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Synthesis, characterization, and structural studies of mercury(II) complexes of new bidentate phosphorus ylide

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ABSTRACT

The reaction of $Ph_2PCH_2CH_2PPh_2$ (dppe) with $BrCH_2C(O)C_6H_4NO_2$ (1:1.05 molar ratio) in acetone produces a mixture of the new monophosphonium salt $[Ph_2PCH_2CH_2PPh_2CH_2C(O)C_6H_4NO_2]Br$ (**1**) and the diphosphonium salt $[NO_2C_6H_4C(O)CH_2PPh_2CH_2CH_2PPh_2CH_2C(O)C_6H_4NO_2]Br_2$ (**2**). Compound **2** was insoluble in acetone and thus easily separated from the solution of **1**. Further, by reacting both the mono- and diphosphonium salts with the appropriate bases the bidentate phosphorus ylides, $[Ph_2PCH_2CH_2PPh_2{=}CHC(O)C_6H_4NO_2]$ (**3**) and $[NO_2C_6H_4C(O)CH{=}PPh_2CH_2CH_2PPh_2{=}CHC(O)C_6H_4NO_2]$ (**4**) were obtained. The reaction of ligand **3** with mercury(II) halides in dry methanol leads to the formation of the P,P-coordinated monomeric complexes $\{HgX_2(Ph_2PCH_2CH_2PPh_2CHC(O)C_6H_4NO_2)_2\}$ [X = Cl (**5**), Br (**6**), I (**7**)]. The structure of complex **7** being unequivocally determined by single crystal X-ray diffraction techniques. Characterization of these species was also performed by elemental analysis, IR spectroscopy and ^{1}H, ^{31}P, and ^{13}C NMR techniques. These analyses being consistent with a 2:1 stoichiometry ylide/Hg(II) for compounds **5** through **7**. Results obtained from theoretical studies are also consistent with a product in which two ylides are coordinated to the Hg(II) center through their phosphine groups, being this product the most stable among all the possible products.

1. Introduction

Phosphorus ylides are important reagents in organic chemistry, this being especially true in the synthesis of naturally occurring products with important biological and pharmacological activities [1]. Moreover, the utility of metalated phosphorus ylides in synthetic chemistry has been well documented [2–6]. Much of the interest in the coordination properties of resonance stabilized phosphorus ylides stemming from their bond versatility due to the presence of different functional groups in their molecular structure [2]. For instance, the α-keto stabilized ylides derived from bisphosphines, viz., $Ph_2PCH_2PPh_2{=}C(H)C(O)R$, $Ph_2P(CH_2)_2PPh_2{=}C(H)C(O)R$ (R = Me, Ph or OMe) [7] and $PhC(O)C(H){=}PPh_2CH_2CH_2PPh_2{=}C(H)\text{-}C(O)Ph$ [8] form an important class of hybrid ligands containing both phosphine and ylide functionalities, and can exist in ylidic and enolate forms. This versatility has allowed the characterization of coordinated ylides in different bonding modes: C-coordinated (through the Cα atom), O-bonded (through the carbonyl O), P-bonded (through the phosphine group), or even situations in which the same ylide shows a combination of bonding modes. For example, for compound $Ph_2PCH_2CH_2PPh_2{=}C(H)C(O)C_6H_4NO_2$ different bonding modes have been observed (Chart 1).

Thus, it is clear that these ligands can engage in different kinds of bonding with different metal ions [7–18]. Recently, Ebrahim et al. [16] have reported the reactivity of mercury(II) halides with the phosphine-ylide ligand with an ethylenic spacer $Ph_2P(CH_2)_2PPh_2{=}C(H)C(O)Ph$, this compound giving place to two different polymeric products. However, in this work we have found quite different patterns of reactivity of similar ligands toward mercury(II) halides. Hence, the goals of this report are (i) the tandem synthesis of mono- and diphosphonium salts and (ii) the synthesis and characterization of new bidentate phosphorous ylides and their corresponding mononuclear Hg(II) complexes. The results of theoretical studies on various potential types of coordination of ligand (**3**) towards Hg(II) metal ions are also discussed in this paper.

2. Experimental

2.1. Materials

All reactions were carried out under nitrogen using standard Schlenk techniques. Solvents were reagent grade and used without

