



Mercury(II) complexes of stabilized phosphine–phosphonium ylide derived from bis(diphenylphosphino)methane: Synthesis, spectra and crystal structures

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ABSTRACT

The reaction of a mixed phosphine–phosphonium ylide, $\text{PPh}_2\text{CH}_2\text{PPh}_2=\text{C}(\text{H})\text{C}(\text{O})\text{Ph}$ with mercury(II) halides in methanol under mild conditions yielded the P, C-chelated complexes, $[\text{HgX}_2(\text{PPh}_2\text{CH}_2\text{PPh}_2\text{C}(\text{H})\text{C}(\text{O})\text{Ph})]$ where X = Cl (**2**), Br (**3**), I (**4**). Single crystal X-ray diffraction studies reveal the presence of mononuclear complexes containing Hg atom in a distorted tetrahedral environment and long Hg–C_{ylide} bond. The five-membered chelate rings in the two independent molecules present in the asymmetric unit of **4** adopt ‘envelope’ and ‘twist’ conformations. Spectroscopic studies also indicate the weaker Hg–C bonding. Additionally, the molecular structure of the free ylide (**1**) is also discussed.

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1. Introduction

Phosphorus ylides with their numerous modifications have been widely employed as reagents in synthetic organic chemistry [1,2]. Much of the interest in the coordination properties of resonance stabilized phosphorus ylides stems from their ligating versatility due to the presence of different functional groups in their molecular skeleton [3]. The monoketo ylides derived from bisphosphines, viz., $\text{Ph}_2\text{PCH}_2\text{PPh}_2=\text{C}(\text{H})\text{C}(\text{O})\text{R}$, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2=\text{C}(\text{H})\text{C}(\text{O})\text{R}$ (R = Me, Ph or OMe) [4] contain a P donor site in addition to C donor (the ylidic C) or O donor (the carbonyl O) sites for coordination, and therefore can engage in different kinds of bonding with metal ions. We have been interested in studying the coordination modes adopted by the resonance stabilized ylides when ligated to Hg(II) and U(VI) [5]. Hg(II) forms C-coordinated complexes with $\text{Ph}_3\text{P}=\text{C}(\text{H})\text{C}(\text{O})\text{Ph}$ [6,7] and $\text{Ph}_3\text{P}=\text{C}(\text{H})\text{CO}(\text{OCH}_2\text{CH}_3)$ [8], whereas, regioselective O-coordination of the acetyl oxygen had been observed with $\text{Ph}_3\text{P}=\text{C}(\text{OPh})(\text{COMe})$ [9]. The remarkable change in reactivity arises from a subtle variation in the molecular–electronic structure of the ylide due to the presence of additional keto stabilization.

Recently, we have observed that the phosphine–phosphonium ylide with an ethylenic spacer, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2=\text{C}(\text{H})\text{C}(\text{O})\text{Ph}$ forms polymeric Hg(II) complexes with HgCl_2 via P, C-bridging

mode. However, HgBr_2 and HgI_2 react with the same ylide giving polymeric halogen bridged phosphine complexes with dangling ylide [10]. Such a versatile reactivity has prompted us to expand our studies to related mixed phosphine–phosphonium ylide with mercuric halides. Furthermore, coordination of ligands towards Hg(II) has assumed importance since, in nature’s mercury detoxification process, the initial Hg–C bond cleavage involves the increase in the coordination number around Hg [11]. In addition, evidence for new classes of metal-binding motifs in enzymes, transcription factors, and regulatory proteins emphasize the need for structural insights about local Hg(II) coordination environments [12]. In this paper, we report the reactivity of $\text{Ph}_2\text{PCH}_2\text{PPh}_2=\text{C}(\text{H})\text{C}(\text{O})\text{Ph}$, benzoylmethylenediphenyldiphenylphosphino methylphosphorane (BDEP), towards mercury(II) halides.

2. Experimental

All reactions were carried out under nitrogen atmosphere. Reactants and reagents were obtained from Aldrich Chemical Company and used without further purification. The solvents were dried and distilled using standard methods [13]. The ^1H and $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra were recorded on a Bruker DPX400 spectrometer at 400.13 and 161.98 MHz, referenced relative to residual solvent and external 85% H_3PO_4 , respectively. The chemical shifts (δ) and the coupling constants (J) were expressed in ppm and Hz, respectively. The IR spectra in the interval of $4000\text{--}400\text{ cm}^{-1}$ were recorded on a Perkin–Elmer 1720X FT-IR spectrophotometer using KBr pellets. Positive mode ESI-Mass spectra were measured on a

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Bruker FTMS 4.7T BioAPEX II instrument using the solution of the complexes in acetonitrile. Elemental analyses were performed at the Ecole d'ingénieurs de Fribourg, Switzerland.

