Synthesis of a new carbbenzyloxymethylenetriparatolylphosphorane ylide and study of its reaction with mercury(II) halides: Spectral and structural characterization

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Abstract

A new carbbenzyloxymethylenetriparatolylphosphorane ylide (BTPY), $\{(p\text{-tolyl})_3PCHCOOCH_2C_6H_5\}$, was synthesized and characterized with elemental analysis as well as various spectroscopic techniques. The reactions of the title ylide with mercury(II) chloride, mercury(II) bromide and mercury(II) iodide in equimolar ratios using dry methanol as solvent have yielded $[BTPY \cdot HgCl_2]_2$ (**1**), $[BTPY \cdot HgBr_2]_2$ (**2**) and $[BTPY \cdot HgI_2]_2$ (**3**), respectively. Single crystal X-ray analysis of **2** reveals the presence of a centrosymmeteric dimeric structure containing the ylide and $HgBr_2$. The analytical data, IR and ^1H, ^{13}C and ^{31}P NMR data for the latter compound are similar to those of **1** and **3**, indicating similar structures. The theoretical studies indicated that, for all three compounds, the observed *trans*-like structure for compound **2**, is more stable than the possible *cis*-like structure in each case.
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Keywords: Phosphorus ylide; Mercury(II) halides complexes; X-ray crystal structure; Theoretical studies

1. Introduction

Phosphorus ylides are reactive compounds, which take part in many reactions of value in the synthesis of organic products [1–4]. They are synthetic targets of interest, because of their value for a variety of industrial, biological and chemical synthetic uses [5–7]. Juxtaposition of the keto group and carbanion in the phosphorus ylide, BTPY allows for the resonance delocalization of the ylidic electron density providing additional stabilization to the ylide species (Scheme 1). This so-called α-stabilization provides BTPY with the potential to act as an ambidentate ligand and thus bond to an Hg(II) centre through the either carbanion (**b**) or the enolate oxygen (**c**).

Although many bonding modes are possible for keto ylides [8], coordination through carbon is more predominant and observed with soft metal ions, e.g., Pd(II), Pt(II), Ag(I), Hg(II), Au(I) and Au(III) [9–13], whereas, O-coordination dominates when the metals involved are hard, e.g., Ti(IV), Zr(IV), and Hf(IV) [14]. In this work we have synthesized benzyloxy stabilized phosphorus ylide and metal complexes with mercury(II) halides. The aims of our present work are (i) to determine and compare the molecular structure of the products formed by the title ylide with mercury(II) halides, and (ii) to characterize all the products by IR, ^1H, ^{13}C and ^{31}P NMR spectra and X-ray crystallography.

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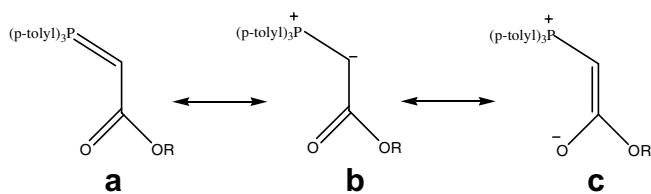
Scheme 1. The canonical forms of BTPY (R = CH$_2$Ph).

2. Experimental section

2.1. Physical measurements and materials

Methanol was distilled over magnesium powder and diethyl ether (Et$_2$O) over a mixture of sodium and benzophenone just before use. All other solvents were reagent grade and used without further purifications. Solution-state ^{1}H, ^{31}P and ^{13}C NMR spectra at ambient temperature were obtained in DMSO-d_6 or CDCl$_3$ using a 200 MHz Bruker spectrometer. Solution-state ^{1}H and ^{31}P NMR spectra at 220 K were obtained in CDCl$_3$ using a 500 MHz Bruker spectrometer operating at 500.13 MHz for ^{1}H, and 202.45 MHz for ^{31}P. Melting points were measured on a SMPI apparatus. Elemental analysis for C, H and N were performed using a PE 2400 series analyzer. IR spectra were recorded on a Shimadzu 435-U-04 spectrophotometer and the measurements were made by the KBr disk method. X-ray analysis was recorded on a STOE IPDS-II diffractometer.

