

## **ORIGINAL PAPER**

# Mercury(II) complexes of new bidentate phosphorus ylides: synthesis, spectra and crystal structures

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The reaction of dppm (1,1-bis(diphenylphosphino)methane) with 2-bromo-4-phenylacetophenone and benzyl bromoacetate in chloroform produces new phosphonium salts,  $[Ph_2PCH_2PPh_2CH_2C(O) C_6H_4Ph]Br$  (I) and  $[Ph_2PCH_2PPh_2CH_2COOCH_2Ph]Br$  (II). By allowing the phosphonium salts to react with the appropriate base, the bidentate phosphorus ylides,  $Ph_2PCH_2PPh_2=C(H)C(O)C_6 H_4Ph$  (III) and  $Ph_2PCH_2PPh_2=C(H)C(O)OCH_2Ph$  (IV), were obtained. The reaction of these ligands with mercury(II) halides in dry methanol led to the formation of the mononuclear complexes {HgX\_2[(Ph\_2PCH\_2PPh\_2C(H)C(O)C\_6H\_4Ph)]} (X = Cl (V); X = Br (VI); X = I (VII)) and {HgX\_2[(Ph\_2PCH\_2PPh\_2C(H)COOCH\_2Ph)]} (X = Cl (VIII); X = Br (IX); X = I (X)). The FTIR and <sup>1</sup>H, <sup>31</sup>P and <sup>13</sup>C NMR spectra were studied. The structure of compound III was unequivocally determined by the single-crystal X-ray diffraction technique. Single-crystal X-ray analysis of the {HgBr\_2[(Ph\_2PCH\_2PPh\_2C(H)C(O)C\_6H\_4Me)]} complex (XI) revealed the presence of a mononuclear complex containing the Hg atom in a distorted tetrahedral environment. In all complexes, the ylides referred to above were coordinated through the ylidic carbon and the phosphine atom. (© 2013 Institute of Chemistry, Slovak Academy of Sciences

Keywords: unsymmetrical phosphorus ylides, Hg(II) complexes, X-ray crystal structure

## Introduction

Multi-functional ligands are organic entities that possess more than one functional group; these ligands have attracted interest due to the wide field of applications based on their multi-functionality (Navarro & Urriolabeitia, 1999). Phosphorus ylides are remarkable and important ligands that have attracted much attention in the synthetic, catalytic and theoretical fields of transition metal chemistry (Johnson, 1993; Sabounchei et al., 2013a). These compounds are very interesting ligands in organometallic chemistry, as well as being useful intermediates in organic synthesis (Kokotos & Aggarwal, 2007; Heinicke et al., 2005; Janardanan & Sunoj, 2007; Kolodiazhnyi, 1997; Heydari et al., 2010). Transition metal complexes of these ligands have attracted much attention due to their versatile coordination chemistry and their application in catalysis (Abu-Gnim & Amer, 1996; Grushin, 2004; Wegman et al., 1987). Much of the interest in the coordination properties of resonance-stabilised phosphorus ylides stems from their ligating versatility due to the presence of different functional groups in their molecular skeleton (Ebrahim et al., 2009; Urriolabeitia, 2008; Falvello et al., 2001; Vicente et al., 2002; Viau et al., 2001). Hence, it is clear that these ligands can engage in different kinds of bonding with different metal ions (Falvello et al., 2010a; Oosawa et al., 1976; Lin et al., 1990; Ebrahim et al.,

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2007; Spannenberg et al., 2000; Saravanabharathi et al., 2003; Usón et al., 1987; Takahashi et al., 1976). The asymmetrical bidentate P,C-coordination of the type  $Ph_2P(CH_2)_nPPh_2CHC(O)R$  (n = 1 or 2; R = Me, Ph or OMe) containing both phosphine and ketostabilised phosphorus ylide moieties was recently observed and their transition metal complexes are mostly confined to mercury halides (Ebrahim et al., 2007, 2009; Sabounchei et al., 2010b, 2010c). The transition metal complexes of keto-stabilised ylides have been well studied and are of interest due to the stability of the ylides as ligands and the ease of detection of the coordination of the ylide carbon to the metal by means of infrared spectroscopy (Koezuka et al., 1974, 1976; Nishiyama et al., 1975; Weleski et al., 1975). It is apparent that the presence of different donor atoms in the same ligand induces different geometries and structures in the Hg(II) complexes. Furthermore, the coordination of ligands to Hg(II)has assumed importance since, in the natural mercury detoxification process, the initial Hg—C bond cleavage involves the increase in the coordination numbers around Hg (Barbaro et al., 1994). Within this context, attention is focused here on studying the coordination mode adopted by the resonance-stabilised ylides when ligated to Hg(II). The results of these studies including the full characterisation of the complexes obtained (performed by elemental analysis, IR, multinuclear NMR techniques and electrochemical data) are presented and discussed in this paper.

