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Structural, theoretical and multinuclear NMR study of mercury(II) complexes with a new ambidentate phosphorus ylide

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ABSTRACT

The reaction of the new ambidentate ylide, $Ph_3PCHCOCH_2COOC_2H_5$ (EAPPY), with HgX_2 (X = Cl, Br and I) in equimolar ratios using methanol as the solvent leads to binuclear complexes of the type $[EAPPY{\cdot}HgX_2]_2$ (X = Cl (**1**), Br (**2**) and I (**3**)). Single crystal X-ray analysis reveals the presence of a centrosymmetric dimeric structure containing the ylide and HgX_2 (X = Br or I). The IR and NMR data of the product $[(EAPPY){\cdot}HgCl_2]_2$ (**1**), formed by the reaction of mercury(II) chloride with the same ylide, are similar to those of **2** and **3**. Analytical data indicate a 1:1 stoichiometry between the ylide and Hg(II) halide in each of the three products. Theoretical studies indicate that the nature of the R group in ylides of the type $Ph_3PCHCOR$ has a weak effect on the Hg–C(ylide) bond length in binuclear $Hg_2L_2I_4$ complexes.

1. Introduction

The organometallic chemistry of phosphorus ylides $R_3P = C(R')(R'')$ (R, R′, R″ = alkyl or aryl groups) has undergone great growth over the last few years, mainly due to their interesting application as reactants in organometallic and metal-mediated organic synthesis [1–4]. Juxtaposition of the keto group and carbanion in the phosphorus ylide EAPPY allows for resonance delocalization of the ylidic electron density, providing additional stabilization to the ylide species (Scheme 1). This so-called α-stabilization provides EAPPY with the potential to act as an ambidentate ligand and thus bond to a metal center through either the carbanion (b) or the enolate oxygen (c). The enolate from (c) may assume either a cis or trans arrangement, the geometry of which will be retained upon bonding to the metal.

In the compounds reported to date, coordination through carbon is more predominant and is observed with soft metal ions, e.g., Hg(II), Pd(II), Pt(II), Ag(I), Au(I) and Au(III) [5–9] and only very few examples of O-coordinated ylides are known [10–13]. Some of these examples contain the ylide O-coordinated to a hard, very oxophilic metal center, such as Sn(IV) [10,11] or group 4 metals with a high oxidation number e.g., Ti(IV), Zr(IV) and Hf(IV) [12]. Only W(0) complexes of the type $W(CO)_5L$ (L = ylide) [13] and Pd(II) complexes of the stoichiometry $[Pd(C_6F_5)L_2)(APPY)](ClO_4)$ [14] [APPY = Ph_3CCOMe; L = PPh_3, PBu_3; L_2 = bipy] contain stable ylides O-linked to a soft metal center.

We have recently focused on the synthesis of binuclear complexes derived from mercury(II) salts and phosphorus ylides [15,16]. The aims of our present work are to describe the preparation and spectroscopic characterization of Hg(II) binuclear complexes. The X-ray crystal structures of complexes **2** and **3** demonstrate C-coordination of the ylide to a metal. We also report here a theoretical study on binuclear $Hg_2L_2I_4$ complexes in which the ligands L are a series of ylides of the type $Ph_3PCHCOR$.

2. Experimental

2.1. Physical measurements and materials

All reactions were performed in air. Methanol was distilled over magnesium powder and diethyl ether over a mixture of sodium and benzophenone just before use. All other solvents were reagent grade and used without further purifications. The ligand was synthesized by the reaction of triphenylphosphine with a chloroform solution of the phosphonium salt and concomitant elimination of HCl by NaOH [17]. Melting points were measured on a Stuart SMP3 apparatus. Elemental analysis for C, H and N were performed using a Perkin-Elmer 2400 series analyzer. Fourier transform IR spectra were recorded on a Shimadzu 435-U-04 spectrophotometer and samples were prepared as KBr pellets. ^1H, ^{31}P and ^{13}C NMR spectra were recorded on 300 MHz Bruker and 90 MHz Jeol spectrometers.

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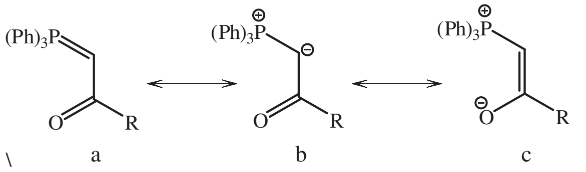


Scheme 1. The canonical forms of EAPPY (R = $CH_2COOC_2H_5$).

2.2. X-ray crystallography

The single crystal X-ray diffraction analysis of suitable crystals of **2** and **3** were performed on a STOE IPDS-II diffractometer at 298 K, using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The data collection was performed using the ω-scan technique and using the STOE X-AREA software package [18]. The crystal structures were solved by direct methods and refined by full-matrix least-squares on F^2 by SHELX [19] and using the X-STEP32 crystallographic software package [20]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted at calculated positions using a riding mode with fixed thermal parameters. Residual densities of 2.485 and −2.228 e Å^{-3} for **2** and 3.572 and −3.173 e Å^{-3} for **3** are near to the heavy Hg atoms (0.95 and 0.91 Å from Hg1 in **2** and 1.25 and 0.79 Å from Hg1 in **3**).

2.3. Computational methods

The geometries of all the compounds were fully optimized at the DFT (B3LYP) [21,22] level of theory using the GAUSSIAN 03 [23] set of programs. Three different standard basis sets LanL2MB, Lanl2DZ and CEP-121G were used in all calculations to study the possible effect of the basis set. All the above basis sets include effective core potentials (ECP) for mercury, phosphorus and halide (Br and I) atoms. In the case of all $Hg_2L_2X_4$ complexes and the corresponding free ligands, the atomic coordinates for DFT calculations were obtained from the data of the X-ray crystal structure analyses [15,16,24,25].