2.2. X-ray crystallography

A block colorless crystal of **2** having approximate dimensions of 0.25 × 0.15 × 0.12 mm was mounted on a glass fiber. All measurements were made on a STOE IPDS-II diffractometer with graphite monochoromated Mo Kα radiation. (λ = 0.7107 nm).

The data were collected at a temperature of 298 K to a maximum θ value of 26.78° and in a series of ω scans in 1degr oscillations with 60 s exposures. Of the 15671 reflections that were collected, 6136 were unique (R_{int} = 0.0345), equivalent reflections were merged. Data were collected and integrated using the STOE X-AREA [15] software package. The numerical absorption coefficient, μ, for Mo Kα radiation is 8.109 mm^{-1}. A numerical absorption correction was applied using X-RED [16] and X-SHAPE [17] softwares, which resulted in transmission factors ranging from 0.242 to 0.378. The data were corrected for Lorentz and polarizing effects. The structure was solved by direct [18] methods. All of the none-hydrogen atoms were refined anisotropically. All of hydrogen atoms were located in the ideal positions. Anomalous description effects were included in F_{calc} [19], the values for Δf′ and Δf″ were those of Creagh and McAuley [20]. The values for the mass attenuation coefficient are those of Creagh and Habbell [21].

2.3. Computational methods

The geometries of all compounds were fully optimized at the Hartree–Fock (HF) (B3LYP) level of theory using the GAUSSIAN98 program [22] on a Pentium-PC computer with 3000 MHz processor. The standard LanL2MB basis set was used for both complexes [23]. This basis set includes effective core potentials (ECP) for both the mercury and phosphorous as well as halide (Cl, Br, I) ions. Vibrational frequency analyses, calculated at the same level of theory, indicate that optimized structures are at the stationary points corresponding to local minima, without any imaginary frequency. Atomic coordinates for ab initio calculations were obtained from the data of the X-ray crystal structure analyses for compound **2**.

2.4. Sample preparation

2.4.1. Synthesis of [(p-tolyl)$_3$PCHCOOCH$_2$C$_6$H$_5$] (BTPY)

Benzylbromoacetate (0.42 g, 2 mmol) was dissolved in 20 ml of chloroform and then a solution of triparatolylphosphine (0.557 g, 2 mmol) in the same solvent (5 ml) was added dropwise to the above solution. The resulting pale yellow solution was stirred for 10 h. The solution was concentrated under reduced pressure to 5 ml, and diethyl ether (20 ml) was added. The yellow solid formed was filtered off, washed with petroleum benzene (10 ml), and dried under reduced pressure. In order to get the final product, all of the crude solid, 0.75 g (81.5%), was transferred to an alkaline solution of 5% NaOH and stirred at 40 °C for about 14 h, yielding the pale white precipitate. The product was washed several times with distilled water and air dried. Yield 0.59 g (85.5%), m.p. 101–103 °C. Anal. Calc. for C$_{30}$H$_{29}$O$_2$P: C, 79.62; H, 6.46. Found: C, 79.78; H, 6.54%.

2.4.2. Synthesis of [(BTPY) · HgCl$_2$]$_2$ (1)

A solution of 0.09 g (0.3 mmol) of HgCl$_2$ in methanol (15 ml) was added to a solution of 0.15 g (0.3 mmol) of BTPY in dry methanol and stirred for 12 h. The white solution was concentrated to 2 ml, and diethyl ether (15 ml) added to precipitate the white complex. Yield 0.202 g (84.2%), m.p. 173–175 °C. Anal. Calc. for C$_{60}$H$_{58}$Cl$_4$Hg$_2$O$_4$P$_2$: C, 49.77; H, 4.04. Found: C, 50.57; H, 3.82%.

2.4.3. Synthesis of [(BTPY) · HgBr$_2$]$_2$ (2)

A solution of 0.14 g (0.4 mmol) of HgBr$_2$ in methanol (15 ml) was added to a solution of 0.172 g (0.4 mmol) of BTPY in dry methanol and stirred for 8 h. The white solution was concentrated to 2 ml, and diethyl ether (15 ml) added to precipitate the white complex, which was recrystallized from chloroform–diethyl ether.

Yield 0.266 g (85.8%), m.p. 176–178 °C. Anal. Calc. for C$_{60}$H$_{58}$Br$_4$Hg$_2$O$_4$P$_2$: C, 44.32; H, 3.6. Found: C, 44.55; H, 3.47%.