### Experimental

#### Materials and methods

All reactions were carried out under an atmosphere of dry nitrogen. Prior to use, methanol and diethyl ether were dried with magnesium powder and a mixture of sodium and benzophenone, respectively. All other solvents were of reagent grade and used without further purification. Melting points were measured on a Stuart SMP3 apparatus (Stuart, USA). IR spectra (in KBr pellets) were recorded on a Shimadzu 435-U-04 spectrophotometer (Shimadzu, Japan). <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectra were recorded on a 300 MHz (Bruker, Germany) and a 90 MHz (Jeol, Japan) spectrometers in DMSO- $d_6$  or CDCl<sub>3</sub> as solvent at 25 °C. Chemical shifts ( $\delta$ ) were referenced against the tetramethylsilane (TMS) as the internal standard and 85~% phosphoric acid as the external standard. Elemental analyses were performed using a Perkin-Elmer 2400 Series II CHNS/O elemental analyser (Perkin-Elmer, USA).

#### X-ray crystal structure determination

The single-crystal X-ray diffraction data of suitable crystals of *III* were collected on a STOE IPDS

II diffractometer (Stoe & Cie, Germany) at 298 K, using graphite monochromic Mo  $K_{\alpha}$  radiation ( $\lambda =$ 0.71073 Å). The data collection was performed using the  $\omega$ -scan technique using the Stoe X-AREA software package (Stoe & Cie, 2005a), while data reduction was carried out using the X-RED program (Stoe & Cie, 2005a). The crystal structure was solved by direct methods and refined by full-matrix least-squares on  $F^2$  using the SHELXS and SHELXL programs, respectively (Sheldrick, 2008) and using the X-STEP<sup>32</sup> crystallographic software package (Stoe & Cie, 2005b). The H atoms were included in calculated positions and treated as riding atoms using SHELXL (Sheldrick, 2008) default parameters. Numerical absorption corrections were applied to III. Data collection from suitable crystals of XI (Sabounchei et al., 2013b) was performed on an Oxford Diffraction single-crystal X-ray diffractometer (Oxford Diffraction, UK) using mirror monochromatic Mo  $K_{\alpha}$  radiation ( $\lambda = 0.71073$  Å) at 130 K. Gaussian absorption corrections were carried out using a multi-faceted crystal model, using CrysAlisPro software (Agilent Technologies, 2011). The structure was solved by direct methods and refined by the full-matrix least-squares method on  $F^2$  using the SHELXTL-97 crystallographic package (Sheldrick, 2008; Dolomanov et al., 2009). All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were inserted at calculated positions using a riding model, with isotropic displacement parameters.

## $[Ph_2PCH_2PPh_2CH_2C(O)C_6H_4Ph]Br$ (I)

A solution of 2-bromo-4-phenylacetophenone (0.36 g, 1.30 mmol) in chloroform (4 mL) was added dropwise to the solution of dppm (0.50 g, 1.30 mmol) in chloroform (8 mL) and the mixture was stirred at ambient temperature for 15 h. The mixture was then concentrated under reduced pressure to approximately 2 mL. Diethyl ether (25 mL) was added and the solid thus formed was filtered and dried under reduced pressure.

## $[Ph_2 PCH_2 PPh_2 CH_2 CO_2 CH_2 Ph]Br$ (II)

A solution of dppm (0.50 g, 1.30 mmol) and benzyl bromoacetate (0.30 g, 1.30 mmol) in chloroform was stirred at ambient temperature for 10 h. The white solid thus formed was filtered and dried under reduced pressure.

## $Ph_2PCH_2PPh_2 = C(H)C(O)C_6H_4Ph$ (III)

The monophosphonium salt (I) (0.33 g, 0.50 mmol) was treated with triethylamine (0.50 mL) in toluene (15 mL) and the triethylamine hydrobromide thus obtained was removed by filtration. Evaporation of toluene to approximately 1 mL and the subsequent

Compound	Formula	$M_{ m r}$	$w_{ m i}({ m calc.})/{ m mass}~\% \ w_{ m i}({ m found})/{ m mass}~\%$		Yield	M.p.	
	Formuta		С	Н	%	°C	
Ι	$\mathrm{C}_{39}\mathrm{H}_{33}\mathrm{BrOP}_{2}$	659.53	$71.02 \\ 70.91$	$5.04 \\ 5.09$	85	180	
II	$\mathrm{C}_{34}\mathrm{H}_{31}\mathrm{BrO}_{2}\mathrm{P}_{2}$	613.46	$66.56 \\ 66.64$	$5.09 \\ 5.11$	82	166	
III	$\mathrm{C}_{39}\mathrm{H}_{32}\mathrm{OP}_2$	578.62	$80.95 \\ 80.86$	$5.57 \\ 5.56$	71	145	
IV	$\mathrm{C}_{34}\mathrm{H}_{30}\mathrm{O}_{2}\mathrm{P}_{2}$	532.55	$76.68 \\ 76.94$	$5.68 \\ 5.77$	62	138	
V	$\rm C_{39}H_{32}Cl_2HgOP_2$	850.11	$55.10 \\ 54.95$	$3.79 \\ 3.72$	67	209	
VI	$\rm C_{39}H_{32}Br_2HgOP_2$	939.02	$49.88 \\ 49.76$	$3.43 \\ 3.49$	68	214	
VII	$\mathrm{C}_{39}\mathrm{H}_{32}\mathrm{I}_{2}\mathrm{HgOP}_{2}$	1033.02	$45.34 \\ 45.21$	$3.12 \\ 3.07$	56	217	
VIII	$\mathrm{C}_{34}\mathrm{H}_{30}\mathrm{Cl}_{2}\mathrm{HgO}_{2}\mathrm{P}_{2}$	804.04	$50.79 \\ 50.95$	$3.76 \\ 3.69$	54	205	
IX	$\mathrm{C}_{34}\mathrm{H}_{30}\mathrm{Br}_{2}\mathrm{HgO}_{2}\mathrm{P}_{2}$	892.95	$45.73 \\ 45.58$	$3.38 \\ 3.43$	58	210	
X	$\mathrm{C}_{34}\mathrm{H}_{30}\mathrm{I}_{2}\mathrm{HgO}_{2}\mathrm{P}_{2}$	986.95	$41.38 \\ 41.54$	$3.06 \\ 3.01$	49	218	