2.4. Sample preparation

2.4.1. Synthesis of EAPPY

To a chloroform solution (10 mL) of triphenylphosphine (0.262 g, 1 mmol) was added ethyl-4-chloroacetoacetate (0.164 g, 1 mmol) and the mixture was stirred for 12 h. The solid product (phosphonium salt) was filtered off, washed with Et_2O and dried under reduced pressure. Further treatment with aqueous NaOH solution led to elimination of HCl, giving the free ligand EAPPY. Yield: 94%, m.p. 86–88 °C. *Anal.* Calc. for $C_{24}H_{23}O_3P$: C, 73.84; H, 5.94. Found: C, 74.21; H, 6.22%. IR (KBr disk) ν (cm^{-1}): 1546 (CO) and 870 ($P^+–C^-$). ^1H NMR ($CDCl_3$, ppm) δ_H: 3.80 (d, $^2J_{PH}$ = 24.19 Hz, 1H, CH), 7.51–7.73 (m, 15H, arom.), 3.33 (s, 2H, CH_2), 4.16 (q, $^3J_{HH}$ = 7.17 Hz, 2H, CH_2), 1.25 (t, $^3J_{HH}$ = 7.17 Hz, 3H, CH_3). ^{31}P NMR ($CDCl_3$, ppm) δ_P: 12.50. ^{13}C NMR ($CDCl_3$, ppm) δ_C: 52.50 (d, $^1J_{PC}$ = 107.30 Hz, CH), 126.58 (d, $^1J_{PC}$ = 90.56 Hz, PPh_3(i)), 133.11 (d, $^2J_{PC}$ = 10.16 Hz, PPh_3(o)), 128.86 (d, $^3J_{PC}$ = 12.21 Hz, PPh_3(m)), 132.13 (s, PPh_3(p)), 60.42 (s, CH_2), 14.23 (s, CH_3), 48.28 (d, $^3J_{PC}$ = 15.41 Hz, CH_2), 170.68 (s, OCO), 184.02 (s, CO).

2.4.2. Synthesis of the Hg(II) halide dimeric complexes

2.4.2.1. General procedure. To HgX_2 (0.5 mmol) dissolved in 10 mL of dried methanol was added the ylide EAPPY (0.195 g, 0.5 mmol) at room temperature. The mixture was stirred for approximately 4 h. The white solid product was filtered, washed with Et_2O and dried under reduced pressure.

2.4.2.2. Data for 1. Yield: 83%, m.p. 178–180 °C. *Anal.* Calc. for $C_{48}H_{46}Cl_4Hg_2O_6P_2$: C, 43.55; H, 3.50. Found: C, 43.28; H, 3.73%. IR (KBr disk) ν (cm^{-1}): 1671 (CO) and 800 ($P^+–C^-$). ^1H NMR (DMSO-d$_6$, ppm) δ_H: 4.82 (br, 1H, CH), 7.66–7.76 (m, 15H, arom.), 3.73 (s, 2H, CH_2), 4.05 (q, $^3J_{HH}$ = 6.98 Hz, 2H, CH_2), 1.16 (t, $^3J_{HH}$ = 6.98 Hz, 3H, CH_3). ^{31}P NMR (DMSO-d$_6$, ppm) δ_P: 20.49. ^{13}C NMR (DMSO-d$_6$, ppm) δ_C: 51.63 (br, CH), 123.60 (d, $^1J_{PC}$ = 89.50 Hz, PPh_3(i)), 133.75 (d, $^2J_{PC}$ = 10.04 Hz, PPh_3(o)), 130.04 (d, $^3J_{PC}$ = 12.07 Hz, PPh_3(m)), 134.05 (s, PPh_3(p)), 60.85 (s, CH_2), 14.52 (s, CH_3), 48.51 (s, CH_2), 168.42 (s, OCO), 191.93 (s, CO).

2.4.2.3. Data for 2. Yield: 83%, m.p. 176–178 °C. *Anal.* Calc. for $C_{48}H_{46}Br_4Hg_2O_6P_2$: C, 38.39; H, 3.09. Found: C, 38.56; H, 3.21%. IR (KBr disk) ν (cm^{-1}): 1667 (CO) and 796 ($P^+–C^-$). ^1H NMR (DMSO-d$_6$, ppm) δ_H: 4.61 (br, 1H, CH), 7.64–7.73 (m, 15H, arom.), 3.60 (s, 2H, CH_2), 4.07 (q, $^3J_{HH}$ = 7.17 Hz, 2H, CH_2), 1.17 (t, $^3J_{HH}$ = 7.17 Hz, 3H, CH_3). ^{31}P NMR (DMSO-d$_6$, ppm) δ_P: 20.09. ^{13}C NMR (DMSO-d$_6$, ppm) δ_C: 52.27 (br, CH), 123.09 (d, $^1J_{PC}$ = 87.77 Hz, PPh_3(i)), 133.16 (d, $^2J_{PC}$ = 9.93 Hz, PPh_3(o)), 129.51 (d, $^3J_{PC}$ = 11.80 Hz, PPh_3(m)), 133.38 (s, PPh_3(p)), 60.39 (s, CH_2), 14.01 (s, CH_3), 47.95 (s, CH_2), 167.99 (s, OCO), 190.03 (s, CO).