2.4.4. Synthesis of [(BTPY) · HgI₂]₂ (3)

A solution of 0.18 g (0.4 mmol) of HgI_2 in methanol (15 ml) was added to a solution of 0.178 g (0.4 mmol) of BTPY in dry methanol and stirred for 6 h. The yellow solution was concentrated to 2 ml, and diethyl ether (15 ml) added to precipitate the pale yellow complex. Yield 0.31 g (86.1%), m.p. 184–187 °C. Anal. Calc. for $C_{60}H_{58}I_4Hg_2O_4P_2$: C, 39.73; H, 3.22. Found: C, 38.94; H, 3.1%.

3. Results and discussion

3.1. Spectroscopy

The $v(CO)$, which is sensitive to complexation, occurs at 1615 cm^{-1} in the parent ylide, as in the case of other resonance stabilized ylides [24]. Coordination of the ylide through carbon causes an increase in $v(CO)$, while, for O-coordination a lowering of $v(CO)$ is expected (Table 1). The infrared absorption bands observed for the three complexes at 1702, 1699 and 1692 cm^{-1} indicate coordination, of the ylide through carbon. The $v(P^+–C^-)$, which is also diagnostic for the coordination occurs at 851 cm^{-1} in $(p\text{-tolyl})_3P^+–C^-H_2$ and at 811 cm^{-1} in $(C_6H_4CH_3)_3$-$PCHCOOCH_2C_6H_5$. In the present study, the $v(P^+–C^-)$ values for all three complexes were shifted to lower frequencies and observed at 805, 806 and 806 cm^{-1} for **1**, **2**, and **3**, respectively, suggesting some removal of electron density in the P–C bond.

The ^{1}H NMR data for the mercury(II) complexes along with those of the parent ylide are listed in Table 2. The signal due to the methine proton, when recorded in CDCl₃, was broad for complexes **1**, **2**, and **3**. This indicates probably, that the ylide dissociate in solution. Compounds wherein the ylide is C-coordinated exhibit a $^2J(PH)$ value 10 or less Hz [12,8,33].

Table 1
v (CO) of selected phosphoranes and their metal complexes

Compound	v (CO) cm^{-1}	Reference
Ph₃PCHCON(CH₃)₂	1530	[24]
Ph₃PCHCOCH₃ (APPY)	1530	[25]
Ph₃PCHCOPh (BPPY)	1525	[26]
(C₆H₄CH₃)₃PCHCOOCH₂C₆H₅ (BTPY)	1615	This work
C-coordination		
BTPY · HgCl₂ (**1**)	1702	This work
BTPY · HgBr₂ (**2**)	1699	This work
BTPY · HgI₂ (**3**)	1692	This work
BPPY · HgCl₂	1635	[12]
BPPY · HgBr₂	1630	[12]
Au [CH(PPh₃)CON(CH₃)₂]	1605	[24]
O-coordination		
[(Sn(CH₃)₃ · BPPY]Cl	1480	[27]
[(SnPh₃) · BPPY]Cl	1470	[27]
[Pd{C₆F₅}(PPh₃)₂(APPY)]ClO₄	1513	[9]

APPY = acetylmethylenetriphenylphosphorane.
BPPY = benzoylmethylenephenylphosphorane.

Table 2
^{1}H and ^{31}P NMR data of BTPY and its complexes with Hg (II) halide ($T = 298$ K; J in Hz; TMS $\delta = 0.00$ ppm)

Compound	δ (CH)	^2J (PH)	δ(P(p-tolyl)₃)	δ (^{31}P)
BTPY[a]	2.88(d)	15.59	7.16–7.88(m)	13.90(s)
BTPY · HgCl₂[a]	4.25(br)	–	7.23–8.21(m)	23.85(s)
BTPY · HgBr₂[a]	4.07(br)	–	7.48–8.11(m)	21.66(s)
BTPY · HgI₂[a]	3.94(br)	–	7.50–8.21(m)	20.96(s)

br, broad; s, singlet; d, doublet; m, multiplet.
[a] In CDCl₃, values (ppm) relative to internal TMS.