2.1. Preparation of compounds

2.1.1. $\text{Ph}_2\text{PCH}_2\text{PPh}_2=\text{C}(\text{H})\text{C}(\text{O})\text{Ph}$ (**1**)

The ylide was prepared by the treatment of triethylamine on the monophosphonium bromide derived from bis(diphenylphosphino)methane as reported previously [4]. X-ray quality crystals were obtained by recrystallization from a toluene-petroleum ether mixture. IR (cm^{-1}): 3054, 2887, 1581, 1523 ($\nu\text{C}=\text{O}$), 1482, 1433, 1385, 1348, 1191, 1102, 1063, 1024, 997, 927, 887, 783, 751, 742, 734, 719, 709, 693, 650, 587, 518, 504, 491, 471. ^1H NMR (CDCl_3): δ 3.67 (d, 2H, PCH_2P , $^2J_{\text{P-H}} = 14.4$), 4.31 (d, 1H, PCHCOPh , $^2J_{\text{P-H}} = 24.4$), 7.23–7.87 (m, 25H, Ph). ^{31}P NMR (CDCl_3): δ -26.64 (d, PPh_2 , $^2J_{\text{P-P}} = 62.1$), 14.47 (d, PCHCOPh , $^2J_{\text{P-P}} = 62.1$).

2.1.2. $[\text{HgCl}_2(\text{PPh}_2\text{CH}_2\text{PPh}_2\text{C}(\text{H})\text{C}(\text{O})\text{Ph})]$ (**2**)

A methanolic solution containing $\text{PPh}_2\text{CH}_2\text{PPh}_2=\text{CHCOPh}$ (0.15 g, 0.29 mmol) and HgCl_2 (0.08 g, 0.29 mmol) was mixed gently for homogenization. The resulting clear colourless solution was allowed to stand at -5°C . The complex was isolated as colourless crystals after two days, washed with ice-cold methanol and dried *in vacuo*. Yield: 0.18 g, 80%. M.p. $> 158^\circ\text{C}$ (decomposes). Anal. Calc. for $\text{C}_{33}\text{H}_{28}\text{Cl}_2\text{HgOP}_2$: C, 51.21; H, 3.65. Found: C, 51.62; H, 3.67%. IR (cm^{-1}): 3053, 2901, 1596, 1566 ($\nu\text{C}=\text{O}$), 1483, 1437, 1329, 1300, 1192, 1157, 1107, 1022, 997, 832, 771, 742, 689, 532, 496, 474. ^1H NMR (CDCl_3): δ 4.15 (t, 2H, PCH_2P , $^2J_{\text{P-H}} = 12.3$), 4.81 (d, 1H, PCHCOPh , $^2J_{\text{P-H}} = 10.0$), 7.34–8.05 (m, 25H, Ph). ^{31}P NMR (CDCl_3): δ 8.65 (d, PPh_2 , $^2J_{\text{P-P}} = 36.1$), 25.09 (d, PCH_2COPh , $^2J_{\text{P-P}} = 38.8$). Mass spectrum: ESI + [m/z , ion, (%): 739.1 [$\text{M}-\text{Cl}$] $^+$ (72).

2.1.3. $[\text{HgBr}_2(\text{PPh}_2\text{CH}_2\text{PPh}_2\text{C}(\text{H})\text{C}(\text{O})\text{Ph})]$ (**3**)

The same procedure as used for the preparation of **2** was followed using the ylide (0.15 g, 0.29 mmol) and HgBr_2 (0.10 g, 0.29 mmol). The resulting clear colourless solution was allowed to stand at room temperature. Colourless crystals were obtained after a day. They were washed with ice-cold methanol and vacuum dried. Yield: 0.22 g, 85%. M.p. $> 156^\circ\text{C}$ (decomposes). Anal. Calc. for

$\text{C}_{33}\text{H}_{28}\text{Br}_2\text{HgOP}_2$: C, 45.93; H, 3.27. Found: C, 44.84; H, 3.01%. IR (cm^{-1}): 3054, 1598, 1568 ($\nu\text{C}=\text{O}$), 1483, 1436, 1326, 1299, 1203, 1188, 1107, 1038, 1022, 998, 872, 833, 772, 742, 688, 531, 498, 469. ^1H NMR (CDCl_3): δ 4.13 (t, 2H, PCH_2P , $^2J_{\text{P-H}} = 11.8$), 4.79 (d, 1H, PCHCOPh , $^2J_{\text{P-H}} = 9.8$), 7.34–8.04 (m, 25H, Ph). ^{31}P NMR (CDCl_3): δ 2.83 (d, PPh_2 , $^2J_{\text{P-P}} = 37.4$), 25.44 (d, PCHCOPh , $^2J_{\text{P-P}} = 42.8$). Mass spectrum: ESI + [m/z , ion, (%): 783.0 [$\text{M}-\text{Br}$] $^+$ (77).