2.4.2.4. Data for 3. Yield: 81%, m.p. 165–167 °C. *Anal.* Calc. for $C_{48}H_{46}I_4Hg_2O_6P_2$: C, 34.18; H, 2.75. Found: C, 34.02; H, 2.88%. IR (KBr disk) ν (cm^{-1}): 1657 (CO) and 786 ($P^+–C^-$). ^{31}P NMR (DMSO-d$_6$, ppm) δ_P: 18.89. ^1H NMR (DMSO-d$_6$, ppm) δ_H: 4.40 (br, 1H, CH), 7.61–7.68 (m, 15H, arom.), 3.46 (s, 2H, CH_2), 4.07 (q, $^3J_{HH}$ = 7.17 Hz, 2H, CH_2), 1.17 (t, $^3J_{HH}$ = 7.17 Hz, 3H, CH_3). ^{13}C NMR (DMSO-d$_6$, ppm) δ_C: 52.02 (br, CH), 124.11 (d, $^1J_{PC}$ = 77.59 Hz, PPh_3(i)), 133.66 (d, $^2J_{PC}$ = 8.45 Hz, PPh_3(o)), 129.95 (d, $^3J_{PC}$ = 11.77 Hz, PPh_3(m)), 133.94 (s, PPh_3(p)), 60.84 (s, CH_2), 14.66 (s, CH_3), 48.85 (s, CH_2), 168.79 (s, OCO), 189.56 (s, CO).

3. Results and discussion

3.1. Spectroscopy

The infrared data of the ligands as well as the corresponding metal complexes are listed in Table 1. The ν_{CO} absorption, which is sensitive to complexation, occurs at 1546 cm^{-1} in the parent ylide, as in the case of other resonance-stabilized ylides [26]. Coordination of the ylide through the carbon atom cause an increase in ν_{CO}, while for O-coordination a lowering of ν_{CO} is expected. The infrared spectra of complexes in the solid state show ν_{CO} in the range 1657–1671 cm^{-1}, at higher frequencies with respect to the free ylide. The $\nu_{P^+–C^-}$ frequency, which is also diagnostic of the coordination, occurs at 870 cm^{-1} for EAPPY. In the present study,

Table 1
Assignment of characteristic FT-IR vibrations of the ligands and their complexes.

Compound	IR bond (cm^{-1}) $\nu_{C=O}$	Ref.
$Ph_3PCHCOPh$ (BPPY)	1525	[27]
$Ph_3PCHCON(CH_3)_2$	1530	[28]
$Ph_3PCHCOCH_3$ (APPY)	1530	[29]
$Ph_3PCHCOCH_2COOC_2H_5$ (EAPPY)	1546	a
C-coordination		
$[(EAPPY){\cdot}HgCl_2]_2$	1671	a
$[(EAPPY){\cdot}HgBr_2]_2$	1667	a
$[(EAPPY){\cdot}HgI_2]_2$	1657	a
$Au[CH(PPh_3)(CON)(CH_3)_2]Cl$	1605	[28]
$BPPY{\cdot}HgCl_2$	1635	[5]
O-coordination		
$[(Sn(CH_3)_3{\cdot}BPPY]Cl$	1480	[17]

[a] This work.

the $\nu_{P^+-C^-}$ values for all the complexes were shifted to lower frequencies and were observed in the range 786–843 cm^{-1}, suggesting some removal of electron density from the P–C bond [27,28].

In the ^1H NMR spectra, the signals due to the methinic protons were broad or unobserved, probably due to the very low solubility of these complexes. The expected higher frequency shifts of the ^{31}P and ^1H signals for the PCH group upon complexation were observed in their corresponding spectra. The $^{31}P\{^1H\}$ NMR spectra show only one sharp singlet between δ 18.89 and 20.49 ppm for these complexes. The ^{31}P chemical shift values for the complexes appear to higher frequency by about δ 6–8 ppm with respect to the parent ylide ($\delta = 12.50$ ppm), indicating coordination of the ylide has occurred (Table 2).

The appearance of one set of signals for the PCH group in both the ^{31}P- and ^1H NMR spectra indicates the presence of only one molecule for all complexes [5], as expected for C-coordination. It must be noted that O-coordination of the ylides generally leads to the formation of cis and trans isomers, giving rise to two different signals in the ^{31}P- and ^1H NMR spectra [12,14].

The most interesting aspect of the ^{13}C NMR spectra of the complexes is the upfield shift of the signals due to the ylidic carbon. Such an upfield shift observed in $PdCl(\eta^3\text{-}2\text{-}XC_3H_4)(C_6H_5)_3PCHCOR$ ($X = H, CH_3$; $R = CH_3, C_6H_5$) was attributed to the change in hybridization of the ylidic carbon [29]. Similar upfield shifts of δ 2–3 ppm with reference to the parent ylide were also observed in the case of $[(C_6H_5)_3PC_5H_4HgI_2]_2$ [30] and our synthesized complexes [27,31]. The ^{13}C shifts of the CO group in the complexes are around 190 ppm, relative to 183.91 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 metal ions was observed at room temperature in the ^1H-, ^{13}C- and ^{31}P NMR spectra for all these complexes. Failure to observe satellites in the above spectra was previously noted in ylide complexes of Hg(II) [32], which had been explained by fast exchange of the ylide with the metal.

3.2. X-ray crystallography

The crystals of complexes **2** and **3** were grown by the slow evaporation of the dimethylsulfoxide solution over several days. The solid state structures of complexes **2** and **3** have been established by single crystal X-ray analysis, which revealed monoclinic and triclinic systems, respectively. Table 3 provides the crystallographic results and refinement for the complexes. The molecular structures are shown in Figs. 1 and 2, and selected interatomic parameters are collected in Table 4. It is to be noted that according to data collection at room temperature, the ethylacetoacetate side chain in **2**, has a high thermal parameter. We tried refining some of these atoms in two positions with a reduced occupancy, but while this model converged satisfactorily, there was no decrease in the R value and therefore we consider that our original refinement is the best that can be achieved and should be reported.