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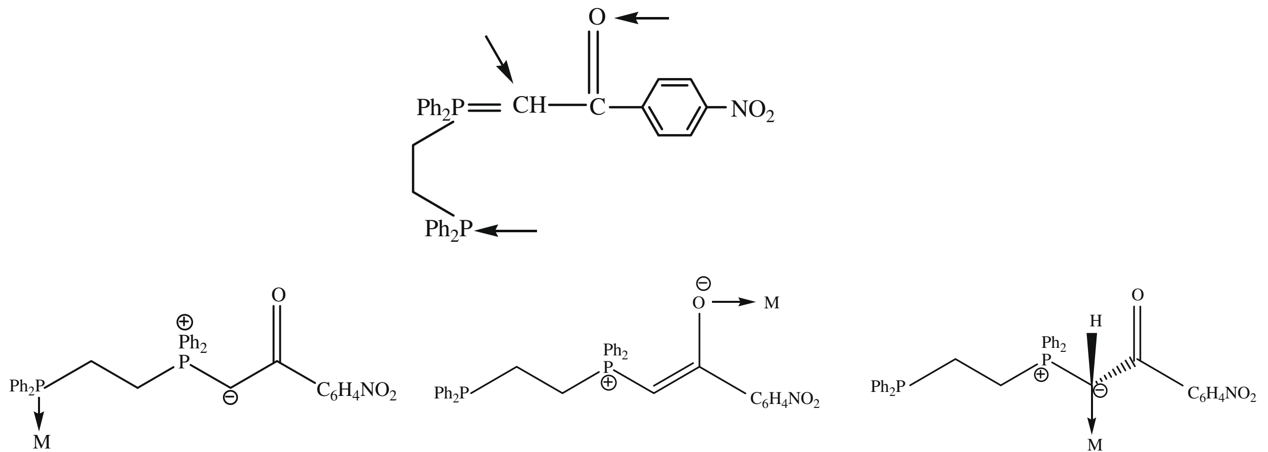
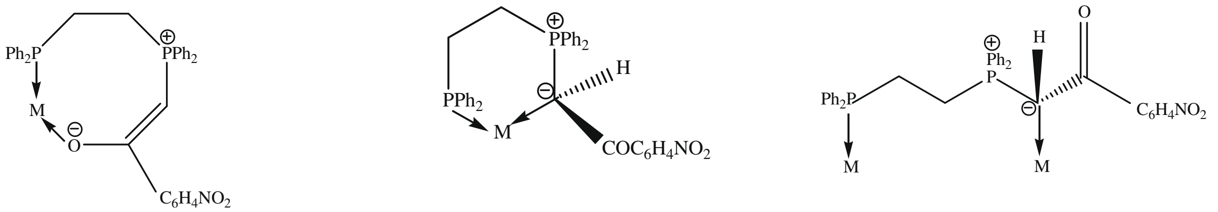
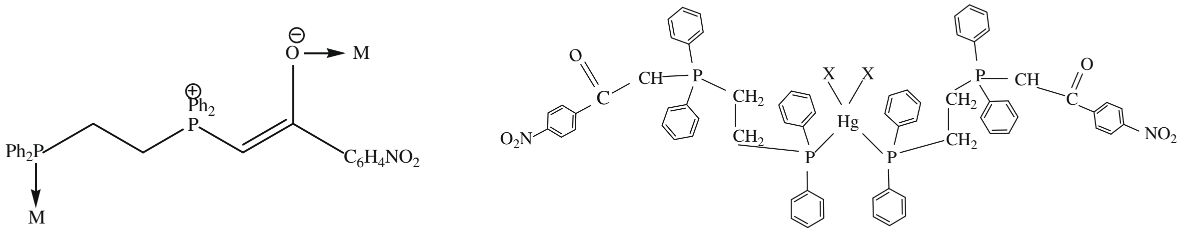


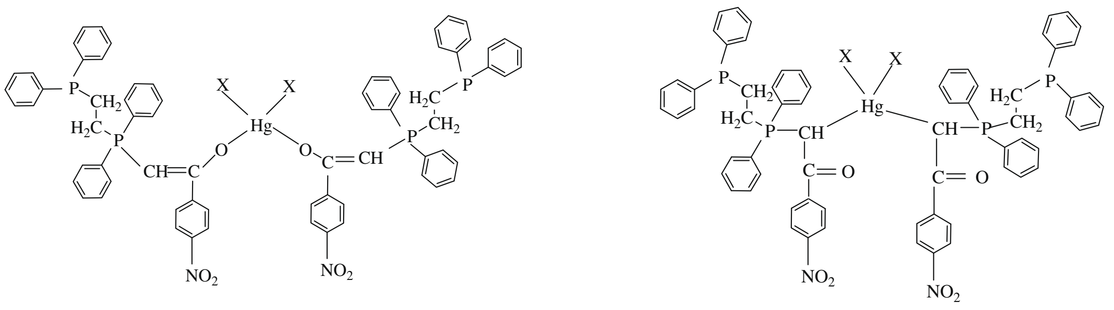
(a) P-bonding (b) O-bonding (c) C-bonding



(d) P, O-bonding, chelate (e) P, C-bonding, chelate (f) P, C-bonding, bridging



(g) P, O-bonding, bridging (h) P, P-bonding



(i) O, O-bonding (j) C, C-bonding

Chart 1. The possible bonding modes of $Ph_2PCH_2CH_2PPh_2{=}CHC(O)C_6H_4NO_2$ to metal M.

further purifications. Reactants and reagents were obtained from Merck Chemical Company and used without further purification. The solvents were dried and distilled using standard methods [19].

2.2. Physical measurements

Melting points were measured on a SMPI apparatus. Elemental analysis was performed using a Perkin–Elmer 2400 series analyzer. IR spectra were recorded on a Shimadzu 435-U-04 FT spectrophotometer from KBr pellets. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded either on a 300 MHz Bruker and a 90 MHz Jeol spectrometer in DMSO-d_6 or $CDCl_3$ as solvents at 25 °C. Chemical shifts (ppm) were reported according to internal TMS (^1H, ^{13}C) and external 85% phosphoric acid (^{31}P). Coupling constants were given in Hz.

Suitable crystals were obtained from dimethylsulfoxide solution by slow evaporation of the solvent and mounted in random

Table 1
Crystallographic data summary for complex $\{HgI_2(Ph_2PCH_2CH_2PPh_2CH\text{-}C(O)C_6H_4NO_2)_2\}$ (**7**).

Compound	$\{HgI_2(Ph_2PCH_2CH_2PPh_2CHC(O)C_6H_4NO_2)_2\}$ (**7**)
Empirical formula	$C_{68}H_{58}I_2HgN_2O_6P_4$
Formula weight	1577.43
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	14.5919(10)
b (Å)	25.1082(18))
c (Å)	17.2604(12)
α (°).	90
β (°)	91.5740(10)
γ (°)	90
Z	4
Absorption coefficient (mm^{-1})	3.566
Index ranges	$-17 \leqslant h \leqslant 17$ $-30 \leqslant k \leqslant 30$ $-20 \leqslant l \leqslant 20$
Reflections collected	51 865
Independent reflections	11 567 [$R_{(int)} = 0.0811$]
Maximum and minimum transmission	0.4140 and 0.2859
Goodness-of-fit on F^2	0.905
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0391$, $wR_2 = 0.0834$
R indices (all data)	$R_1 = 0.0581$, $wR_2 = 0.0876$
Largest difference in peak and hole (e $Å^{-3}$)	3.481 and −0.607

Table 2
Selected bond lengths (Å) and bond angles (°) for **7**.