The expected downfield shifts of ^{31}P and ^{1}H signals for the PCH group upon complexation were observed in their corresponding spectra. The appearance of single signals for the PCH group in both the ^{31}P and ^{1}H NMR at ambient temperature indicates the presence of only one molecule for all the three complexes as expected for C-coordination. It must be noted that O-coordination of the ylide sometimes leads to the formation of *cis* and *trans* isomers giving rise to two different signals in the ^{31}P and ^{1}H NMR [9,14]. The resonances of the ^{31}P NMR complexes **1**, **2**, and **3** were observed to occur at a lower field with respect to the free ylide (Table 2). Comparison of the ^{31}P spectra of the three complexes at ambient temperature indicates that decreases in the order **1** > **2** > **3**. At low temperature (220 K), exhibit satellites due to coupling to ^{199}Hg (8% intensity each, $^2J_{P–Hg} \sim 201$ Hz).

The ^{13}C NMR data of the complexes and the title ylide are listed in Table 3 along with possible assignments. The most interesting aspect of the ^{13}C spectra of the complexes is the upfield shift of the signals due to the ylidic carbon. Such upfield shifts observed in PdCl $(\eta^3\text{-}2\text{-}XC_3H_4)$ $(C_6H_5)_3PCHCOR$ (X = H, CH₃; R = CH₃, C₆H₅) was attributed to a change in hybridization of the ylidic carbon [28]. Similar upfield shifts of 4–9 ppm with reference to the parent ylide were also observed [29] in the case of $[(C_6H_5)_3PC_5H_4HgI_2]_2$, and in our synthesized mercury complexes [30]. The ^{13}C shifts of the CO group in the complexes are around 169 ppm, which is higher than the 170 ppm shift noted for the same carbon in the parent ylide, indicating much higher shielding of the carbon of the CO group in the complexes. No coupling to Hg was observed at room temperature in ^{1}H, ^{13}C and ^{31}P NMR spectra of all these complexes.

3.2. X-ray crystallography

Table 4 provides the crystallographic results and refinement information for complex **2**. The refinement was performed using the X-STEP32 [31] crystallographic software package. The molecular structure of **2** is shown in Fig. 1a. Fractional atomic coordinates and equivalent isotropic displacement coefficients (U_{eq}) for the non-hydrogen atoms of complex **2** (are shown in Table S1). Table 5 lists key bond lengths and angles for complex **2**.

The dimeric structure adopted by complexes **1**, **2**, and **3** is in contrast to the O-coordinated trinuclear mercury(II) complex of the phosphorus ylide Ph₃PCHCOPh, [32] but

Table 3
^{13}C NMR data of BTPY and its complexes with mercury (II) halides

Possible assignments	BTPY[a]	BTPY · HgCl$_2$[b]	BTPY · HgBr$_2$[a]	BTPY · HgI$_2$[b]
(CH)	30.5(d)	br	br	br
^1J(PC)	125.03	–	–	–
CH$_2$	63.37(s)	66.32(s)	67.18(s)	51.4(s)
CH$_3$	21.66(s)	21.01(s)	21.72(s)	21.06(s)
(CH$_2$–Ph)(i)	144.85(s)	144.44(s)	144.96(s)	144.11(s)
(CH$_2$–Ph)(o)	127.56(s)	128.00(s)	128.91(s)	130.26(s)
(CH$_2$–Ph)(m)	127.26(s)	128.00(s)	128.22(s)	128.75(s)
(CH$_2$–Ph)(p)	126.50(s)	128.00(s)	127.86(s)	127.95(s)
P(p-tolyl)$_3$(i)	124.41(d)	118.72(d)	119.46(d)	119.74(d)
^1J(PC)	94.16	91.66	92.18	92.72
P(p-tolyl)$_3$(o)	132.51(d)	133.13(d)	133.47(d)	133.04(d)
^2J(PC)	10.21	10.38	9.48	10.48
P(p-tolyl)$_3$(m)	129.02(d)	130.07(d)	130.54(d)	130.00(d)
^3J(PC)	12.66	12.80	13.00	11.78
P(p-tolyl)$_3$(p)	138.44(s)	135.55(s)	136.13(s)	133.27(s)
(CO)	170.39(s)	168.62(s)	169.46(s)	169.66(s)

s, singlet; d, doublet; (o), ortho; (m), meta; (i), ipso carbon; br, broad.
[a] Record in CDCl$_3$.
[b] Record in DMSO-d_6.