2.1.4. $[\text{HgI}_2(\text{PPh}_2\text{CH}_2\text{PPh}_2\text{C}(\text{H})\text{C}(\text{O})\text{Ph})]$ (**4**)

This complex was prepared in the same way as used for **2** and **3** using HgI_2 (0.13 g, 0.29 mmol). Yield: 0.25 g, 88%. M.p. 166–168 $^\circ\text{C}$. Anal. Calc. for $\text{C}_{33}\text{H}_{28}\text{I}_2\text{HgOP}_2$: C, 41.42; H, 2.95. Found: C, 41.16; H, 2.71%. IR (cm^{-1}): 3051, 2953, 2893, 1600, 1564 ($\nu\text{C}=\text{O}$), 1482, 1437, 1325, 1298, 1197, 1183, 1104, 1033, 1023, 997, 873, 832, 771, 760, 740, 722, 688, 649, 528, 492, 472. ^1H NMR (CDCl_3): δ 4.14 (dd, 2H, PCH_2P , $^2J_{\text{P-H}} = 10.1$), 4.79 (d, 1H, PCHCOPh , $^2J_{\text{P-H}} = 11.0$), 7.31–8.02 (m, 25H, Ph). ^{31}P NMR (CDCl_3): δ -9.20 (br, PPh_2), 25.53 (d, PCHCOPh , $^2J_{\text{P-P}} = 46.4$). Mass spectrum: ESI + [m/z , ion, (%): 831.0 [$\text{M}-\text{I}$] $^+$ (100).

2.2. X-ray crystallography

Single crystals were grown as described above and were removed directly from the mother liquor and mounted in an inert oil using a cryoloop. The intensity data were collected at 173 K (-100°C) on a Stoe Mark II-Image Plate Diffraction System [14] equipped with a two-circle goniometer and using Mo $\text{K}\alpha$ graphite monochromated radiation. The structures were solved by direct methods using the program SHELXS-97 [15]. The refinement and all further calculations were carried out using SHELXL-97 [15]. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2 . In complex **2**, the phenyl ring atoms C9–C14 were constrained to have thermal parameters equal to that of the *ipso* carbon atom and the C–O distance in the two solvent methanol molecules was restrained to the theoretical value. Complex **3** crystallized in monoclinic space group $P2_1/c$ and was refined as a twin [final BASF value = 0.115]. The C–O distances in the co-crystallized methanol molecules were restrained to the theoretical values. In complex

Table 1
Crystal data and refinement details for compounds **1–4**.

Compound	1	2 · 2MeOH	3 · 2MeOH	4 · CH₂Cl₂
Empirical formula	$\text{C}_{33}\text{H}_{28}\text{OP}_2$	$\text{C}_{33}\text{H}_{28}\text{Cl}_2\text{HgOP}_2 \cdot 2(\text{CH}_3\text{OH})$	$\text{C}_{33}\text{H}_{28}\text{Br}_2\text{HgOP}_2 \cdot 2(\text{CH}_3\text{OH})$	$\text{C}_{33}\text{H}_{28}\text{HgI}_2\text{OP}_2 \cdot \text{CH}_2\text{Cl}_2$
Formula weight	502.49	838.07	926.99	1041.81
Temperature (K)	223(2)	173(2)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P2_1/c$
<i>a</i> (Å)	10.0742(12)	11.1951(9)	11.2610(6)	17.3598(11)
<i>b</i> (Å)	10.5950(12)	16.9989(11)	17.1507(7)	21.5815(9)
<i>c</i> (Å)	13.7296(16)	17.7694(17)	20.5164(11)	19.8451(12)
α ($^\circ$)	81.723(14)	90	90	90
β ($^\circ$)	89.236(14)	93.297(11)	119.908(4)	109.451(5)
γ ($^\circ$)	63.240(12)	90	90	90
Volume (Å ³)	1292.7(3)	3376.0(5)	3434.7(3)	7010.6(7)
<i>Z</i>	2	4	4	8
Absorption coefficient (mm^{-1})	0.193	4.846	6.934	6.422
Crystal size (mm)	$0.38 \times 0.19 \times 0.12$	$0.25 \times 0.25 \times 0.20$	$0.33 \times 0.23 \times 0.14$	$0.40 \times 0.20 \times 0.10$
Reflections collected	10195	26103	33393	61806
Independent reflections	4712	6572	12653	12496
Goodness-of-fit on F^2	0.815	0.784	1.128	0.909
R_1 ($I > 2\sigma(I)$)	0.0318	0.0415	0.0547	0.0421
wR_2 (All data)	0.0698	0.0870	0.1677	0.0959