Table 1. Characterisation data of compounds I-X



Fig. 1. Reaction scheme for synthesis of phosphine–phosphonium ylides. Reaction conditions: i) chloroform, ambient temperature, 24 h; ii) triethylamine, toluene; Ph = phenyl.

addition of diethyl ether (25 mL) resulted in precipitation of the desired ligand (bidentate phosphorus ylide) as a white solid.

## $Ph_2PCH_2PPh_2 = CHCO_2CH_2Ph$ (IV)

This phosphorus ylide was obtained using the procedure adopted for the preparation of III starting from monophosphonium salt (II) (0.31 g, 0.50 mmol).

# General procedure for preparation of complexes V-X

A solution of *III* or *IV* (0.35 mmol) in methanol (4 mL) was added dropwise at  $0^{\circ}$ C to a solution of HgX<sub>2</sub> (0.35 mmol) in methanol (8 mL) and the mixture was stirred for 2 h. The resulting solid, admixed with grey material, was treated with dichloromethane (25 mL) and filtered through a short plug of Celite. The addition of an excess volume of methanol to the concentrated filtrate caused precipitation of the prod-

ucts as solids. Characterisation data of compounds I-X are given in Table 1.

## **Results and discussion**

#### Synthesis and spectral determination

The ligands were synthesised by allowing bis(diphenylphosphino)methane to react with 2-bromo-4phenylacetophenone and benzyl bromoacetate and removal of the proton from the phosphonium salts by triethylamine (Fig. 1) (Oosawa et al., 1976).

Reactions of HgX<sub>2</sub> with ylides *III* and *IV* in a 1 : 1 stoichiometry afforded the P,C-bonding complexes V-X with a chelating structure (Fig. 2). All complexes were soluble in dichloromethane and were obtained with fair yields (49–68 %). The spectral data of compounds I-X are given in Table 2.

The <sup>1</sup>H NMR spectrum of *I* exhibited, in addition to the aromatic resonances, two doublets at  $\delta = 5.91$ (<sup>2</sup>*J*<sub>P,H</sub> = 12.15 Hz) and  $\delta = 4.27$  (<sup>2</sup>*J*<sub>P,H</sub> = 14.85 Hz)



Fig. 2. Reaction of ylides III and IV with Hg(II) halides. Reaction conditions: i) MeOH, N<sub>2</sub> atmosphere, 0 °C, 2 h.