Table 2
^{31}P and ^1H NMR data of the ligands and their mercury(II) halide complexes.

Compound	$^{31}P\{^1H\}$ NMR[a]	CH	$^2J_{(P-H)}$
EAPPY[b]	12.50 (s)	3.80 (d)	24.19
$[EAPPY{\cdot}HgCl_2]_2$[c]	20.49 (s)	4.82 (br)	
$[EAPPY{\cdot}HgBr_2]_2$[c]	20.09 (s)	4.61 (br)	
$[EAPPY{\cdot}HgI_2]_2$[c]	18.89 (s)	4.40 (br)	

s, Singlet; d, doublet; br, broad.

[a] $T = 298$ K; TMS $\delta = 0.00$ ppm; shifts relative to internal TMS and external 85% phosphoric acid.

[b] Record in $CDCl_3$.

[c] Record in DMSO-d_6.

Table 3
Crystal data and refinement details for **2** and **3**.

Empirical formula	$C_{48}H_{46}Br_4Hg_2O_6P_2$	$C_{48}H_{46}Hg_2I_4O_6P_2$
Formula weight	1501.57	1689.57
T (K)	298(2)	120(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	triclinic
Space group	*Pc*	$P\bar{1}$
Unit cell dimensions		
a (Å)	10.4551(9)	10.2208(7)
b (Å)	11.8372(9)	10.8141(7)
c (Å)	20.9539(17)	12.9264(8)
α (°)		72.206(5)
β (°)	98.658(7)	72.207(5)
γ (°)		73.452(5)
V ($Å^3$)	2563.7(4)	1266.11(14)
Z	2	1
Calculated density (mg/m^3)	1.945	2.216
Absorption coefficient (mm^{-1})	9.205	8.602
F(0 0 0)	1424	784
Crystal size (mm)	0.15 × 0.11 × 0.10	0.29 × 0.23 × 0.21
θ Range for data collection (°)	1.72–29.27	1.70–29.18
Limiting indices	$-14 \le h \le 10$ $-16 \le k \le 16$ $-28 \le l \le 28$	$-14 \le h \le 13$ $-14 \le k \le 14$ $-17 \le l \le 17$
Reflections collected/unique	19 869/11 878 [$R_{int} = 0.0927$]	14 537/6741 [$R_{int} = 0.0438$]
Completeness (%)	98.8	98.7
Absorption correction	numerical	numerical
Maximum and minimum transmission	0.401 and 0.310	0.956 and 0.915
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	11 787/3/561	6741/0/280
Goodness-of-fit (GOF) on F^2	1.130	1.099
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0759$, $wR_2 = 0.1738$	$R_1 = 0.0334$, $wR_2 = 0.0876$
R indices (all data)	$R_1 = 0.1088$, $wR_2 = 0.2003$	$R_1 = 0.0344$, $wR_2 = 0.0882$
Largest difference in peak and hole (e $Å^{-3}$)	2.485 and −2.228	3.572 and −3.173
Flack parameter	0.013(15)	

Single crystal X-ray diffraction analysis showed that complex **2** crystallized in the trigonal chiral *Pc* space group with a flack parameter of 0.013(15) throughout, with $Z = 2$, so that one merucry dimer complex is crystallographically independent. On the other hand, complex **3** crystallized in the $P\bar{1}$ space group throughout, with $Z = 1$, so that 1/2 of the complex is crystallographically independent. The dimeric structures adopted by the mercury complexes are in contrast to the O-coordinated trinuclear mercury(II) complex of the phosphorus ylide $Ph_3PCHCOPh$ [33], but they are similar to the structure of trans-di-μ-iodo-diiodobis(tri-phenylphosphoniumcyclopentadienylide) dimercury(II) reported by Baenziger et al. [34] and the C-coordinated dinuclear mercury(II) halide complexes of $Ph_3CHCOPh$ (BPPY) [5]. The C-coordination of EAPPY is in stark contrast to the O-coordination of the phosphorus ylide, $Ph_3PC(COMe)(COPh)$ (ABPPY) to a Hg(II) center [35]. The difference in the coordination mode of ABPPY and the present ylide to Hg(II) can be rationalized in terms of the electronic properties and steric requirements of the ylides.

The nucleophilicity of the carbanion in ABPPY is less than for EAPPY; this is due to the additional delocalization of the ylide electron density in ABPPY which is facilitated by the second carbonyl group. This will reduce the ability of ABPPY to bind via the ylidic carbon. Facchin and co-workers have studied the steric influences on the coordination modes of ylide molecules to Pt(II) systems [36]. This research group concluded that the preferred coordination takes place via the ylidic C-atom, but that steric hindrance around the metal center or the ylidic C-atom will necessitate O-coordination. Indeed, this trend is reflected here, both BPPY and