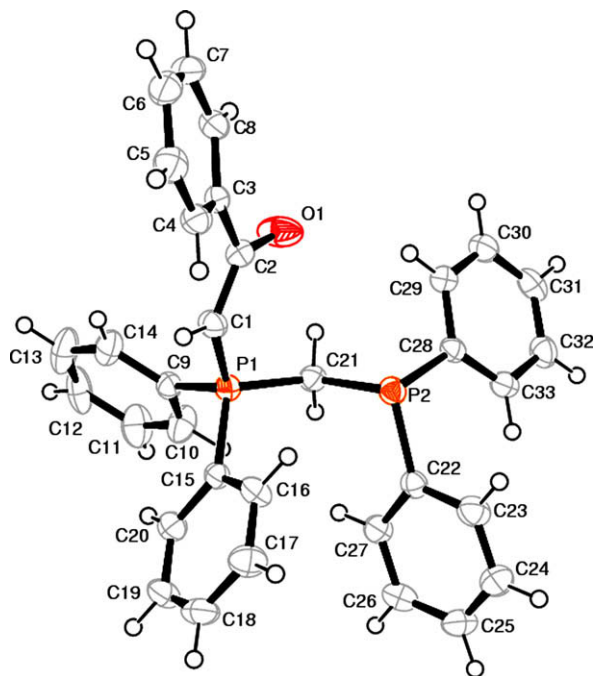


Fig. 1. Molecular structure of $\text{Ph}_2\text{PCH}_2\text{PPh}_2=\text{CHCOPh}$ (**1**) at 50% probability ellipsoids. Selected bond lengths (Å) and angles ($^\circ$): C(1)–P(1) 1.705(2), C(1)–C(2) 1.404(3), C(2)–O(1) 1.249(2), C(2)–C(3) 1.506(3), C(2)–C(1)–P(1) 124.41(15), O(1)–C(2)–C(1) 124.93(18), O(1)–C(2)–C(3) 117.90(17), P(1)–C(1)–C(2)–O(1) $-2.5(3)$.

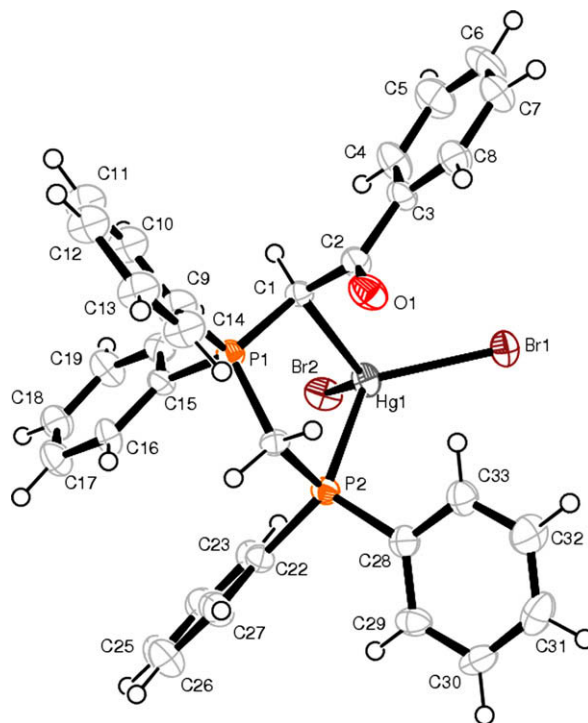


Fig. 3. Molecular structure of $[\text{HgBr}_2(\text{PPh}_2\text{CH}_2\text{PPh}_2\text{C}(\text{H})\text{C}(\text{O})\text{Ph})]$ (**3**) with 30% probability ellipsoids. The two methanol solvent molecules have been omitted for clarity.