**Table 2.** Spectral data of compounds I - X

Compound	Spectral data <sup><math>a</math></sup>				
Ι	IR, $\tilde{\nu}/\text{cm}^{-1}$ : 1669 (C=O) <sup>1</sup> H NMR (CDCl <sub>3</sub> ), $\delta$ : 4.27 (d, 2H, PCH <sub>2</sub> P, <sup>2</sup> J <sub>P,H</sub> = 14.85 Hz), 5.91 (d, 2H, PCH <sub>2</sub> CO, <sup>2</sup> J <sub>P,H</sub> = 12.15 Hz), 7.20–8.25 (m, 29H, H <sub>arom</sub> ) <sup>13</sup> C NMR (CDCl <sub>3</sub> ), $\delta$ : 22.00 (dd, PCH <sub>2</sub> P, <sup>1</sup> J <sub>P,C</sub> = 51.01 Hz, <sup>1</sup> J <sub>P,C</sub> = 34.33), 36.34 (dd, PCH <sub>2</sub> , <sup>1</sup> J <sub>P,C</sub> = 60.50 Hz, <sup>3</sup> J <sub>P,C</sub> = 5.02 Hz), 117.93–147.05 (C <sub>arom</sub> ), 191.70 (s, C=O) <sup>31</sup> P NMR (CDCl <sub>3</sub> ), $\delta$ : -29.25 (d, PPh <sub>2</sub> , <sup>2</sup> J <sub>P,P</sub> = 63.42 Hz), 21.09 (d, PCH <sub>2</sub> CO, <sup>2</sup> J <sub>P,P</sub> = 63.58 Hz)				
II	IR, $\tilde{\nu}/cm^{-1}$ : 1729 (C=O) <sup>1</sup> H NMR (CDCl <sub>3</sub> ), $\delta$ : 4.28 (d, 2H, PCH <sub>2</sub> P, <sup>2</sup> J <sub>P,H</sub> = 15.21 Hz), 4.99 (d, 2H, PCH <sub>2</sub> CO, <sup>2</sup> J <sub>P,H</sub> = 13.50 Hz), 4.78 (s, 2H, CH <sub>2</sub> O), 6.85–7.92 (m, 25H, H <sub>arom</sub> ) <sup>13</sup> C NMR (CDCl <sub>3</sub> ), $\delta$ : 21.13 (dd, PCH <sub>2</sub> P, <sup>1</sup> J <sub>P,C</sub> = 51.03 Hz, <sup>1</sup> J <sub>P,C</sub> = 36.00 Hz), 32.35 (dd, PCH <sub>2</sub> , <sup>1</sup> J <sub>P,C</sub> = 57.00 Hz, <sup>3</sup> J <sub>P,C</sub> = 2.02 Hz), 68.11 (s, CH <sub>2</sub> O), 116.71–134.70 (C <sub>arom</sub> ), 164.27 (s, C=O) <sup>31</sup> P NMR (CDCl <sub>3</sub> ), $\delta$ : -29.55 (d, PPh <sub>2</sub> , <sup>2</sup> J <sub>P,P</sub> = 65.78 Hz), 20.17 (d, PCH <sub>2</sub> CO, <sup>2</sup> J <sub>P,P</sub> = 65.05 Hz)				
III	IR, $\tilde{\nu}/\text{cm}^{-1}$ : 1565 (C=O) <sup>1</sup> H NMR (CDCl <sub>3</sub> ), $\delta$ : 3.70 (d, 2H, CH <sub>2</sub> , <sup>2</sup> J <sub>P,H</sub> = 14.22 Hz), 4.36 (brs, 1H, CH), 7.27–8.02 (m, 29H, H <sub>arom</sub> ) <sup>13</sup> C NMR (CDCl <sub>3</sub> ), $\delta$ : 24.52 (dd, PCH <sub>2</sub> P, <sup>1</sup> J <sub>P,C</sub> = 57.64 Hz, <sup>1</sup> J <sub>P,C</sub> = 32.28 Hz), 49.94 (d, CH, <sup>1</sup> J <sub>P,C</sub> = 114.46 Hz), 124.89–141.84 (Carom), 184.60 (s, C=O) <sup>31</sup> P NMR (CDCl <sub>3</sub> ), $\delta$ : -29.78 (d, PPh <sub>2</sub> , <sup>2</sup> J <sub>P,P</sub> = 63.67 Hz), 11.32 (d, PCH, <sup>2</sup> J <sub>P,P</sub> = 63.24 Hz)				
IV	IR, $\tilde{\nu}/\text{cm}^{-1}$ : 1583 (C=O) <sup>1</sup> H NMR (CDCl <sub>3</sub> ), $\delta$ : 3.39 (d, 2H, CH <sub>2</sub> , <sup>2</sup> J <sub>P,H</sub> = 13.77 Hz), 3.00 (brs, 1H, CH), 4.86 (s, 2H, CH <sub>2</sub> O), 7.02–7.85 (m, 25H, H <sub>arom</sub> ) <sup>13</sup> C NMR (CDCl <sub>3</sub> ), $\delta$ : 21.13 (dd, PCH <sub>2</sub> P, <sup>1</sup> J <sub>P,C</sub> = 55.08 Hz, <sup>1</sup> J <sub>P,C</sub> = 40.12 Hz), 53.31 (d, CH, <sup>1</sup> J <sub>P,C</sub> = 107.28 Hz), 67.24 (s, CH <sub>2</sub> O), 117.18–132.87 (C <sub>arom</sub> ), 156.17 (s, C=O) <sup>31</sup> P NMR (CDCl <sub>3</sub> ), $\delta$ : -30.63 (d, PPh <sub>2</sub> , <sup>2</sup> J <sub>P,P</sub> = 64.62 Hz), 12.69 (d, PCH, <sup>2</sup> J <sub>P,P</sub> = 64.84 Hz)				