Table 4
Crystal data and refinement parameter for **2**

Empirical formula	C$_{60}$H$_{58}$Br$_4$Hg$_2$O$_4$P$_2$
Formula weight	1625.78
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	
a (Å)	11.2864(12)
b (Å)	10.3313(7)
c (Å)	25.149(3)
α (°)	90
β (°)	96.751
γ (°)	90
Volume	2912.1(5) Å^3
Z, Calculated density	2, 1.854 Mg/m^3
Absorption coefficient	8.109 mm^{-1}
$F(000)$	1560
Crystal size	0.25 × 0.15 × 0.12 mm
Theta range for data collection	1.63–26.78°
Limiting indices	$-14 \leqslant h12$, $-11 \leqslant k \leqslant 13$, $-31 \leqslant 1 \leqslant 31$
Reflections collected/unique	15671/6136 [$R_{int} = 0.0345$]
Completeness to theta = 23.78	98.60%
Absorption correction	Numerical
Maximum and minimum transmission	0.378 and 0.242
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6136/0/325
Goodness-of-fit on F^2	1.07
Final R indices	R_1[a] = 0.0313, wR_2[b] = 0.0582
R indices (all data)	$R_1 = 0.0401$, $wR_2 = 0.0608$
Largest difference in peak and hole	3.179 and -0.740 e Å^{-3}

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ for reflection with $I > 2\sigma I$.
[b] $wR_2 = [\sum(w(F_o^2 - F_c^2)^2) / \sum w(F_o^2)^2]^{1/2}$.

is similar to the structure of μ-dichlorobis[chloro-(benzoylmethylenetri-n-butylphosphorane)palladium(II)] reported by Albanese et al. [33] and the C-coordinated dinuclear mercury(II) halide complexes of Ph$_3$PCHCOPh

(BPPY) [12]. The C-coordination of BTPY is in stark contrast to the O-coordination of the phosphorus ylide Ph$_3$PC(COMe)(COPh) (ABPPY) to the Hg(II) centre [34]. The difference in coordination mode between ABPPY and BTPY 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 BTPY; 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. Belluco et al. have studied steric influences on the coordination modes of ylide molecules to Pt(II) systems [35]. These authors concluded that the preferred coordination mode is via the ylidic carbon, but that steric hindrance around the metal centre or the ylidic carbon will necessitate O-coordination.