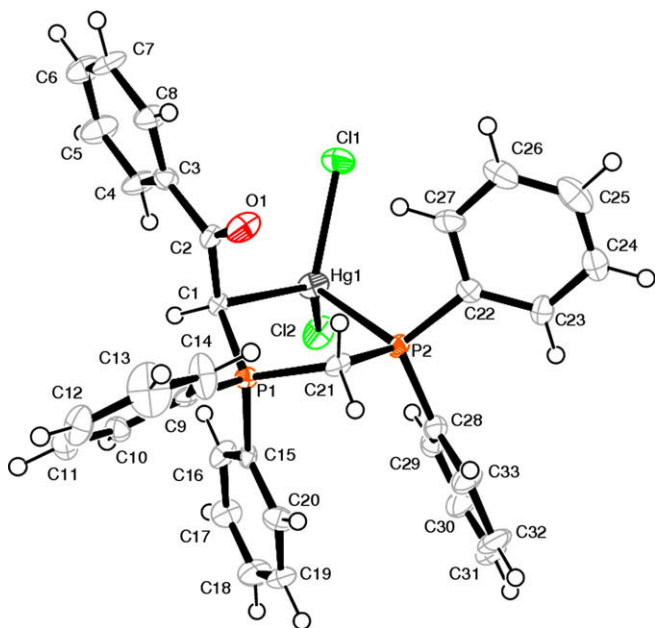


Fig. 2. Molecular structure of $[\text{HgCl}_2(\text{PPh}_2\text{CH}_2\text{PPh}_2\text{C}(\text{H})\text{C}(\text{O})\text{Ph})]$ (**2**) with 30% probability ellipsoids. The two methanol solvent molecules have been omitted for clarity.

4, the co-crystallized dichloromethane molecule was found to be disordered over two positions (C68/C68A). The refinement of the site occupancy factor leads to 55.2% occupancy for the major component. Further crystallographic data are given in Table 1. The molecular structure and crystallographic numbering schemes are illustrated in ORTEP [16] drawings, Figs. 1–4.

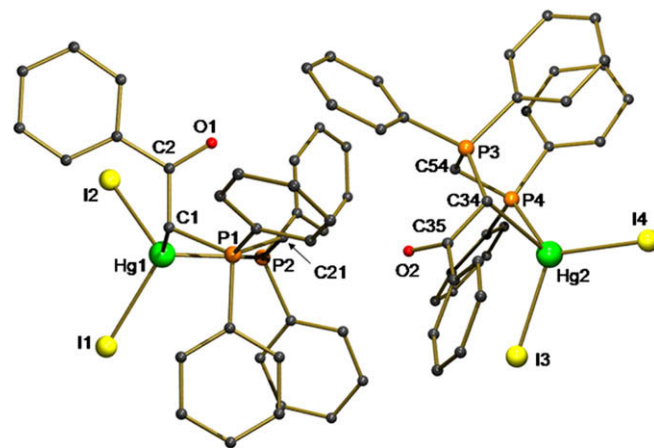


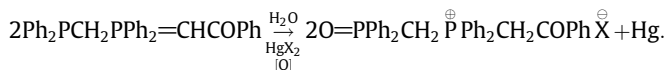
Fig. 4. Molecular structure of the two independent molecules of complex **4**. The figure shows 'envelope' (**4**) and 'twist' (**4'**) conformation of the five-membered chelate rings.

3. Results and discussion

3.1. Synthesis

Complexes **2–4**, in crystalline form, were obtained in good yields (80–88%) by gentle mixing of methanolic solutions of the ylide and mercuric halide and allowing to stand at room temperature or at -5°C . However, when stirred, the same reaction in methanol gave a grey solid, due to metallic mercury, together with a mixture of unidentified products. In this case, lowering the reaction temperature, protection from light and change in solvent to dichloromethane, did not prevent the decomposition. That no such reduction has been reported for the complexes of this ylide with

Pd(II) [4], Pt(II) [4] and Rh(I) [17] suggests that Hg(II) brings about a special reactivity causing the formation of metal. It is likely that Hg(0) is produced following the oxidation of phosphine by trace amount of water leading to the formation of phosphonium salt as shown below.



The ^{31}P NMR of the product gives some evidence for the formation of the phosphine oxide-phosphonium salt (*vide infra*). In fact, catalytic oxidation of bis(diphenylphosphino)methane (dppm) by Hg^{2+} to dppmO and dppmO₂ has been noted previously [18].