V	IR, $\tilde{\nu}/\text{cm}^{-1}$ : 1594 (C=O) <sup>1</sup> H NMR (DMSO- $d_6$ ), $\delta$ : 4.69 (brs, 2H, CH <sub>2</sub> ), 5.31 (brs, 1H, CH), 7.44–8.15 (m, 29H, H <sub>arom</sub> ) <sup>13</sup> C NMR (DMSO- $d_6$ ), $\delta$ : 24.27 (brs, CH <sub>2</sub> ), 33.64 (brs, CH), 126.63–135.66 (C <sub>arom</sub> ), 191.87 (s, C=O) <sup>31</sup> P NMR (DMSO- $d_6$ ), $\delta$ : 8.25 (brs, PPh <sub>2</sub> ), 26.58 (d, PCH, <sup>2</sup> J <sub>P,P</sub> = 41.12 Hz)				
VI	IR, $\tilde{\nu}/\text{cm}^{-1}$ : 1594 (C=O) <sup>1</sup> H NMR (DMSO- $d_6$ ), $\delta$ : 4.64 (brs, 2H, CH <sub>2</sub> ), 5.34 (brs, 1H, CH), 7.43–8.01 (m, 29H, H <sub>arom</sub> ) <sup>13</sup> C NMR (DMSO- $d_6$ ), $\delta$ : 23.97 (brs, CH <sub>2</sub> ), 33.89 (brs, CH), 125.96–135.78 (C <sub>arom</sub> ), 190.94 (s, C=O) <sup>31</sup> P NMR (DMSO- $d_6$ ), $\delta$ : 0.20 (brs, PPh <sub>2</sub> ), 26.96 (d, PCH, <sup>2</sup> $J_{P,P} = 45.29$ Hz)				
VII	IR, $\tilde{\nu}/\text{cm}^{-1}$ : 1593 (C=O) <sup>1</sup> H NMR (DMSO- $d_6$ ), $\delta$ : 4.48 (brs, 2H, CH <sub>2</sub> ), 5.23 (brs, 1H, CH), 7.40–8.13 (m, 29H, H <sub>arom</sub> ) <sup>13</sup> C NMR (DMSO- $d_6$ ), $\delta$ : 24.11 (brs, CH <sub>2</sub> ), 31.17 (brs, CH), 124.88–136.14 (C <sub>arom</sub> ), 189.73 (s, C=O) <sup>31</sup> P NMR (DMSO- $d_6$ ), $\delta$ : -13.36 (brs, PPh <sub>2</sub> ), 26.53 (d, PCH, <sup>2</sup> $J_{P,P} = 53.70$ Hz)				
VIII	IR, $\tilde{\nu}/\text{cm}^{-1}$ : 1673 (C=O) <sup>1</sup> H NMR (DMSO- $d_6$ ), $\delta$ : 4.34 (brs, 2H, CH <sub>2</sub> ), 5.11 (brs, 1H, CH), 4.81 (s, 2H, CH <sub>2</sub> O), 7.08–8.09 (m, 25H, H <sub>arom</sub> ) <sup>13</sup> C NMR (DMSO- $d_6$ ), $\delta$ : 22.18 (brs, CH <sub>2</sub> ), 35.87 (brs, CH), 64.38 (s, CH <sub>2</sub> O), 118.56–131.67 (C <sub>arom</sub> ), 162.25 (s, C=O) <sup>31</sup> P NMR (DMSO- $d_6$ ), $\delta$ : 6.20 (brs, PPh <sub>2</sub> ), 25.71 (d, PCH, <sup>2</sup> J <sub>P P</sub> = 42.64 Hz)				
IX	IR, $\tilde{\nu}/\text{cm}^{-1}$ : 1667 (C=O) <sup>1</sup> H NMR (DMSO- $d_6$ ), $\delta$ : 4.29 (brs, 2H, CH <sub>2</sub> ), 4.99 (brs, 1H, CH,), 4.85 (s, 2H, CH <sub>2</sub> O), 7.01–8.14 (m, 25H, H <sub>arom</sub> ) <sup>13</sup> C NMR (DMSO- $d_6$ ), $\delta$ : 22.95 (brs, CH <sub>2</sub> ), 34.11 (brs, CH), 65.12 (s, CH <sub>2</sub> O), 118.37–132.18 (C <sub>arom</sub> ), 160.27 (s, C=O) <sup>31</sup> P NMR (DMSO- $d_6$ ), $\delta$ : 1.76 (brs, PPh <sub>2</sub> ), 25.48 (d, PCH, <sup>2</sup> J <sub>P,P</sub> = 43.92 Hz)				
Х	IR, $\tilde{\nu}/\text{cm}^{-1}$ : 1659 (C=O) <sup>1</sup> H NMR (DMSO- $d_6$ ), $\delta$ : 4.36 (brs, 2H, CH <sub>2</sub> ,), 4.87 (brs, 1H, CH), 4.92 (s, 2H, CH <sub>2</sub> O), 7.12–8.23 (m, 25H, H <sub>arom</sub> ) <sup>13</sup> C NMR (DMSO- $d_6$ ), $\delta$ : 23.17 (brs, CH <sub>2</sub> ), 31.27 (brs, CH), 62.17 (s, CH <sub>2</sub> O), 119.18–132.29 (C <sub>arom</sub> ), 157.74 (s, C=O) <sup>31</sup> P NMR (DMSO- $d_6$ ), $\delta$ : -10.27 (brs, PPh <sub>2</sub> ), 26.04 (d, PCH, <sup>2</sup> $J_{P,P} = 49.83$ Hz).				