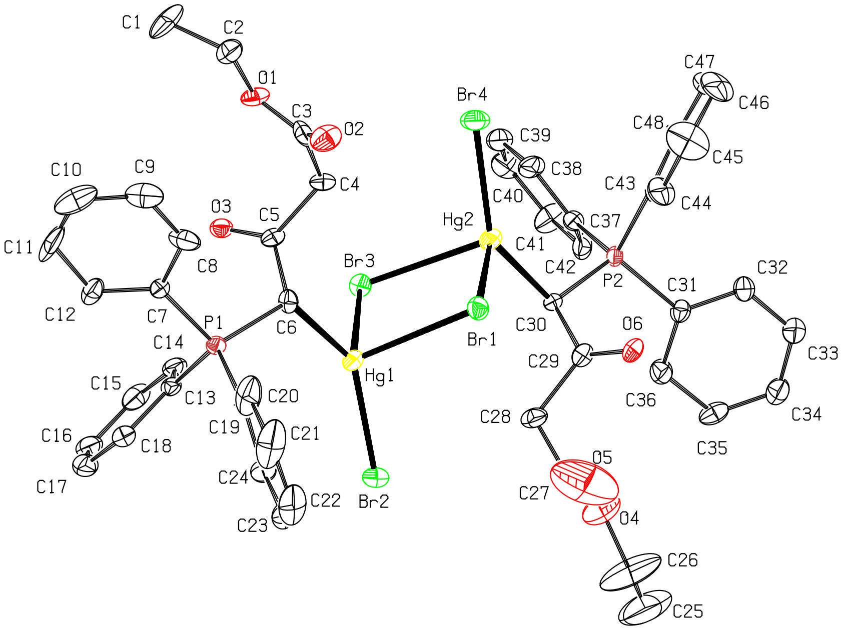


Fig. 1. Thermal ellipsoid plot of **2** (30% probability level) showing the numbering scheme. H atoms are omitted for clarity.

EAPPY are slightly less sterically demanding than ABPPY, and both are C-coordinated to Hg(II).

The Hg(II) center forms four close contacts with sp^3 hybridization and has a four-coordinate environment with one short Hg–X, one Hg–C bond and two asymmetric bridging Hg–X bonds at distances of 2.779(2) and 2.831(2) Å in **2** and 2.8411(3) and 3.0348(4) Å in **3**. The significant shortening of the Hg–C bond length, 2.205(19) Å in **2** and 2.234(4) Å in **3**, compared to analogous distances in $[EPPY{\cdot}HgBr_2]_2$ [5,24] and in $[(C_5H_4P(C_6H_5)_3HgI_2]_2$ [37] (2.224(5) and 2.292(8) Å , respectively) must be attributed to the use of mercury orbitals with high s character for bonding to the ylidic carbon. The use of non-equivalent hybrid orbitals with high s character to bond to low electronegative atoms was proposed by Bent in the concept of isovalent hybridization to account for the variation in bond lengths and bond angles around a central atom [38].

The terminal Hg–X bond lengths, 2.490(3) Å in **2** and 2.6950(4) Å in **3**, are comparable to the value of 2.578 Å observed in the case of $C_{22}H_{21}O_2PHgBr_2$, which has a tetrahedral coordination environment around mercury with a bridging structure [24]. The two bridged Hg–X bonds fall within the range 2.779(2)–2.859(2) Å for **2** and 2.8411(3)–3.0348(4) Å for **3** reported for other structures [39] containing bromo and iodo bridged mercury.

The angles around mercury vary from 87.61(6)° to 140.9(4)° for **2** and 91.819(10)° to 125.83(10)° for **3**, a much distorted tetrahedral environment. This distortion must be due to the higher s character of the sp^3 hybrid mercury orbitals involved in the above bonds and the formation of a strong halogen bridge between the Hg atoms, which requires the internal XHgX angle to be considerably smaller.

The stabilized resonance structure for EAPPY is destroyed by the complexes formation. Thus, the C(5)–C(6) bond length of 1.50(2) Å in **2** and the C(20)–C(19) bond length of 1.483(5) Å in **3** are significantly longer than the corresponding bond found in a similar uncomplexed phosphorane (1.407(8) Å) [40]. On the other hand, the P(1)–C(6) bond length in **2** and C(19)–P(1) bond length in **3** in the similar ylide is 1.706 Å [14], which shows that the above bond is considerably elongated to 1.776(17) and 1.792(4) Å, respectively, in the complexes. The internuclear distances between the mercury atoms were found to be 4.046(7), 4.091 and 4.014(1) Å in the structures **2**, **3** and $[BPPY{\cdot}HgBr_2]_2$, respectively These distances are much longer than the sum of Van der Waals radii (1.5 Å) of two mercury atoms [41], indicating the absence of any significant bonding interactions between the mercury atoms in the molecular structures. The adaptation of dimeric structures in Hg(II) ylide complexes may be explained by both the preference of Hg(II) to have four coordination and the stability of the 18 electron configuration around Hg(II).

3.3. Theoretical studies

In our previous works we have reported the relative stability of trans-like isomers versus cis-like isomers for a number of binuclear metal ylide complexes [15,31,42]. In addition we have compared C-coordination versus O- and P-coordination for a number of ylides [43]. The reaction of a solvent molecule with binuclear metal ylide complexes producing the corresponding mononuclear complexes also has been previously studied [42,44,45]. In this work we have compared the structure and metal–ylide bond strength in a number of binuclear metal ylide complexes. We were interested to compare the characteristic bond distances in compounds **2** and **3** with those in a number of metal complexes containing similar ylides. Also we were interested to see how much the energy of reaction (1) is different for various ylides. Thus we chose a number of binuclear complexes of Hg(II) with similar ylides for which the X-ray crystal structures and related CIFs were available (see Scheme 2).

$$2Hg^{2+} + 2L + 4X^{-} \rightarrow Hg_2L_2X_4 \qquad (1)$$

The optimized structures of all the complexes are shown in Fig. 3. A comparison between the selected calculated bond lengths (Å) for the complexes with the corresponding experimental values are presented in Table 5. The calculated electronic energies (Hartree) for the studied complexes and their components using different basis sets are given in Table 6. As can be seen in Table 5, the calculated bond lengths using all basis sets are slightly longer than the measured ones, but the results of CEP-121G calculations are closer to the experimental data. Interestingly, the results of all calculations, similar to experimental data, show that the longest P–C(ylide) bond length exists in $Hg_2L^E{}_2I_4$. Also the results of LanL2MB and LanL2DZ calculations show that, similar to the solid state, the longest Hg–C(ylide) bond length exists in $Hg_2L^E{}_2I_4$. On the other