Indeed, this trend is reflected here, both BPPY and BTPY are slightly less sterically demanding than ABPPY, and are both C-coordinated to Hg(II). The Hg(II) in **2** is sp3 hybridized and has a tetrahedral coordination environment with one short Hg–Br bond, one Hg–C bond and two asymmetric bridging Hg–Br bonds at the distances of 2.753(5) and 2.780(5) Å. The significant of the Hg–C bond of length, 2.226(4) Å compared to analogous distances in [BPPY. HgI$_2$]$_2$ (**4**) [12] and in [(C$_6$H$_5$)$_3$PC$_5$H$_4$ · HgI$_2$]$_2$ [28] (2.312(13) and 2.292(8) Å, respectively) must be attributed to the use of Hg (II) orbitals with high s character for bonding to 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. As expected on the basis of the same concept, the Hg–C bonds in **2** and [BPPY. HgCl$_2$]$_2$ (**5**) [12] are much shorter than in **4**, because of the very low difference in electronegativity between carbon and iodine.
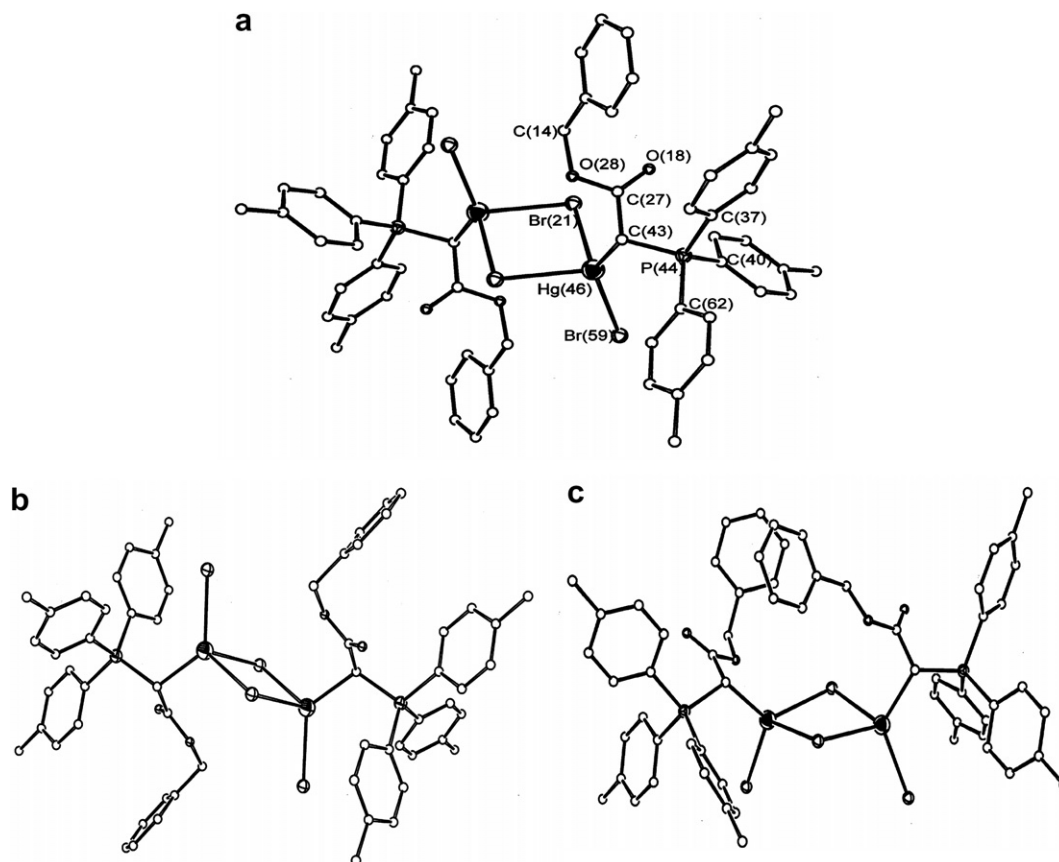
Fig. 1. (a) ORTEP view of X-ray crystal structure of **2**, (b) calculated molecular structure of *trans*- [BTPY · HgBr$_2$]$_2$ and (c) calculated molecular structure of *cis*-[BTPY · HgBr$_2$]$_2$.

The internuclear distances between mercury atoms were found to be 3.951(5), 4.014(1), and 3.810(2) Å in structures **2**, **4**, and **5**, respectively. These distances are much longer than the sum of Van der Waals radii (1.5 Å) of the two mercury atoms [36] indicating the absence of 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) for four coordination and the stability of the 18 electron configuration around Hg(II).

3.3. Theoretical studies

As mentioned in Section 2.3, the analytical and spectroscopic data for compound **2** are similar to those of the other two complexes synthesized here. We were interested to see whether the observed *trans*-like structure for compound **2** is more stable than its possible *cis*-like isomer and whether this is the case for other compounds. Thus the observed geometry of compound **2** was considered for ab initio calculations. The optimized structure of this compound is shown in Fig. 1b and the selected bond lengths and bond angles are given in Table 5. As can be seen, the calculated bond lengths are slightly longer than measured bond lengths but the similarity of calculated and measured

bond angles reflects the similar geometrical structures for this compound in both the solid state and gas-phase. It is clear that the dimeric structure with general formula [BTPY · HgX$_2$]$_2$ can be considered as both the observed *trans*-like or possible *cis*-like isomers. Thus we changed the geometrical structure of compound **2**, by replacement of positions of one terminal bromine atom with one coordinated ylide group, to obtain a *cis*-like isomer. The minimization of this isomer at same level of theory gave the desired *cis*-like isomer as it has been shown in Fig. 1c. But we found that this structure is about 5.4 kcal/mol less stable than *trans*-like structure. We have also studied the gas phase structures of [BTPY · HgCl$_2$]$_2$ and [BTPY · HgI$_2$]$_2$ complexes in a similar way. We could optimize a *cis*-like isomer for the former complex which was about 5.9 kcal/mol less stable than *trans*-like isomer (Fig. 2). On the other hand we never were able to optimize a *cis*-like isomer for compound **3**. It was very interesting that any considered *cis*-like structure for this compound, has been changed to a *trans*-like structure (Fig. 3).