a)  $H_{arom}$  and  $C_{arom}$  mean aromatic protons and carbons of phenyl moieties, respectively; brs means broad signal.

due to the PCH<sub>2</sub>CO and PCH<sub>2</sub>P groups, respectively (Navarro & Urriolabeitia, 1999). The <sup>31</sup>P NMR spectrum exhibited two doublets at  $\delta = 21.09$  and  $\delta =$ -29.25, indicating the PCH<sub>2</sub>CO and PPh<sub>2</sub> groups, respectively. In the <sup>13</sup>C NMR spectrum, two doublet of doublet signals were registered at  $\delta = 22.0 \ (^{1}J_{\rm P,C} =$ 51.01 Hz,  ${}^{1}J_{\rm P,C} = 34.33$  Hz) and  $\delta = 36.34$  ( ${}^{1}J_{\rm P,C} =$ 60.50 Hz,  ${}^3J_{\rm P,C} = 5.02$  Hz) due to the PCH<sub>2</sub>P and PCH<sub>2</sub> groups, respectively. The carbonyl signal appeared as a singlet at  $\delta = 191.70$ . The <sup>1</sup>H NMR spectrum of II showed two doublets at  $\delta = 4.28 \ (^2J_{\rm P,H})$ = 15.21 Hz) and  $\delta$  = 4.99 (<sup>2</sup>J<sub>P,H</sub> = 13.50 Hz), which were assigned to the PCH<sub>2</sub>P and PCH<sub>2</sub>CO groups, respectively (Navarro & Urriolabeitia, 1999). A signal appearing at  $\delta = 4.81$  (singlet) was attributed to the CH<sub>2</sub>O group. The <sup>31</sup>P NMR spectrum exhibited two doublets at  $\delta = 20.17$  and  $\delta = -29.55$ , indicating the  $PCH_2CO$  and  $PPh_2$  groups, respectively. In the  ${}^{13}C$ NMR spectrum, two doublet of doublet signals were observed at  $\delta = 21.13$  ( ${}^{1}J_{\rm P,C} = 51.03$  Hz,  ${}^{1}J_{\rm P,C} = 36.00$  Hz) and  $\delta = 32.35$  ( ${}^{1}J_{\rm P,C} = 57.00$  Hz,  ${}^{3}J_{\rm P,C} =$ 2.02 Hz) due to the PCH<sub>2</sub>P and PCH<sub>2</sub> groups, respectively. The carbonyl signal appeared as a singlet at  $\delta$ = 164.27. A signal appearing at  $\delta = 68.11$  as a singlet was attributed to the CH<sub>2</sub>O group.

In the <sup>1</sup>H NMR spectra of *III* and *IV*, the CH signals of the ylides are shifted upfield compared with those of the phosphonium salts due to the electron density increasing in the P-C bonds and this interpretation holds true the increase of  ${}^{2}J_{\rm P,H}$  for III (Falvello et al., 2003). The <sup>31</sup>P NMR spectra showed two doublets around  $\delta = 11$  and  $\delta = -30$ , which were assigned to the PCH and PPh<sub>2</sub> groups, respectively (Vicente et al., 1991). In the  ${}^{13}C$  NMR spectra, a downfield shift for the CH signal was observed for ylides, suggesting low shielding of carbon atoms (replacing the  $CH_2$  group with the CH group) but increasing the electron density in the P—C bond. An upfield shift of C=O signals was also observed for ylides, which is due to the electron density increasing on the carbon atom.

The <sup>1</sup>H NMR spectrum of V exhibited, in addition to the aromatic resonances, two broad signals at  $\delta = 5.31$  related to a CH group bonded to the mercury atom and shifted downfield relative to the parent ylide III and signal at  $\delta = 4.69$  attributed to CH<sub>2</sub> group (Sabounchei et al., 2010d). The <sup>31</sup>P NMR spectrum exhibited a doublet at  $\delta = 26.58$  with a coupling constant  ${}^{2}J_{\rm P,P}$  of 41.12 Hz and a broad signal at  $\delta =$ 8.25, attributable to the PCH<sub>2</sub> and PPh<sub>2</sub> groups, respectively. The  ${}^{13}C$  NMR spectrum of V exhibited, in addition to the aromatic resonances, two broad signals at  $\delta = 24.27$  and  $\delta = 33.64$  due to the CH<sub>2</sub> and CH groups, respectively. The carbonyl signal appearing at  $\delta = 191.87$  was shifted downfield relative to the parent ylide. The <sup>1</sup>H NMR spectrum of VIII showed two broad signals at  $\delta = 4.34$  and  $\delta = 5.11$ , which were assigned to the PCH<sub>2</sub>P and CH groups, respectively.