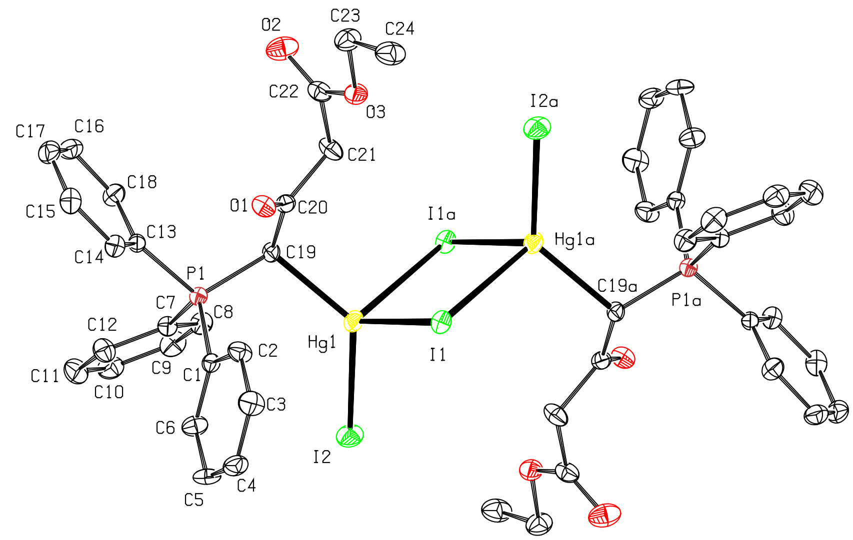
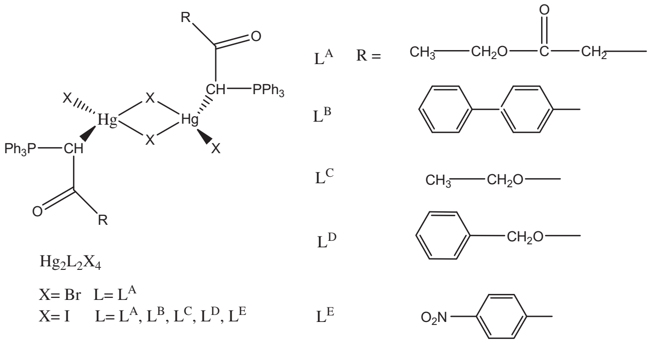


Fig. 2. Thermal ellipsoid plot of **3** (50% probability level) showing the numbering scheme. H atoms are omitted for clarity. Symmetry code; a: −*x* + 1, −*y* + 1, −*z*+.

Table 4
Selected bond lengths (Å) and bond angles (°) for **2** and **3**.

Bond distances			
2		**3**	
C5–C6	1.50(2)	C20–C19	1.483(5)
C6–P1	1.776(17)	C19–P1	1.792(4)
C6–Hg1	2.205(19)	C19–Hg1	2.234(4)
C5–O3	1.21(2)	C20–O1	1.217(5)
C4–C5	1.51(3)	C21–C20	1.523(5)
C7–P1	1.824(19)	C13–P1	1.801(4)
C13–P1	1.803(19)	C1–P1	1.805(4)
C19–P1	1.769(15)	C7–P1	1.796(4)
Br1–Hg1	2.831(2)	I1–Hg1	2.8411(3)
Br2–Hg1	2.490(3)	I2–Hg1	2.6950(4)
Br3–Hg1	2.779(2)	I1a–Hg1	3.0348(4)
Br1–Hg2	2.812(2)		
Br3–Hg2	2.859(2)		
Br4–Hg2	2.503(3)		
Bond angles			
C5–C6–P1	113.0(13)	C20–C19–P1	112.5(3)
C5–C6–Hg1	107.6(11	C20–C19–Hg1	110.3(3)
P1–C6–Hg1	112.7(9)	P1–C19–Hg1	109.52(18)
O3–C5–C6	123.0(16)	O1–C20–C19	123.2(4)
O3–C5–C4	120.3(15)	O1–C20–C21	120.4(4)
C6–C5–C4	116.6(15)	C19–C20–C21	116.4(3)
C6–Hg1–Br2	140.9(4)	C19–Hg1–I2	125.83(10)
C6–Hg1–Br1	99.3(5)	C19–Hg1–I1	100.74(10)
Br2–Hg1–Br3	106.48(9)	I2–Hg1–I1a	103.469(12)
Br1–Hg1–Br3	88.82(6)	I1–Hg1–I1a	91.819(10)
Br1–Hg2–Br3	87.61(6)	I2 Hg1–I1	112.036(11)
Br4–Hg2–Br1	103.67(9)	Hg1–I1–Hg1a	88.180(9)
C30–Hg2–Br1	106.4(4)		
C30–Hg2–Br4	140.5(4)		

See Figs. 1 and 2 for the atom numbering. Symmetry code; a: −*x* + 1, −*y* + 1, −*z* + 1.