In the *trans*-like structures of compounds **1**, **2**, and **3** the internuclear distances between mercury atoms were calculated to be 4.091, 4.250, and 4.420 Å, indicating the absence of significant bonding interactions between the mercury atoms in the molecular structures (Tables 5 and 6). The Hg–C bond length in the latter structures are

Table 5
A comparison between the calculated bond lengths (Å) and bond angles (°) for the compound **2** with corresponding experimental values

	X-ray	HF/Lanl2mb
Bond lengths		
Hg(46)–Br(21)	2.7533 (5)	2.947
Hg(46)–Br(21) #1	2.7800 (5)	2.986
Hg(46)–Br(59)	2.5255 (6)	2.778
P(44)–C(62)	1.805 (4)	1.960
P(44)–C(37)	1.789 (4)	1.916
P(44)–C(43)	1.791 (4)	1.925
P(44)–C(40)	1.800 (4)	1.929
Hg(46)–C(43)	2.226 (4)	2.248
Bond angles		
Hg(46)–Br(21)–Hg(46)	91.14	91.50
Br(21)–Hg(46)–C(43)	104.790	106.846
Br(59)–Hg(46)–Br(59)	106.00	107.85
Br(21)–Hg(46)–Br(21) #1	88.864	88.502
Br(21)–Hg(46)–Br(59)	114.001	107.305
C(43)–Hg(46)–Br(57)	104.886	110.830
C(43)–Hg(46)–Br(59)	130.095	128.181
Br(21)–Hg(46)–Br(59) #1	106.004	107.851
Hg(46)–Br(57)–Hg(46) #1	91.136	91.496
Br(57)–Hg(46)–Br(21)	88.86	88.50
O(18)–C(27)–O(28)	123.445	125.448
O(18)–C(27)–C(43)	124.866	126.265
O(28)–C(27)–C(43)	111.683	108.283
C(14)–O(28)–C(27)	114.858	113.071
C(43)–P(44)–C(40)	114.72	111.13
C(62)–P(44)–C(40)	108.10	109.66
C(37)–P(44)–C(40)	109.29	110.28
C(43)–P(44)–C(37)	109.23	110.25
C(62)–P(44)–C(37)	108.32	108.04
C(62)–P(44)–C(43)	106.99	109.46
P(44)–C(43)–Hg(46)	114.005	114.353

calculated to be 2.244, 2.248, and 2.251 Å, respectively, indicating the slight decreasing in the *s* character of the Hg(II) orbitals in bonding to ylidic carbon with decreasing electronegativity of coordinated halide ligands.

The optimized molecular structure of the ligand BTPY (is shown in Fig. S1), along with selected calculated bond lengths (is shown in Table S2). As can be seen in Scheme 1, the ylides in their free forms can be shown as three pos-

sible structures. Obviously upon C-coordination to metal ions the structure (b) will be the unique or predominant structure. This was confirmed by comparison of the calculated bond lengths for C(27)–C(43) (Fig. 1) in the free ylide, 1.509 Å, and its complexes **1**, **2**, and **3**, 1.537, 1.538, 1.538 Å, respectively.

4. Conclusions

A new ylide (BTPY), and its mercury(II) complexes with the general formula [BTPY · HgX$_2$]$_2$ (X = Cl, Br, I) have been synthesized. Theoretical studies on the gas phase structures of the latter complexes, confirm the *trans*-like dimeric structure for compound **2** obtained by X-ray crystal structure analyses. The observation of similar analytical and spectroscopic data after further support the presence of a centrosymmeteric dimeric structure containing the ylide and HgX$_2$.
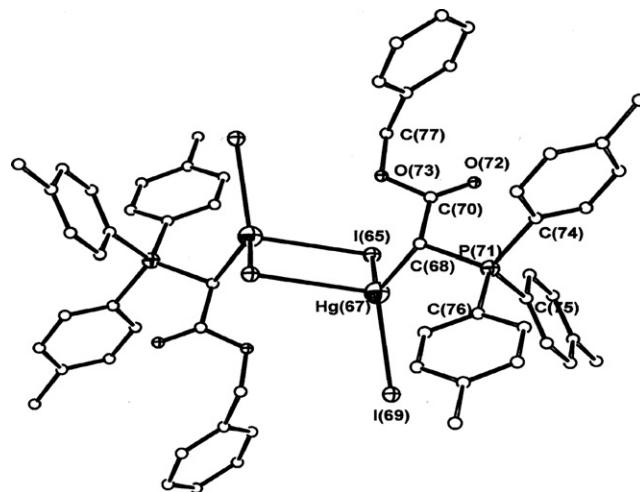