The CH group bonded to the mercury atom resulted in a downfield shift relative to the parent vlide IV. A singlet at  $\delta = 4.81$  was attributed to the CH<sub>2</sub>O group. The <sup>31</sup>P NMR spectrum of VIII showed a doublet at  $\delta = 25.71$  with a coupling constant of 42.64 Hz and a broad signal at  $\delta = 6.20$ , attributable to the coordinated PPh<sub>2</sub> and to the uncoordinated phosphine atoms, respectively. The <sup>13</sup>C NMR spectrum of this complex exhibits, in addition to the aromatic resonances, two broad signals at  $\delta = 22.18$  and  $\delta = 35.87$ due to the CH<sub>2</sub> and CH groups, respectively. The carbonyl signal appearing at  $\delta = 162.25$  was shifted downfield relative to the parent ylide. A singlet at  $\delta = 64.38$ was attributed to the CH<sub>2</sub>O group. The NMR data of complexes IX and X were similar to those of VIII (Table 2).

The IR data (Table 2) confirmed the formation of the phosphorus ylides with the disappearance of the C=O bands at 1669 cm<sup>-1</sup> and 1729 cm<sup>-1</sup> in phosphonium salts I and II and the presence of new strong C=O bands at 1565 cm<sup>-1</sup> and 1583 cm<sup>-1</sup> of stabilised ylides III and IV, respectively (Sbovata et al., 2008; Vicente et al., 1991). The upward frequency shift of the  $\nu$ (C=O) absorption in complexes, with reference to the free ylides III and IV, strongly indicates coordination of the ylides through the ylidic carbon atom (Sabounchei et al., 2010c; Kalyanasundari et al., 1995).

## X-ray crystallography

The crystallographic results and refinement information for compounds III and XI are summarised in Table 3. Colourless crystals of *III* were obtained from a toluene solution by slow evaporation of the solvent. An ORTEP plot (Fig. 3) shows that the geometry of molecule III around the P atom is almost tetrahedral, and the O atom is *cis*-oriented to the P(1) atom. The P1—C14 (1.722(3) Å) and C13—C14 (1.409(4))Å) bond lengths are shorter than the  $(P^+ - C(sp^3))$ (1.800 Å) and  $(C - C(sp^3) (1.511 \text{ Å})$  normal values, respectively. This is due to the ylidic resonance and intermediate between the common values for the single P-C bond (1.80 Å) and double P=C bond (1.66 Å). The C=O bond (1.253(3) Å) is also longer than the normal value (1.210 Å). This bond distance suggests electron delocalisation in this molecule (Sabounchei et al., 2010d). The relevant bond lengths and angles of III are given in Table 4.

As for the slightly higher *R*-factors observed for compound *III*, it should be noted that some atoms have a high thermal parameter due to the data being collected at ambient temperature. An attempt was made to refine these atoms in two positions with reduced occupancy but, while this model converged satisfactorily, there was no decrease in *R*-value, hence it was concluded that the original refinement represented the best that could be achieved and should be

Table 3. Crystal data and refinement details for III and XI

Demonster	Compound III	Compound XI		
rarameter	Value	Value		
Empirical formula	$C_{39}H_{32}OP_2$	$C_{34}H_{30}OP_2Br_2Hg$		
Formula mass	578.59	876.93		
Temperature, $T(\mathbf{K})$	298(2)	129.98(10)		
Wavelength (Å)	0.71073	0.71073		
Crystal system	Triclinic	monoclinic		
Space group	P1	$P2_1/c$		
a (Å)	10.4034(18)	12.9904(3)		
b (Å)	11.964(2)	16.2273(3)		
c (Å)	13.943(2)	15.6988(3)		
$\alpha$ (°)	108.260(13)	90.007(3)		
$\beta$ (°)	98.298(13)	106.953(3)		
$\gamma$ (°)	103.846(14)	90.004(3)		
Formula per unit cell, $Z$	2	4		
Absorption coefficient, $\mu \ (mm^{-1})$	0.170	3.457		
$\theta$ range for data collection (°)	1.58 to 29.22	3.56 to 77.21		
Index ranges	$-14 \leq h \leq 14$	$-16 \leq h \leq 16$		
	$-15 \leq k \leq 16$	$-20 \leq k \leq 19$		
	$-19 \leq l \leq 19$	$-14 \leq l \leq 19$		
Reflections collected	17402	32394		
Independent reflections	$8330 \ [R(int) = 0.0800]$	$6675 \ [R(int) = 0.0529]$		
Refinement method	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$		
Goodness-of-fit on $F^2$	1.036	1.060		
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.1011, wR_2 = 0.2111$	$R_1 = 0.0328, wR_2 = 0.0858$		
R indices (all data)	$R_1 = 0.1234, wR_2 = 0.2146$	$R_1 = 0.0382, wR_2 = 0.0909$		
Largest diff. peak and hole $(e \cdot A^{-3})$	0.872  and  -0.356	2.07  and  -1.18		