Scheme 2. Schematic illustration of complexes studied here.

hand, both the experimental data and the CEP-121G calculations show that amongst all the $Hg_2L_2I_4$ complexes, the $Hg_2L^A{}_2I_4$ complex **3** has the shortest Hg–C(ylide) bond length. However, a comparison of experimental data for $Hg_2L_2I_4$ complexes indicates that the difference between the shortest and longest Hg–C(ylide) bond length in the solid state is about 0.058 Å. We note that the ylides studied in this work are of the type $Ph_3PCHCOR$. Thus the above results shows that the nature of the R group in the coordinated ylide has a weak effect on the Hg–C(ylide) bond length. Except in the case of the longest and shortest bond lengths in the series of $Hg_2L_2I_4$ complexes, one can hardly find an agreement between the trends for increasing the bond lengths around the metal ion in the solid state with that in the gas phase. Thus it is probable that in addition to the nature of coordinated ylide (which is not very important), crystal packing has also an effect on the bond lengths around the metal atom in these complexes. The calculated energies for the formation of $Hg_2L_2I_4$ complexes according to reaction (1) and considering the different ylides are given in Table 7. As can be seen, in the case of all basis sets the least amount of released energy is calculated for $Hg_2L^E{}_2I_4$. We remember that the latter complex has the longest Hg–C(ylide) bond length in both the solid state and gas phase. Except in the latter case, one can hardly find an agreement between the trend for increasing the Hg–C(ylide) bond length in the solid state and decreasing the energy of formation of the $Hg_2L_2I_4$ complexes in the gas phase. Furthermore, the difference between the maximum amount of released energy and minimum one in the series of these complexes is about 15–20 kcal/mol, depending on the type of basis set. Thus once again it confirms that the nature of the R group in the coordinated ylide has only a weak effect on the strength of the Hg–C(ylide) bond length. The second reason for this fact that the changes in the energy of reaction (1) are not consistent with the changes in Hg–C(ylide) bond length, is the difference in the relaxation energy of the different ligands from their geometry in the complex to the equilibrium geometry. Obviously, different ligands have different strain energies in the complex and this affects the energy of reaction (1).

Now let us study the effect of the coordinated halide ion on both the Hg–C(ylide) bond length and energy of reaction (1). As can be

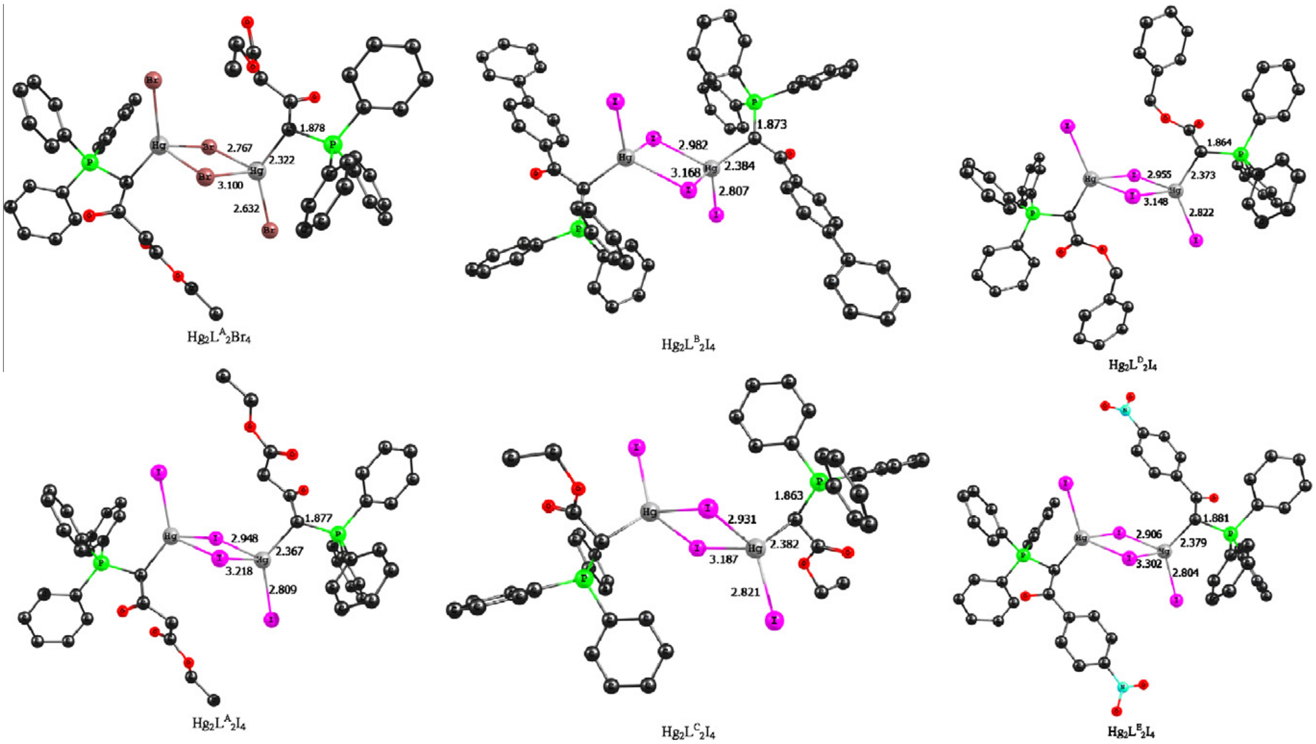


Fig. 3. Optimized structures for the $Hg_2L_2X_4$ complexes studied here at the B3LYP/CEP-121G level of theory.

Table 5
A comparison between selected calculated bond lengths with the corresponding experimental data for $Hg_2L_2X_4$ complexes.