3.2. Spectroscopy

The upward frequency shift of the $\nu(\text{CO})$ absorption in complexes **2**, **3** and **4** at 1566, 1568 and 1564 cm^{-1} , respectively, with reference to the free ylide (1523 cm^{-1}), strongly suggests coordination of the ylidic carbon to form an Hg–C_{ylide} bond. Significantly, the coordination shifts [$\Delta\nu = \nu(\text{CO})_{\text{complex}} - \nu(\text{CO})_{\text{free ylide}}$] of $\sim 40 \text{ cm}^{-1}$ are much lower than the corresponding shifts (88–110 cm^{-1}) observed in the other C-bonded Hg(II) complexes containing $\text{Ph}_3\text{PC}(\text{H})\text{C}(\text{O})\text{Ph}$ [6] and $\text{Ph}_3\text{P}=\text{C}(\text{H})\text{CO}(\text{OCH}_2\text{CH}_3)$ [8]. This perhaps signals a weaker Hg–C bonding in these complexes.

The initial NMR measurement of the complexes in DMSO-*d*₆ solution showed extensive dissociation and decomposition, which is in contrast to the stability of [$\text{Ph}_3\text{PCHCOPh.HgX}_2$]₂ (X = Cl, Br, I) [6] complexes in the same solvent. The ^1H NMR spectra of all complexes in CDCl_3 exhibit a doublet in the region of 4.80 ppm due to the methine protons. The observed downfield shifts and decrease in $^2J_{\text{P-H}}$ coupling constants when compared to the free ylide are in accordance with the reduction in P–C bond order, a consequence of the C-coordination of the ylide. In the ^{31}P NMR spectra (CDCl_3) the signal due to phosphonium group appears as a doublet around 25.35 ppm. The significant downfield shift of this signal from that of the free ylide (δ 14.47) is in agreement with the C-bonding of the ylide. The coordination of phosphine is also clearly evident from the strong downfield shifts of the signal due to 'PPh₂' group when compared to that of same signal in the free ylide (δ –26.64). The doublet signals at 8.65 ppm and 2.83 ppm, respectively, for **2** and **3**, as well as the broad resonance centered at –9.20 ppm for **4**, sig-

nify the halogen dependence of the chemical shifts which agrees well with the situation encountered in mercury(II)-phosphine complexes [19]. However, ^{199}Hg satellites could not be observed in CDCl_3 solution due to exchange decoupling caused by presumable fast exchange, as noted previously in the case of some Hg(II)-phosphine complexes [20,21]. The spectral data thus indicate the bidentate coordination of the ligand through both P and C atoms.

It is interesting to note that, in addition to the major resonances discussed above, the ^{31}P NMR spectra in CDCl_3 show the presence of two other minor species. One set of two doublets in the region of 26.06 ppm and 21.75 ppm in the ^{31}P NMR spectra can be attributed to $[\text{O}=\text{PPh}_2\text{CH}_2\text{P}^+\text{Ph}_2\text{CH}_2\text{COPh}]\text{X}^-$ (where X = anion concerned). The assignment has been confirmed by comparison of the spectral properties with that of $[\text{O}=\text{PPh}_2\text{CH}_2\text{P}^+\text{Ph}_2\text{CH}_2\text{COPh}]\text{Br}^-$ which displays essentially the same features (see [Supplementary information](#)). The origin of another set of minor doublets (35.18 and 8.36 ppm, $^2J_{\text{P-P}} = 24 \text{ Hz}$), is not immediately apparent. However, if one considers the cleavage of the ylide to form $\text{Ph}_2\text{PCH}_2\text{PPh}_2$, the subsequent mono oxidation and coordination to Hg^{2+} could possibly explain the observed additional signals.

Interestingly, the ^{31}P NMR spectra when measured in CD_3CN are clean and show only a negligible amount of $\text{O}=\text{PPh}_2\text{CH}_2\text{P}^+\text{Ph}_2\text{CH}_2\text{COPh}\cdot\text{X}^-$ in the spectrum of **3** and an almost complete absence in **2** and **4**, indicating the stability of the complexes in the above solvent. The ^1H and ^{31}P NMR spectra in CD_3CN (data provided as [Supplementary information](#)) are consistent with the P, C-mode of coordination of ylide and show the expected solvent dependent differences in chemical shifts. The most important aspect in the ^{31}P NMR spectra is the observation of Hg–P coupling for complex **4**. The $^1J_{\text{P-Hg}}$ coupling constant of 1881 Hz is in the range similar to that of the reported Hg(II)-phosphine complexes [18]. The P, C-chelated monomeric structure is also supported by +ESI-mass spectra, the fragmentation pattern of the peaks at *m/z* 739.1, 783.0 and 831.0, respectively, for complexes **2**, **3**, and **4**, fits the calculated isotopic pattern of the pseudomolecular ion, $[\text{HgX}_2\text{L-X}]^+$ (X = Cl, Br, I).