Bond lengths (Å)	Bond angle (°)
Hg–P(2)	2.5285(13)
Hg–P(3)	2.5050(14)
Hg–I(1)	2.7921(4)
Hg–I(2)	2.7970(5)
O(1)–C(1)	1.252(6)
O(4)–C(49)	1.277(6)
C(1)–C(2)	1.379(7)
C(49)–C(50)	1.358(7)
P(1)–C(2)	1.711(5)
P(4)–C(50)	1.744(5)
P(3)–Hg–P(2)	117.21(4)
P(3)–Hg–I(1)	103.21(3)
P(3)–Hg–I(2)	112.53(3)
P(2)–Hg–I(1)	112.95(3)
P(2)–Hg–I(2)	103.19(3)
I(1)–Hg–I(2)	107.65(15)
C(23)–P(2)–Hg	120.92(17)
C(43)–P(3)–Hg	116.80(2)
C(1)–C(2)–P(1)	121.00(4)
C(49)–C(50)–P(4)	120.9(4)

orientation on glass fibers. The X-ray intensity data were measured at 298 K on a Bruker SMART APEX CCD-based three-circle X-ray diffractometer system using graphite mono-chromated Mo Kα ($\lambda = 0.71073$ Å) radiation. The detector was placed at a distance of 4.837 cm from the crystals in all cases. A total of 1800 frames were collected with a scan width of 0.3° in ω and an exposure time of 10 s/frame. The frames were integrated with the Bruker SAINT software package [20a] using a narrow-frame integration algorithm. The integration of the data was done using a monoclinic unit cell to yield a total of 51 865 reflections to a maximum 2θ angle of 50.00° (0.93 Å resolution), of which 11 567 were independent. Analysis of the data showed in all cases negligible decays during

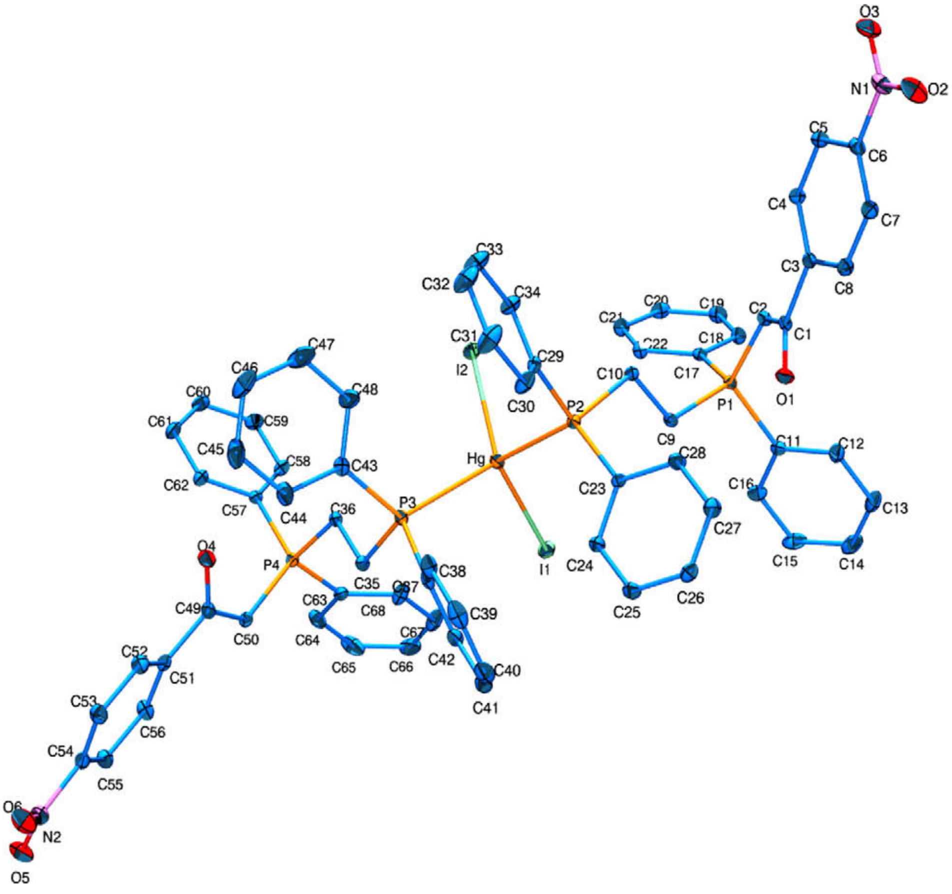


Fig. 1. ORTEP view of X-ray crystal structure of **7**. The hydrogen atoms have been omitted for clarity.

data collections. The structures were solved by Patterson method using SHELXS-97 [20b] program. The remaining atoms were located via a few cycles of least squares refinements and difference Fourier maps using $P2_1/n$ space group with $Z = 4$. Hydrogen atoms were input at calculated positions, and allowed to ride on the atoms to which they are attached. Thermal parameters were refined for hydrogen atoms on the phenyl groups with $U_{iso}(H) = 1.2\ U_{eq}$ of the parent atom in all cases. The final cycle of refinement was carried out on all non-zero data using SHELXL-97 [20c] and anisotropic thermal parameters for all non-hydrogen atoms. The details of the structure determination are given in Table 1 and selected bond distances and angles in Table 2. The numbering of the atoms is shown in Fig. 1 (ORTEP) [20d].

2.3. Computational method

The geometry of the metal complex **7** as determined by X-ray crystal structure analysis (see Fig. 1) was fully optimized at DFT (B3LYP) [21,22] level of theory using the GAUSSIAN 03 [23] set of programs. The standard CEP-31G basis set was used in all calculations.