Compound	Bond length (Å)	LanL2 MB	LanL2DZ	CEP-121G	X-Ray
$Hg_2L^A_2Br_4$	Hg–C	2.331	2.498	2.319	2.205(19)[a]
	Hg–Br (terminal)	2.811	2.706	2.634	2.490(3)
	Hg–Br (bridged)	3.026	2.985	3.058	2.831(2)
	Hg–Br (bridged)	2.991	2.853	2.780	2.779(2)
	P–C	1.974	1.848	1.879	1.776(17)
$Hg_2L^A_2I_4$	Hg–C	2.333	2.518	2.367	2.234(4)[a]
	Hg–I (terminal)	3.005	2.874	2.809	2.695(4)
	Hg–I (bridged)	3.179	3.067	2.948	2.841(3)
	Hg–I (bridged)	3.310	3.150	3.218	3.035(4)
	P–C	1.972	1.848	1.878	1.792(4)
$Hg_2L^B_2I_4$	Hg–C	2.354	2.513	2.384	2.270(8)[b]
	Hg–I (terminal)	3.019	2.868	2.807	2.709(9)
	Hg–I (bridged)	3.184	3.094	2.982	2.816(7)
	Hg–I (bridged)	3.272	3.153	3.168	3.079(8)
	P–C	1.981	1.847	1.873	1.771(8)
$Hg_2L^C_2I_4$	Hg–C	2.337	2.504	2.382	2.276(7)[c]
	Hg–I (terminal)	3.035	2.879	2.821	2.735(5)
	Hg–I (bridged)	3.220	3.066	2.931	2.803(5)
	Hg–I (bridged)	3.306	3.145	3.187	3.019(5)
	P–C	1.971	1.833	1.863	1.786(7)
$Hg_2L^D_2I_4$	Hg–C	2.338	2.499	2.373	2.263(6)[d]
	Hg–I (terminal)	3.013	2.898	2.821	2.672(9)
	Hg–I (bridged)	3.161	3.044	2.955	2.841(9)
	Hg–I (bridged)	3.325	3.141	3.148	3.130(8)
	P–C	1.969	1.835	1.864	1.783(6)
$Hg_2L^E_2I_4$	Hg–C	2.355	2.528	2.378	2.292(5)[e]
	Hg–I (terminal)	3.017	2.867	2.804	2.685(7)
	Hg–I (bridged)	3.146	3.029	2.906	2.790(6)
	Hg–I (bridged)	3.301	3.193	3.302	3.192(6)
	P–C	1.984	1.850	1.881	1.793(4)

[a] This work.
[b] [22].
[c] [21].
[d] [13].
[e] [12].

Table 6
Calculated electronic energies (Hartree) for the studied complexes and their components using different basis sets.

Compound	LanL2MB	LanL2DZ	CEP-121G
Br^-	−13.2064239	−13.2371155	−13.4633275
I^-	−11.4491618	−11.4721101	−11.5372418
Hg^{2+}	−41.7410709	−41.7934727	−152.7585572
L^A	−1145.9355197	−1160.360478	−203.5430001
L^B	−1299.8621332	−1315.9404314	−217.9604358
L^C	−995.2882319	−1007.734925	−175.0982868
L^D	−1184.6632265	−1199.4389067	−204.5004601
L^E	−1273.3085339	−1289.3945752	−222.7987857
$Hg_2L^A{}_2Br_4$	−2430.3842423	−2459.1270171	−768.39909
$Hg_2L^A{}_2I_4$	−2423.264557	−2452.0013356	−760.6599385
$Hg_2L^B{}_2I_4$	−2731.1109945	−2763.1599004	−789.4909531
$Hg_2L^C{}_2I_4$	−2121.9836911	−2146.7578878	−703.7751327
$Hg_2L^D{}_2I_4$	−2500.7156233	−2530.16679	−762.5806091
$Hg_2L^E{}_2I_4$	−2677.9916739	−2710.0519014	−799.1531352

Table 7
Calculated energies (kcal/mol) for the formation of $Hg_2L_2X_4$ complexes according to the reaction $2Hg^{2+} + 2L + 4X^- \rightarrow Hg_2L_2X_4$ using different basis sets.

Compound	LanL2MB	LanL2DZ	CEP-121G
$Hg_2L^A{}_2Br_4$	−1383.88	−1173.85	−1219.04
$Hg_2L^A{}_2I_4$	−1327.01	−1132.65	−1197.19
$Hg_2L^B{}_2I_4$	−1322.75	−1131.80	−1194.77
$Hg_2L^C{}_2I_4$	−1335.61	−1137.45	−1200.10
$Hg_2L^D{}_2I_4$	−1324.28	−1138.04	−1200.80
$Hg_2L^E{}_2I_4$	−1315.14	−1121.58	−1185.66

seen in Table 5, $Hg_2L^A{}_2Br_4$, both in the gas phase and in the solid state, has a shorter Hg–C(ylide) bond length than $Hg_2L^A{}_2I_4$, indicating the slight decrease in the s character of the Hg(II) orbitals on bonding to the ylidic carbon with decreasing electronegativity of the coordinated halide ligands. We note that the difference between the Hg–C(ylide) bond lengths in $Hg_2L^A{}_2Br_4$ and $Hg_2L^A{}_2I_4$ complexes is only 0.023 Å. Thus it seems that the halide ion has also a weak effect on the Hg–C(ylide) bond length. Therefore, the difference between the energy of reaction (1) for $Hg_2L^A{}_2Br_4$ and $Hg_2L^A{}_2I_4$ complexes depends mainly on the type of coordinated halide rather than strength of the bond between Hg(II) and the ylide.

4. Conclusions

The present study describes the synthesis and characterization of some binuclear Hg(II) complexes of a new phosphorus ylide. On the basis of the physico-chemical and spectroscopic data we propose that the ligand herein exhibits monodentate C-coordination to the metal center. Both the experimental and theoretical studies show amongst all the five binuclear $Hg_2L_2I_4$ complexes studied here, complex **3** ($Hg_2L^A{}_2I_4$) has the shortest Hg–C(ylide) bond length in both the solid state and gas phase. However, the nature of the R group in the ylides of the type $Ph_3PCHCOR$ has a weak effect on the Hg–C(ylide) bond length in the above complexes.

Acknowledgements

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Appendix A. Supplementary data

CCDC 751708 and 778462 contain the supplementary crystallographic data for complexes **2** and **3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2011.06.033.

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