**Table 4.** Selected bond lengths (Å) and bond angles (°) for III and  $XI^a$ 

Compound	Bond	Bond length	Bond	Bond angle
III	C14—P1	1.722(3)	C14—P1—C27	111.33(13)
	C13—C14	1.409(4)	C14—P1—C15	107.30(13)
	C13—O1	1.253(3)	C27—P1—C15	108.92(14)
	C27—P1	1.801(3)	C14—P1—C21	115.40(14)
	-	_	C27—P1—C21	107.10(13)
	_	_	C15—P1—C21	106.56(13)
XI	C1—Hg1	2.407(3)	C1—Hg1—P2	90.69(8)
	P2—Hg1	2.504(1)	C1—Hg1—Br2	113.71(8)
	Hg1—Br2	2.5581(5)	P2— $Hg1$ — $Br2$	115.82(2)
	Hg1—Br1	2.6059(4)	C1—Hg1—Br1	108.44(8)
	C2—O1	1.234(4)	P2—Hg1—Br1	117.67(2)
	C1—P1	1.759(4)	Br2—Hg1—Br1	109.20(2)
	-	_	C2-C1-P1	113.1(2)
	-	_	C34— $P2$ — $Hg1$	101.0(1)
	_	_	C1—P1—C34	112.2(2)

a) Standard deviations in parentheses.

reported. On the other hand, this compound slowly decomposed even under perfluoropolyether oil and the crystal used for data collection incurred some damage.

Suitable crystals of XI were obtained from dimethyl sulphoxide solution by slow evaporation of the solvent for twenty days. The molecular structure of complex XI is shown in Fig. 4 and the relevant bond lengths and bond angles are given in Table 4. The Hg(II) atom is located in a distorted tetrahedral environment with 'P' and 'C' atoms. The remaining positions are occupied by the bromide atoms. The coordination environment around Hg(II) closely resembles those found in {HgI<sub>2</sub>[(PPh<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>C(H)C(O)Ph)]} (Ebrahim et al., 2009) and {HgI<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)]} (Sabounchei et al., 2010c). The ligand coordinates to the metal via 'P' and ylidic 'C' atoms to form a five-membered chelate. The Hg—P bond length in XI (2.504(1) Å) is comparable with the analogous distance in Hg(II)–phosphine complexes such as {HgI<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>NO<sub>2</sub>)]}

**Table 5.** Short contacts distances (Å) for XI

Short contacts	$C12 \cdot \cdot \cdot H24$	$Br1 \cdot \cdot \cdot H27$	$Br1 \cdot \cdot \cdot H15$	$Br1 \cdot \cdot \cdot H34A$	$C5 \cdot \cdot \cdot H34B$	$H5 \cdot \cdot \cdot O1$	$H5 \cdot \cdot \cdot H34B$	$H9B \cdot \cdot \cdot O1$
Distances/Å	2.796	2.822	2.894	2.814	2.839	2.414	2.276	2.652



Fig. 3. Molecular structure of *III* with ellipsoids at 50 % probability level.



Fig. 4. Molecular structure of XI with ellipsoids at 50 % probability level. Hydrogen atoms are omitted for clarity.

(2.5199(19) Å) (Sabounchei et al., 2010b) and {HgBr<sub>2</sub> [(PPh<sub>3</sub>)<sub>2</sub>]} (2.550(4) Å) (Kubicki et al., 2001). The terminal Hg—Br distances in XI (2.5581(5) Å and 2.6059(4) Å) are comparable with analogous distances in {HgBr<sub>2</sub>[(PPh<sub>3</sub>)<sub>2</sub>]} (2.626(8) Å and 2.633(6) Å) (Bell et al., 1983) and {HgI<sub>2</sub>[(Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>C(H)  $C(O)C_6H_4Cl)$ ]} (2.7270(14) Å and 2.7483(3) Å) (Sabounchei et al., 2010c). The resonance-stabilised structures in the parent ylide are destroyed by the complex formation, hence the C1—C2 bond length of 1.456(5) Å is longer than the corresponding distances



Fig. 5. Representation of intermolecular contacts of XI. Dashed lines represent short contacts.

found in similar uncomplexed phosphoranes such as  $[Ph_2PCH_2PPh_2C(H)C(O)Ph]$  (1.404(3) Å) (Ebrahim et al., 2009). Similarly, the C14—P1 bond length in uncoordinated ylide *III* is 1.722(3) Å, indicating that the corresponding bond lengths (C1—P1) in *XI* are considerably elongated to 1.759(4) Å. The structure of *XI* has short contacts between the adjacent molecules. In this case, the interactions between the O atom and H atoms of the phenyl and methyl groups (2.414 Å and 2.652 Å, respectively) assume great importance to form the packing structure (Fig. 5). The lengths of all short contacts are reported in Table 5.

#### Conclusions

The present study describes the synthesis and characterisation of a series of chelate mercury(II) complexes derived from mercuric halides and new mixed phosphine–phosphonium ylides. The physicochemical and spectroscopic data indicate that the ligands exhibit bidentate P,C-coordination to the metal centre.

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## Supplementary data

Crystallographic data for compounds III and XI are deposited in the Cambridge Crystallographic Data Centre, CCDC no. 856742 and CCDC no. 879884, respectively. Copies of the information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data\_request/cif).

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