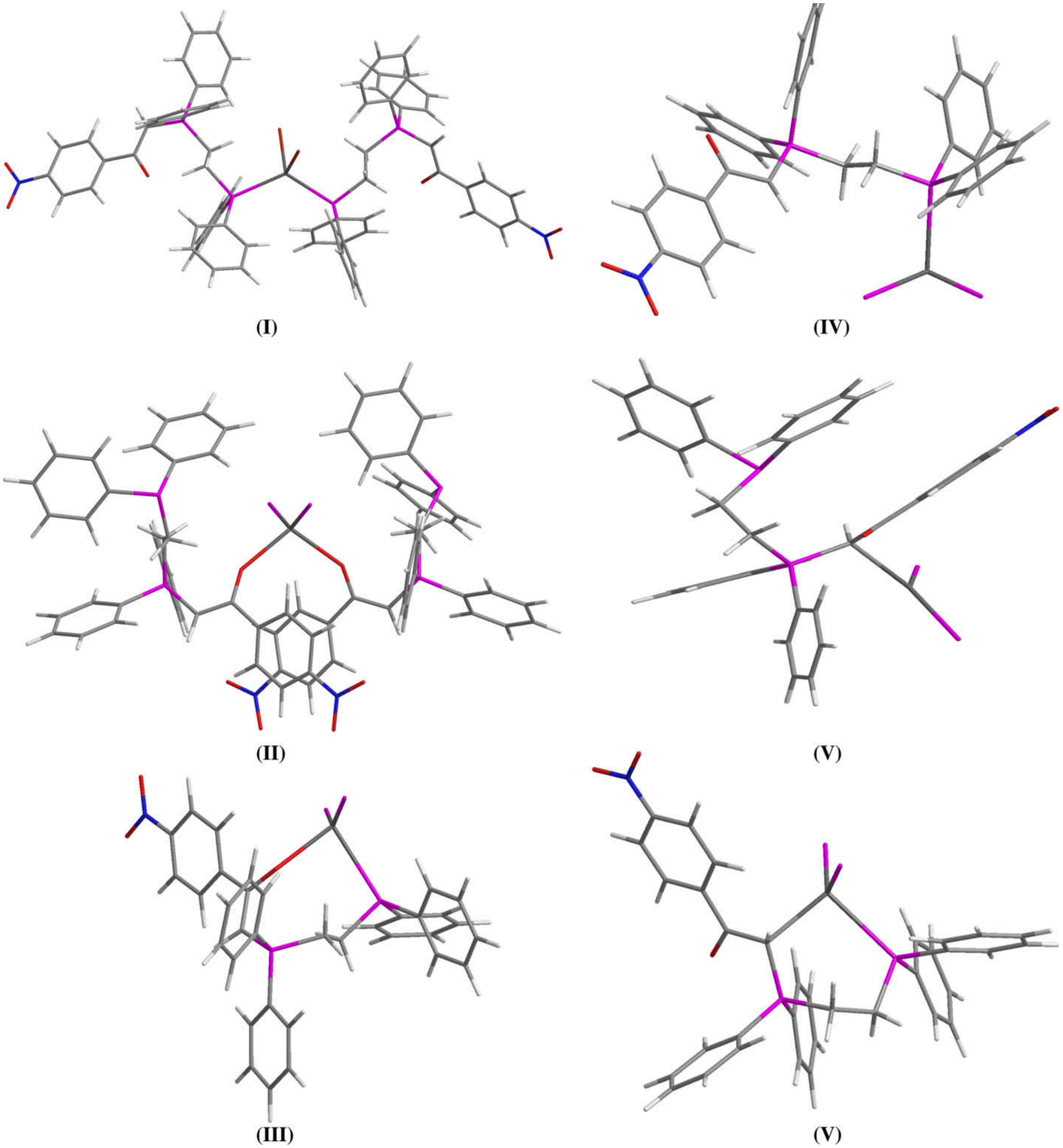

(I) (IV) (II) (V) (III) (V)

Fig. 2. Illustrations of possible isomers for complex **7.**

This basis set includes effective core potentials (ECP) for both the mercury and phosphorus atoms as well as halide (Cl, Br, and I) ions. The observed geometry of compound **7** was used as a basis of DFT calculations for compounds **5** and **6**. The geometries of other possible isomers for compound **7** (Fig. 2, isomers (**I** and **II**)) and/or possible isomer for 1+1 product of reaction between HgI_2 and **3** (Fig. 2, isomers (**III–VI**)) were also optimized at same level of theory. A starting molecular-mechanics for isomers (**II–VI**) for the *ab initio* calculations was obtained using the HYPERCHEM 5.02 program [24]. Calculations were performed on a Pentium-PC computer with a 4400 MHz processor.

2.4. Sample preparation

2.4.1. Synthesis of mono- and diphosphonium salts

General procedure: A solution of bis(diphenylphosphino)ethane (dppe) (0.398 g, 1 mmol) and 4-nitrophenacyl bromide (0.256 g, 1.05 mmol) in acetone (30 mL) was stirred at room temperature overnight. The resulting yellow suspension, consisting of a mixture of both the mono- and diphosphonium salts was filtered to remove the diphosphonium salt (**2**) from the solution as yellow solid. The resulting solid was washed with diethyl ether (10 mL), and dried under vacuum. The residual solution was concentrated under reduced pressure to 5 mL, and crashed with diethyl ether (20 mL). The resulting orange solid was filtered off, washed with petroleum diethyl ether, and dried under vacuum to afford the monophosphonium salt (**1**).

*2.4.1.1. Data for **1**.* Yield: 0.546 g, 85%. M.p. 169–171 °C. *Anal.* Calc. for $C_{34}H_{30}BrNO_3P_2$: C, 63.56; H, 4.71; N, 2.18. Found: C, 64.09; H, 4.42; N, 2.55%. IR (KBr, cm^{-1}): 1683 (C=O), ^1H NMR ($CDCl_3$): $\delta_H = 2.24$ (m, 2H, CH_2); 3.24 (m, 2H, CH_2); 6.26 (d, 2H, PCH_2CO, $^2J_{PH} = 12.27$); 7.27–8.42 (m, 24H, Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta_P = -15.05$ (br, PPh_2); 20.93 (d, PCH_2CO, $^3J_{PP} = 43.18$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta_C = 19.20$ (br, CH_2); 36.43 (d, PCH_2CO, $^1J_{PC} = 58.48$); 116.80–150.78 (Ph); 191.52 (d, CO, $^2J_{PC} = 6.04$).