3.3. Crystal structures

3.3.1. Molecular structure of $\text{Ph}_2\text{PCH}_2\text{PPh}_2=\text{C}(\text{H})\text{C}(\text{O})\text{Ph}$ (**1**)

The molecular structure of the ligand is shown in [Fig. 1](#). As shown, both the phosphine and ylidic components are devoid of steric

Table 2
Selected bond distances (Å) and angles (°) in compounds **2**, **3** and **4**.

	X = Cl (2)	X = Br (3)	X = I	
			4	4'
Hg(1)–C(1)	2.345(7)	2.415(12)	2.418(8)	[Hg(2)–C(34) = 2.616(7)]
Hg(1)–P(2)	2.569(2)	2.546(3)	2.5688(19)	[Hg(2)–P(4) = 2.505(2)]
Hg(1)–X(1)	2.493(2)	2.5612(14)	2.7673(6)	[Hg(2)–I(4) = 2.7113(7)]
Hg(1)–X(2)	2.450(2)	2.5773(15)	2.7436(7)	[Hg(2)–I(3) = 2.6932(6)]
P(1)–C(1)	1.766(7)	1.769(12)	1.760(8)	[P(3)–C(34) = 1.719(8)]
P(1)–C(21)	1.811(7)	1.829(13)	1.815(7)	[P(3)–C(54) = 1.811(8)]
P(2)–C(21)	1.834(7)	1.829(13)	1.823(8)	[P(4)–C(54) = 1.824(7)]
O(1)–C(2)	1.248(9)	1.244(16)	1.245(9)	[O(2)–C(35) = 1.247(9)]
C(1)–C(2)	1.469(10)	1.431(18)	1.454(11)	[C(34)–C(35) = 1.435(10)]
C(1)–Hg(1)–X(2)	123.79(19)	119.4(3)	109.03(18)	[C(34)–Hg(2)–I(4) = 109.07(16)]
C(1)–Hg(1)–X(1)	111.70(18)	110.8(3)	111.50(16)	[C(34)–Hg(2)–I(3) = 102.41(18)]
X(2)–Hg(1)–X(1)	105.36(7)	107.10(5)	107.20(2)	[I(3)–Hg(2)–I(4) = 114.64(2)]
C(1)–Hg(1)–P(2)	90.12(18)	89.2(3)	88.24(18)	[P(4)–Hg(2)–C(34) = 86.65(18)]
X(2)–Hg(1)–P(2)	113.03(7)	112.62(8)	120.07(5)	[P(4)–Hg(2)–I(4) = 112.94(5)]
X(1)–Hg(1)–P(2)	112.41(7)	117.46(9)	118.92(5)	[P(4)–Hg(2)–I(3) = 124.89(5)]
C(2)–C(1)–P(1)	112.8(5)	113.6(9)	112.8(5)	[C(35)–C(34)–P(3) = 117.5(6)]
C(2)–C(1)–Hg(1)	104.4(5)	105.6(8)	104.2(5)	[C(35)–C(34)–Hg(2) = 99.4(5)]
P(1)–C(1)–Hg(1)	103.7(3)	102.5(5)	103.2(3)	[P(3)–C(34)–Hg(2) = 103.8(3)]
P(1)–C(1)–C(2)–O(1)	21.0(10)	18.2(17)	–28.1(10)	[P(3)–C(34)–C(35)–O(2) = –25.2(10)]

restrictions and can interact with metal ions and reagents. The P(1)–C(1) [1.706(2) Å], C(2)–O(1) [1.249(2) Å] and C(1)–C(2) [1.401(3) Å] bond lengths within the ylidic fragment are comparable to those observed for the other monoketo ylides [22,23]. No steric or electronic effects due to the presence of –CH₂PPh₂ is thus anticipated. The 1,4-P,O intramolecular interaction, indicated by the short contact [3.107(2) Å] as well as by the *cis* orientation [P(1)–C(1)–C(2)–O(1) –2.5(3)°] of the P⁺ and O[–] centers, is also present in this ylide as observed for other keto-stabilized ylides [24].

