respectively, to the metal ion. However, in remaining three cases, the ylide acts as a monodentate ligand coordinated

#### Table 4

A comparison between the selected calculated bond lengths (Å) and bond angles (°) for compounds **3**, **4** and **5** and corresponding experimental values for complexes **4** and **5**.

	Cl-	Br-		I-	
	CEP-31G	CEP-31G	X-ray	CEP-31G	X-ray
Bond lengths					
Hg(1)-C(26)	2.463	2.490	2.412	2.507	2.424
Hg(1)-P(1)	2.885	2.901	2.498	2.949	2.543
Hg(1)-X(2)	2.547	2.666	2.601	2.831	2.748
Hg(1)-X(1)	2.506	2.620	2.568	2.787	2.727
Bond angles					
P(1)-Hg(1)-C(26)	85.247	83.571	90.296	82.657	89.426
P(1)-Hg(1)-X(2)	114.435	103.139	116.597	103.403	113.180
P(1)-Hg(1)-X(2)	109.821	110.208	117.889	111.828	116.261
C(26)-Hg(1)-X(2)	102.477	116.149	112.583	116.895	113.799
C(26)-Hg(1)-X(2)	107.770	110.852	108.928	112.104	111.541
X(1)-Hg(1)-X(2)	127.638	124.352	109.060	122.055	111.041

#### Table 5

Calculated energies for HOMO and LUMO molecular orbitals, hardness and energy gap between the HOMO and LUMO of **3**, **4** and **5** complexes.

х	HOMO (hartree)	LUMO (hartree)	$\eta$ (eV)	Gap (eV)
Cl-	-0.23002	-0.07384	2.12	4.25
I–	-0.22174 -0.21084	-0.07479	1.99	3.99 3.64

through C, P, or O atoms, Fig. 3, isomers **III**, **IV** and **V**, respectively, to the metal ion. For compound **5** the isomer **I** is the unique isomer which was characterized by X-ray crystal structure analysis. The optimized structures of isomers I-V are also shown in Fig. 3. As can be seen in the Table 3 the isomer **I** is the most stable one between all five possible isomers for compound **5**. Thus, it seems that the complexes **4** and **5** have adopted the most stable structure in the solid state (see description of X-ray crystal structure for **4** and **5**).

It is clear than **I** is the most stable structure, probably due to the chelate effect. The structures **IV** and **V** are the highest in energy, and are not reachable at room temperature. However, the structures **I**, **II** and **III** differ only on a small amount of energy (0.6 and 1.2 kcal mol<sup>-1</sup>), therefore these structures can be considered as isoenergetic. Thus, the latter three structures should be present in solution at room temperature, in equilibrium, since the thermal energy is enough to promote the change from one to another one. This fact is in very good agreement with the NMR data, since no <sup>199</sup>Hg satellites were observed in the <sup>31</sup>P, <sup>1</sup>H and <sup>13</sup>C NMR spectra, meaning that the Hg–P and Hg–C bonds probably are breaking and forming quickly.

The geometry of complexes **3**, **4** and **5** were also fully optimized at density functional (B3LYP) level of theory (see Figs. 3 (I) and 4). A comparison between the calculated bond lengths (Å) and bond angles (°) with corresponding experimental values is presented in Table 4. The calculated structures for both complexes **4** and **5** in the gas phase agree well with the structures determined by X-ray crystallography.

The calculated energies for HOMO and LUMO of **3**, **4** and **5** complexes are also given in Table 5. The hardness  $\eta$  of a molecule is defined as Eq. (1):



Fig. 5. Illustration of Calculated HOMO (a, c, and e) and LUMO (b, d, and f) molecular orbitals for compounds 3, 4 and 5, respectively.

$$\eta = \frac{(I-A)}{2} \tag{1}$$

where I and A are the ionization potential and the electron affinity of the system, respectively. Obviously the energy gap between the HOMO and LUMO is equal to (I - A). Thus, we can easily calculate the hardness of the present molecules using Eq. (2) [41].

$$\eta = \frac{(E_{\text{LUMO}} - E_{\text{HOMO}})}{2} \tag{2}$$

We note that hard molecules have a large HOMO-LUMO gap and soft molecules have a small one [42]. The result of CEP-31G calculation show that both the HOMO and LUMO are demonstrated with negative charges (see Table 5). Furthermore, the calculated energy gap between the latter orbitals for the complex 5 containing iodine is smaller than that for other complexes. Thus, the latter complex is softer than the other complexes described here. This is completely consistent with this fact that a hard group makes molecule hard and a soft groups makes it soft. The HOMO and LUMO for all three mononuclear complexes are illustrated in Fig. 5.

# 4. Conclusion

The present study describes the synthesis and characterization of a series of chelate mercury(II) complexes derived from mercuric halides and a bifunctionalized phosphorus ylide. On the basis of the physicochemical and spectroscopic data we propose that ligands herein exhibit monodentate P, C-coordination to the metal centre, which is further confirmed by the X-ray crystal structure of the complexes. The Hg-C bond in these complexes is longer than normal Hg-C<sub>vlide</sub> bond found in mononuclear and binuclear complexes. The result of theoretical study showed that the experimentally determined structure of the complex 5 is more stable than its other bonding modes.

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# **Appendix A. Supplementary material**

CCDC 703482 and 703480 contain the supplementary crystallographic data for **4** and **5**. 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.2010.05.004.

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