*2.4.1.2. Data for **2**.* Yield: 0.079 g, 9%. M.p. 250–252 °C. *Anal.* Calc. for $C_{42}H_{36}Br_2N_2O_6P_2$: C, 56.90; H, 4.09; N, 3.16. Found: C, 57.32; H, 3.92; N, 2.87%. IR (KBr, cm^{-1}): 1682 (C=O), ^1H NMR (DMSO-d_6): $\delta_H = 3.85$ (m, CH_2, 2H merged with residual H_2O); 6.24 (br, 2H, PCH_2CO); 7.74–8.31 (m, 14H, Ph). $^{31}P\{^1H\}$ NMR (DMSO-d_6): $\delta_P = 26.66$ (s, PPh_2); $^{13}C\{^1H\}$ NMR (DMSO-d_6): $\delta_C = 20.67$ (br, CH_2); 49.69 (br, CH); 123.24–148.33 (Ph); 182.37 (s, CO).

2.4.2. Synthesis of bidentate phosphorus ylides

*2.4.2.1. Synthesis of **3**.* The monophosphonium salt (**1**) (0.231 g, 0.36 mmol) was treated with triethyl amine (0.36 mL) in toluene (10 mL). The triethyl amine hydrobromide thus obtained was filtered off. Concentration of the toluene layer to 3 mL and subsequent addition of petroleum ether (20 mL) resulted in the precipitation of the desired ligand as pale orange solid. Yield: 0.138 g, 68%. M.p. 145–147 °C. *Anal.* Calc. for $C_{34}H_{29}NO_3P_2$: C, 72.72; H, 5.21; N, 2.49. Found: C, 72.21; H, 5.36; N, 2.24%. IR (KBr, cm^{-1}): 1530 (C=O), ^1H NMR ($CDCl_3$): $\delta_H = 2.23$ (m, 2H, CH_2); 2.85 (m, 2H, CH_2); 4.23 (br, 1H, CH); 7.37–8.14 (m, 24H, Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta_P = -15.22$ (d, PPh_2, $^3J_{PP} = 48.11$); 14.71 (d, PCH, $^3J_{PP} = 46.81$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta_C = 20.82$ (br, CH_2); 49.69 (br, CH); 123.24–148.33 (Ph); 182.37(s, CO).

*2.4.2.2. Synthesis of **4**.* The diphosphonium salt (**2**) (0.319 g, 0.36 mmol) was treated with an aqueous solution of NaOH (0.1 M, 10 mL) leading to the elimination of HBr to produce the free ligand **4**. Yield: 0.227 g, 87%. M.p. 211–214 °C. *Anal.* Calc. for $C_{42}H_{34}N_2O_6P_2$: C, 69.61; H, 4.73; N, 3.87. Found: C, 69.83; H, 4.41; N, 4.01%. IR (KBr, cm^{-1}): 1527 (C=O), ^1H NMR ($CDCl_3$): $\delta_H = 3.56$ (m, 2H, CH_2); 4.29 (br, 1H, CH); 7.56–8.15 (m, 14H, Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta_P = 15.24$ (s, PPh_2); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta_C = 18.47$ (br, CH_2); 51.22 (d, CH, $^1J_{PC} = 107.4$); 123.30–148.32 (Ph); 182.54 (s, CO).

2.4.3. Synthesis of Hg(II) halide complexes

General procedure: To a solution of HgX_2 (0.36 mmol) in methanol (8 mL), a solution of **3** (0.202 g, 0.36 mmol) in the same solvent (8 mL) was added dropwise at 0 °C and the reaction allowed to proceed under stirring for 2 h. The resulting solid, admixed with gray material was treated with dichloromethane (25 mL) and filtered through a short plug of Celite®. Addition of excess methanol to the concentrated filtrate caused the precipitation of the products as yellow solids.

*2.4.3.1. Data for **5**.* Yield: 0.236 g, 47%. M.p. >135 °C (decomposes). *Anal.* Calc. for $C_{68}H_{58}Cl_2HgN_2O_6P_4$: C, 58.56; H, 4.19; N, 2.01. Found: C, 58.92; H, 3.98; N, 2.18%. IR (KBr, cm^{-1}): 1532 (C=O), ^1H NMR (DMSO-d_6): $\delta_H = 3.06$ (m, CH_2, 4H merged with residual H_2O); 4.61 (d, 1H, CH, $^2J_{PH} = 23.31$); 7.57–8.17 (m, 24H, Ph). $^{31}P\{^1H\}$ NMR (DMSO-d_6): $\delta_P = 17.85$ (d, PCH, $^3J_{PP} = 59.57$); 26.38 (br, PPh_2). $^{13}C\{^1H\}$ NMR (DMSO-d_6): $\delta_C = 18.92$ (br, CH_2); 48.84 (d, CH, $^1J_{PC} = 108.45$); 123.55–148.28 (Ph); 181.35 (s, CO).