3.3.2. Molecular structures of chelate complexes **2**, **3** and **4**

The molecular structures of complexes **2–4** are shown in Figs. 2–4. Selected bond distances and angles are listed in Table 2. The asymmetric unit in each of the complexes **2** and **3** contains a molecule of the complex along with two molecules of methanol. The asymmetric unit of **4** is composed of two symmetry independent molecules (**4** and **4'**) and a molecule of solvent dichloromethane. The X-ray analysis reveals the P,C-chelate mode of coordination of the ligand, Ph₂PCH₂PPh₂=C(H)C(O)Ph to Hg atom in all the three complexes. The Hg atom is surrounded by one P atom of the PPh₂ unit, one ylidic C atom and two halogen atoms leading to a distorted tetrahedral geometry around the metal. In fact, the major deviation from the ideal geometry is exhibited by the ligand bite angle, C(1)–Hg(1)–P(2) 88.5(2)° (average). The stereogenic center formed due to C-bonding adopts same absolute configuration (*R* for C1) in the both **2** and **3**, whereas in complex **4** it is found to be inverted (*S* for C1).

A comparison of the structural features in the present complexes with those of the dinuclear or trinuclear Hg–phosphoylide compounds [6–8,25] reveal striking dissimilarities, the most important being the significantly long Hg–C bond whose distances are 2.345(7), 2.415(12) and [2.418(8) and 2.616(7)] Å in complexes **2**, **3** and **4**, respectively (Table S1, Supplementary information). In addition, the P–C_{ylide} distance is found to be shorter (Table 2) than the corresponding distances in C-coordinated Hg(II)–phosphorus ylide complexes which lie in the range, 1.786(10)–1.806(10) Å [6–8]. Surprisingly, the C=O (keto) distances of 1.248(9), 1.244(16) and [1.245(9) and 1.247(9)] Å in **2**, **3** and **4**, respectively, are found to be close to that of the same distance in the parent ylide [1.249(2) Å]. All these data perhaps indicate that the chelating ylide does not complex well when compared to the non-chelating ylides.

The Hg–P distances range from 2.505(2)–2.569(2) Å in complexes **2–4**. These values are well within the range of 2.39(1)–2.606(3) Å observed previously for the majority of Hg(II)–phosphine complexes [26]. In known Hg(II) chelate complexes containing P, O and P, S donors, the Hg–P distances vary from 2.404(1) Å, as in *trans*-[Hg{Ph₂PNP(O)Ph₂}₂] [27], to 2.503(5) Å as in [Hg(I)₂{Ph₂PCH₂P(S)Ph₂}] [28]. The Hg–Cl distances of 2.493(2) and 2.450(2) Å in **2** as well as the Hg–Br distances of 2.561(1) and 2.577(1) Å in **3** are in agreement with the values reported in the literature [29].

The five-membered chelate rings in **2** and **3** display an envelope conformation. The deviation of the atom P(1) from the basal plane defined by the other four atoms C(21), P(2), Hg(1) and C(1) being 0.742 and 0.750 Å in **2** and **3**, respectively. In complex **4**, the two independent molecules in the asymmetric unit (**4** and **4'**), show different conformations of the five-membered chelate rings. In molecule **4**, the ring adopts an envelope conformation, with atom P(1) 0.765 Å out of the plane of the other four atoms [C(21), P(2), Hg(1) and C(1)]. In molecule **4'** the ring exhibits an half-chair or twist conformation with atoms P(3) and C(54) being out of the plane (by 0.387 Å and –0.413 Å, respectively), and on opposite sides, of the plane defined by atoms P(4), Hg(2), and C(34). Furthermore, the bond parameters in molecules **4** and **4'** vary considerably. Molecule **4** contains a shorter Hg–C bond and a longer Hg–

P bond, whereas in molecule **4'** an opposite trend is observed with a long Hg–C and a short Hg–P bond (Table 2). The Hg–I distances in both the molecules are comparable to those of 2.733(1) and 2.763(1) Å found in [HgI₂(PPh₃)₂] [30], and the terminal Hg–I distances of 2.671(2) and 2.684(2) Å in dimeric [{HgI₂(PPh₃)₂}₂] [31].

In summary, the ylide, PPh₂CH₂PPh₂=CHCOPh reacts with mercury(II) halides in mild conditions to form P,C-chelated complexes. The crystal structures of the above complexes reveal the formation of puckered five-membered chelate rings. The Hg–C bond in these complexes are longer than normal Hg–C_{ylide} bonds, and consists of a carbene ligated to Hg(II). This fact underlines the potential of these complexes in displaying reactivity similar to those exhibited by organomercurials and metalated ylides.

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Appendix A. Supplementary material

CCDC 662092, 662093, 662094 and 662095 contain the supplementary crystallographic data for **1**, **2**·2MeOH, **3**·2MeOH, **4**·2CH₂Cl₂, respectively. 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.jorgchem.2008.11.051.

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