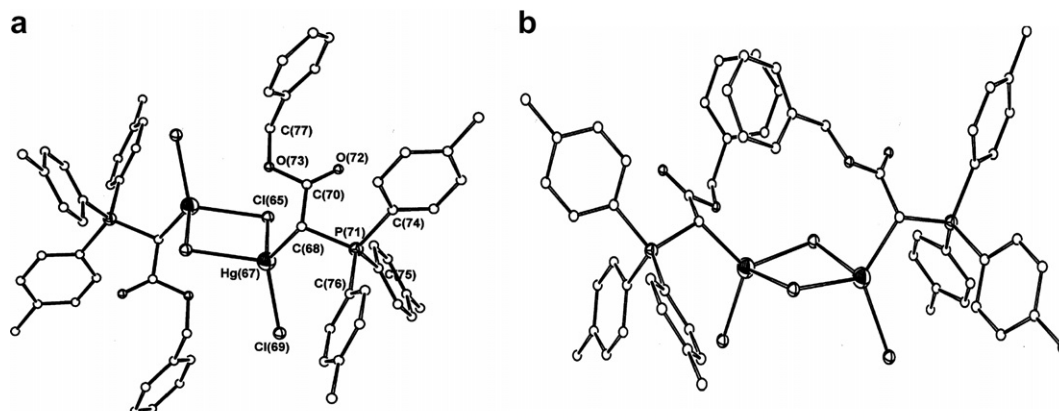Fig. 3. Calculated molecular structure of *trans*-[BTPY · HgI$_2$]$_2$.

Fig. 2. Calculated molecular structure of (a) *trans*- [BTPY · HgCl$_2$]$_2$ and (b) *cis*-[BTPY · HgCl$_2$]$_2$.

Table 6
Selected theoretical bond lengths (Å) and bond angles (°) for the calculated *trans*-like molecular structures of **1** and **3** at HF/LanL2MB level of theory

	X = Cl	X = I
Bond lengths		
X(66)–Hg(67)	2.743	3.236
X(65)–Hg(67)	2.818	3.141
X(69)–Hg(67)	2.618	2.975
P(71)–C(74)	1.929	1.931
P(71)–C(75)	1.916	1.918
P(71)–C(76)	1.925	1.922
P(71)–C(68)	1.959	1.958
C(70)–O(72)	1.217	1.217
C(70)–O(73)	1.384	1.383
Hg(67)–C(68)	2.244	2.251
Bond angles		
Hg(14)–X(66)–Hg(67) #1	94.711	87.730
X(65)–Hg(67)–X(66)	85.289	92.269
X(65)–Hg(67)–C(68)	105.583	112.091
X(65)–Hg(67)–X(69)	107.777	109.918
X(66)–Hg(67)–C(68)	116.998	104.882
X(66)–Hg(67)–X(69)	107.179	106.711
C(68)–Hg(67)–X(69)	125.853	125.369
Hg(67)–C(68)–C(70)	108.500	110.650
Hg(67)–C(68)–P(71)	113.891	113.699
C(68)–C(70)–O(72)	126.478	126.377
C(68)–C(70)–O(73)	108.087	108.223
O(72)–C(70)–O(73)	125.425	125.395
C(70)–O(73)–C(77)	113.096	113.172
O(73)–C(77)–C(84)	112.018	112.081
C(68)–P(71)–C(74)	111.642	111.250
C(68)–P(71)–C(75)	109.551	108.993
C(68)–P(71)–C(76)	108.187	110.251
C(74)–P(71)–C(75)	109.518	109.962
C(74)–P(71)–C(76)	108.018	106.235
C(75)–P(71)–C(76)	109.893	110.128

Acknowledgement

Appendix A. Supplementary material

CCDC 622775 contains the supplementary crystallographic data for **2**. 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.jorganchem.2007.02.027.

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