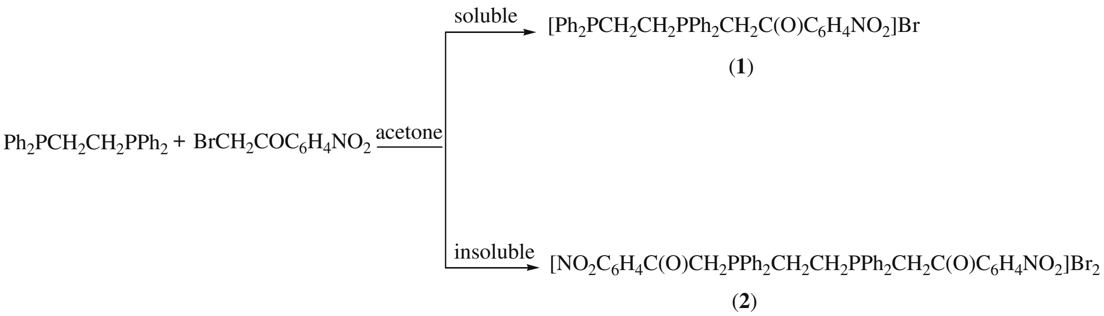
*2.4.3.2. Data for **6**.* Yield: 0.269 g, 51%. M.p. >152 °C (decomposes). *Anal.* Calc. for $C_{68}H_{58}Br_2HgN_2O_6P_4$: C, 58.05; H, 3.94; N, 1.89. Found: C, 58.25; H, 3.78; N, 1.77%. IR (KBr, cm^{-1}): 1530 (C=O), ^1H NMR (DMSO-d_6): $\delta_H = 3.11$ (m, CH_2, 4H merged with residual H_2O); 4.56 (d, 1H, CH, $^2J_{PH} = 23.03$); 7.49–7.88 (m, 24H, Ph). $^{31}P\{^1H\}$ NMR (DMSO-d_6): $\delta_P = 17.89$ (d, PCH, $^3J_{PP} = 57.32$); 24.68 (br, PPh_2). $^{13}C\{^1H\}$ NMR (DMSO-d_6): $\delta_C = 19.76$ (br, CH_2); 48.71 (d, CH, $^1J_{PC} = 105.65$); 123.56–148.30 (Ph); 181.38 (s, CO).

*2.4.3.3. Data for **7**.* Yield: 0.339 g, 60%. M.p. >168 °C (decomposes). *Anal.* Calc. for $C_{68}H_{58}I_2HgN_2O_6P_4$: C, 51.77; H, 3.71; N, 1.78. Found: C, 51.64; H, 3.63; N, 1.61%. IR (KBr, cm^{-1}): 1529 (C=O), ^1H NMR (DMSO-d_6): $\delta_H = 3.21$ (m, $CH_{2,}$ 4H merged with residual H_2O); 4.59 (d, 1H, CH, $^2J_{PH} = 25.26$); 7.50–8.17 (m, 24H, Ph). $^{31}P\{^1H\}$ NMR (DMSO-d_6): $\delta_P = 18.28$ (d, PCH, $^3J_{PP} = 56.08$); 11.08 (br, PPh_2). $^{13}C\{^1H\}$ NMR (DMSO-d_6): $\delta_C = 19.80$ (br, CH_2); 48.611 (d, CH, $^1J_{PC} = 108.67$); 123.57–148.32 (Ph); 181.51 (s, CO).

3. Results and discussion

3.1. Synthesis

The overnight reaction of dppe with 4-nitrophenacyl bromide in acetone at room temperature led to the formation of a mixture of mono- and diphosphonium salts (Scheme 1). Thus, the $^{31}P\{^1H\}$ NMR spectra of the above reaction always shows three singlets: one at 24.38 ppm attributable to the diphosphonium salt, and two at −14.14 ppm ($^3J_{PP} = 44.16$) and 23.48 ppm ($^3J_{PP} = 44.16$) for the monophosphonium derivative. However, we found that the diphosphonium salt will be produced under different experimental conditions, such as higher temperatures (30–40 °C), shorter reaction times (2–8 h) or using different solvents such as chloroform and dichloromethane. However, in all cases the product of the reaction always affords the same three peaks in different ratios. Further experimentation, lead to find acetone to be the best solvent for the reaction of dppe with 4-nitrophenacyl bromide due to the fact that in this solvent the diphosphonium salt is insoluble and thus can be easily isolated by plain filtration from the monophosphonium salt which remains in solution. It should be noted that the reaction of dppe with 2 equivalents of 4-nitrophenacyl bromide affords exclusively the diphosphonium salt.



Scheme 1. Synthetic route for the preparation of the mono- and diphosphonium salts **1** and **2**.

Further, the bidentate phosphorus ylides (**3** and **4**) can be prepared from the corresponding phosphonium salts by reaction with the appropriate bases (Scheme 2).

With the aim to investigate the reactivity of the bidentate phosphorus ylides (**3**) and (**4**) towards metallic substrates, we have reacted these compounds with mercury(II) halides. The reaction of mercury(II) halides with **3** yielded the formation of P,P-coordinated monomeric complexes of the type $\{HgX_2(Ph_2PCH_2CH_2PPh_2CHC(O)C_6H_4NO_2)_2\}$ [X = Cl (**5**), Br (**6**), I (**7**)] (Scheme 3). Analogous reactions with ligand **4** failed to proceed.

3.2. Spectroscopy

The IR data confirms the complete formation of the carbonylic bidentate ylides Hg(II) complexes with the disappearance of the phosphonium CO bands at ν 1683 and 1682 cm^{-1} for **1** and **2**, respectively, and the appearance of new strong CO bands relative to a carbonyl stabilized ylides at ν 1530 and 1527 cm^{-1} for **3** and **4**, respectively. As we have reported previously [25], the coordination of the ylide *via* carbon or oxygen causes a significant increase or decrease in the ν(CO), respectively. Thus, the IR data obtained indicates that the interaction of the ligands with mercury(II) halides is only through the PPh_2 group [16], as proved by the crystal structure of **7** (vide supra).

The $^{31}P\{^1H\}$ NMR spectrum of **1** results more informative and exhibits two doublets at δ 23.49 and −15.05 ppm that indicate the presence of the PCH_2CO and PPh_2 groups in the molecule. The ^1H NMR spectrum exhibits a doublet at δ 6.26 ppm, with a $^2J_{PH}$ of 12.27 Hz, related to a CH_2 group of the 4-nitrophenacyl bromide system bonded to a phosphonium moiety [15]. On the other hand, the $^{31}P\{^1H\}$ NMR spectrum of **2** shows only one sharp singlet at δ 26.66 ppm. In the ^1H NMR spectra of this compound a doublet at 6.24 ppm can be observed due to the PCH_2CO group. The presence of a single signal for the PCH_2CO group in each of the corresponding $^{31}P\{^1H\}$ and ^1H NMR spectra indicates the presence of only one symmetrical molecule of **2** [26].

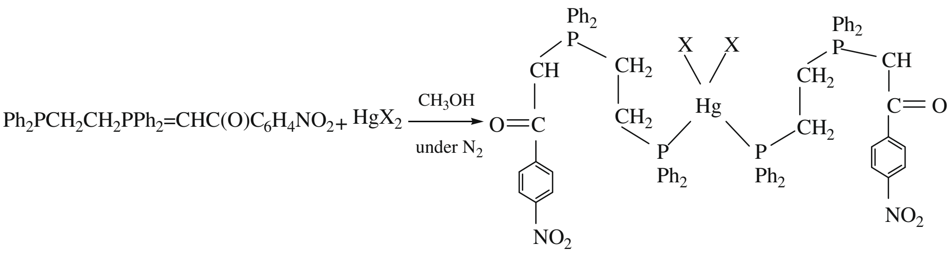
The $^{31}P\{^1H\}$ NMR spectrum for all complexes exhibit the presence of the PCH group as a doublet around δ 17 ppm, this chemical shift being very similar to that observed for the corresponding free ylide (**3**) (δ 14.71 ppm). The coordination of the PPh_2 group is also evident from the strong downfield shifting of the signal when compared to that of the free ylide (δ −15.22 ppm). Analogously, in the ^1H NMR spectra of all complexes, the doublets due to the methine proton around δ 4.58 ppm, appear in the same region as observed for the free ligand (δ 4.23 ppm). In the $^{13}C\{^1H\}$ NMR spectra of all complexes, the signals attributed to the CO group remain unaffected due to complexation. Hence, these spectral data are also consistent with the monodentate coordination of the ligand towards the metal center through the PPh_2 group [16].

When the reactions were carried at room temperature no coordination to Hg(II) was observed, this observation was confirmed by ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR techniques, and can be rationalized due to fast exchange of the ylide with the metal [27].

$$[Ph_2PCH_2CH_2PPh_2CH_2C(O)C_6H_4NO_2]Br \xrightarrow[-[HNEt_3]Br]{NEt_3} \underset{(\mathbf{3})}{Ph_2PCH_2CH_2PPh_2{=}CHC(O)C_6H_4NO_2}$$

$$[NO_2C_6H_4C(O)CH_2PPh_2CH_2CH_2PPh_2CH_2C(O)C_6H_4NO_2]Br_2 \xrightarrow[-2\,HBr]{NaOH} \underset{(\mathbf{4})}{NO_2C_6H_4C(O)CH{=}PPh_2CH_2CH_2PPh_2{=}CHC(O)C_6H_4NO_2}$$

Scheme 2. Synthetic route for preparation of the bidentate phosphorus ylides **3** and **4**.



X = Cl (**5**), Br (**6**), I (**7**)

Scheme 3. Reaction of **3** with Hg(II) halides.

3.3. X-ray crystallography

Table 1 provides the crystallographic results and refinement information for complex {$HgI_2(Ph_2PCH_2CH_2PPh_2CHC(O)C_6H_4NO_2)_2$} (**7**). The molecular structure is shown in Fig. 1. Pertinent bond distances and angles for **7** 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,P-coordination mode of the ligand **3** to the Hg(II) atom in this complex. The mercury atom is coordinated to two halogens and two PPh_2 groups. The angles subtended by the ligand at the Hg(II) center in **7** vary from 103.19(3) to 117.21(4) indicating a slightly distorted tetrahedral environment.

Table 3
A comparison between the calculated energies for the six possible products of reaction between ligand (**3**) and HgI_2.

Isomer	Type of coordination	Type of product	*E* (Hartree)	Δ*E* (kcal mol^{-1})
I	P,P-coordinated	1+2	−736.305341	0.0
II	O,O-coordinated	1+2	−736.293325	7.5
III	P,O-coordinated	1+1	−736.281216[a]	15.1
IV	P-coordinated	1+1	−736.2735417	19.9
V	C-coordinated	1+1	−736.2710918	21.5
VI	P,C-coordinated	1+1	−736.2695346	22.5

[a] The energy of one molecule of free ylide (−279.7504816 (Hartree)) is included in the electronic energy of 1+1 molecules.

The Hg–P distances of 2.505(14) and 2.528(13) Å in this complex are consistent with the values reported for monomeric Hg(II)–phosphine complexes [28]. The two terminal Hg–I bond lengths in **7** (2.792(4) and 2.797(5) Å) are comparable to analogous in [$HgI_2(PPh_3)_2$] (2.733(1) and 2.763(1) Å) [29], [$HgI_2(PPh_2CH_2PPh_2C(H)C(O)Ph)$] (2.767(6) and 2.743(7) Å) [14] and [$HgI_2(dppeO)$]$_n$ (2.700(3) and 2.709(3) Å) [30]. As observed previously for α-stabilized phosphorus ylides [31], the phosphorus and oxygen atoms are *cis* oriented due to significant interaction between P^+ and O^- centers, as shown by the appropriate length (see Table 2).

3.4. Theoretical studies

For the reaction between the HgI_2 and ligand (**3**) we can consider two possible products, 1+1 or 1+2. For both the later products there are several isomers depending on which atom(s) of the ligand are coordinated to the metal ion. We note that each ylide can be coordinated to the metal ion as a bidentate (P, C- or P, O-coordinated) or as a monodentate (P-, C- or O-coordinated) ligand. Thus, if we assume that one ylide will be coordinated to the Hg(II) metal ion, then for the resulting 1+1 product, five isomers can be considered. On the other hand, if we assume that two monodentate ylides are coordinated to the metal ion, then for the resulting 1+2 product, three asymmetrical isomers and three symmetrical isomers can be considered. Obviously, if the first ligand is coordinated through the P atom then most probably the second one will also be coordinated through the same atom, and this is the case for C and O atoms. Thus, the asymmetrical isomers in which one ligand is coordinated through the atom X and the second one is coordinated

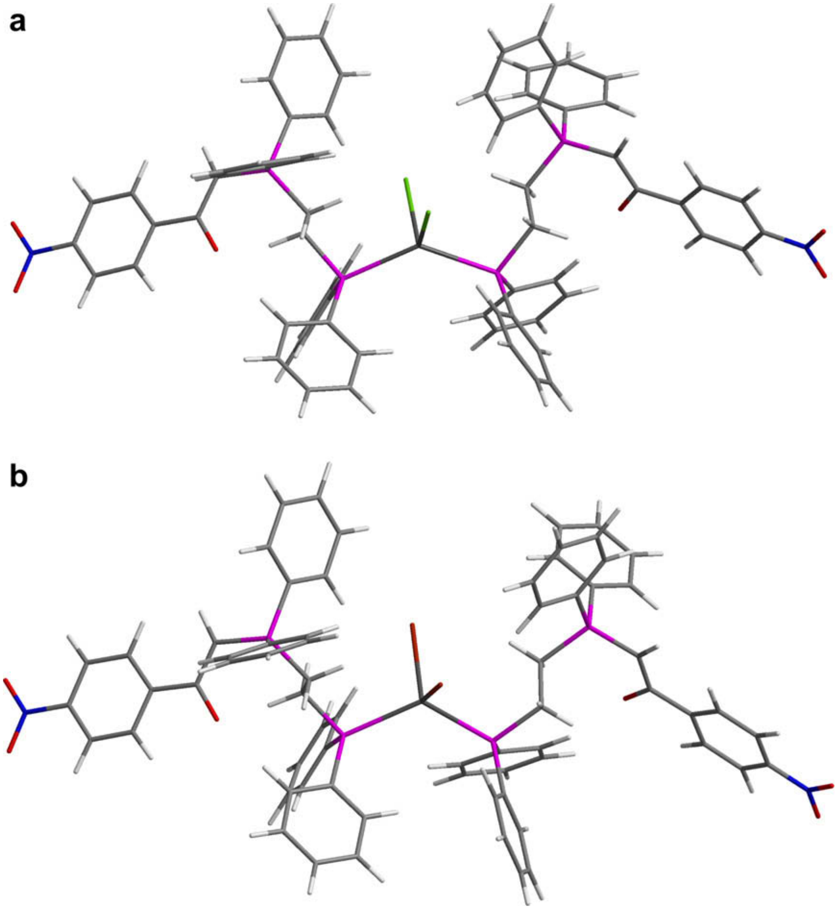


Fig. 3. Calculated molecular structures of complexes: (a) **5** and (b) **6.**

Table 4
A comparison between the selected calculated bond lengths (Å) and bond angles (°) for compounds **5**, **6**, and **7** and corresponding experimental values for complex **7**.

	5	**6**	**7**	
	CEP-31G	CEP-31G	CEP-31G	**X-ray**
Bond lengths				
P(2)–Hg	2.610	2.653	2.699	**2.529**
P(3)–Hg	2.610	2.653	2.702	**2.505**
X(1)–Hg	2.634	2.719	2.865	**2.792**
X(2)–Hg	2.634	2.719	2.874	**2.797**
Bond angles				
P(2)–Hg–X(1)	109.005	109.712	109.770	**112.95**
P(3)–Hg–X(1)	97.507	102.304	104.803	**103.21**
P(2)–Hg–X(2)	97.511	102.295	104.270	**103.20**
P(3)–Hg–X(2)	109.011	109.703	109.302	**112.53**
X(1)–Hg–X(2)	105.058	109.573	112.929	**107.65**
P(2)–Hg–P(3)	135.940	123.004	116.012	**117.21**

through atom Y can be ignored. Therefore, herein we have studied the five possible isomers for 1+1 product and the three symmetrical isomers for 1+2 product. From the all above isomers we could not optimize O-coordinated isomer for 1+1 product and C,C-coordinated isomer for 1+2 product. While the O-coordinated isomer was not minimized after one month, the C,C-coordinated isomer was converted to C-coordinated isomer of 1+1 product and one molecule of free ligand. Thus it seems that, in the present case, the formation of a product in which two ligands are coordinated through the ylidic carbon is not possible (Fig. 2).

As can be seen in Table 3 from the six remaining isomers, the isomer (**I**) is the most stable isomer. We note that the latter isomer is the observed isomer for compound **7** in the solid state. Thus, it seems that the complex **7** has adopted the most stable structure in the solid state (see description of X-ray crystal structure for compound **7**). Thus according to result of above theoretical studies and due to same spectroscopic data between the complexes **5**–**7**, we can assume that the structures of complexes **5** and **6** would be the same as that exhibited by compound **7**. The geometry of complexes **5**, **6**, and **7** were also fully optimized at density functional (B3LYP) level of theory (Fig. 3). A comparison between the calculated bond lengths (Å) and bond angles (°) for compounds **5**–**7** with corresponding experimental values for compound **7** is presented in Table 4. The calculated structure for complex **7** in the gas phase agrees well with the structure determined by X-ray crystallography. As can be seen in Table 4, the Hg–P bond lengths in compound **5**, **6**, and **7** are 2.610, 2.653, (2.699 and 2.702), respectively. Thus it seems that the coordination halide has a slightly effect on the Hg–P bond length.

4. Conclusions

The present study describes a new method for the synthesis of the mono- and diphosphonium salts simultaneously. This study also presents the synthesis and characterization of a new series of mononuclear Hg(II) complexes of bidentate phosphorus ylide. On the basis of the physical–chemical and spectroscopic data we propose that the ligands described herein exhibit monodentate P,P-coordination to the metal center, coordination that has been unequivocally confirmed by the X-ray crystal structure of complex **7**. The results suggest that the interaction of Hg(II) with different phosphines remain an active field of research leading to complexes with new structures. The theoretical studies show that the observed structure for compound **7** is the most stable structure between the all studied structures.

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Appendix A. Supplementary material

CCDC 739884 contains the supplementary crystallographic data for **7**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://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.2010.01.024.

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