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

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The reaction of the title ylide, $Ph_3P{=}CHCOOCH_2Ph$ (BAPPY), with mercury(II) halides in equimolar ratios using methanol as a solvent produces the mercurated complexes $[(BAPPY)\cdot HgCl_2]_2$ (**1**), $[(BAPPY)\cdot HgBr_2]_2$ (**2**) and $[(BAPPY)\cdot HgI_2]_2$ (**3**) in good yields. Single crystal X-ray analysis of **3** reveals the presence of a centrosymmetric dimeric structure containing the ylide and HgI_2. The IR, ^1H, ^{13}C and ^{31}P NMR data for the latter compound are similar to those of **1** and **2**, indicating similar structures. Elemental analysis indicate a 1:1 stoichiometry between the ylide and Hg(II) halide in each of the three products.

1. Introduction

Carbonyl-stabilized phosphorus ylides are very versatile ligands for three reasons: (i) they have two alternate modes of coordination, **A** [1] and **B** [2] (Scheme 1); (ii) they give stable complexes in spite of their low nucleophilicity (arising from electron delocalization through resonance forms **a–c** (Scheme 1)); and (iii) they allow the synthesis of unusual types of complexes [3].

The preparation and characterization of α-stabilized phosphorus ylides, and metal complexes incorporating in this type of ylides, has attracted much attention in recent years. This interest has been driven primarily by the necessity to develop new reagents for chemical synthesis that exhibit enhanced properties [4]. It is the requirement to satisfy this need that has provided the impetus for our work, which has been directed towards evaluating the ligating behavior of phosphorus ylides. In the compounds reported to date, the chemical behavior of the α-keto phosphorus ylides has been clearly dominated by the C-coordinated form [5], and very few examples of O-coordinated ylides are known [6].

Some of these examples contain the ylide O-coordinated to a hard metal, which means there is a very oxophilic metal center, such as Sn(IV) [6a] or a group with a high oxidation number [6b]. Only W(0) complexes of the type $W(CO)_5L$ (L = ylide) [6c] and Pd(II) complexes of the stoichiometry $[Pd(C_6H_5)L_2(APPY)]ClO_4$ [10] [APPY = Ph_3CCOMe; L_2 = PPh_3, PBu_3, bipy] contain stable ylides O-linked to a soft metal center. Other attempts to obtain this kind of O-coordination to “classical” soft metals such as Pd(II), Pt(II) or Hg(II) [7] invariably gave C-coordination.

Phosphorus ylides are known to demonstrate rich coordination chemistry. One of the significance aspects of our work is to ascertain the preferred coordination modes of BAPPY to the Hg metal. In this study, we describe the preparation, spectroscopic characterization (IR and NMR) of mercury(II) complexes with the title ylide. By a comparison of the data collected and single crystal X-ray diffraction of **3**, it demonstrates C-coordination of the ylide to the metal.

2. Experimental

2.1. Materials

Methanol was distilled over magnesium powder and diethyl ether (Et_2O) was distilled over a mixture of sodium and benzophenone just before use. All other solvents were reagent grade and used without further purification. Mercury halides, bromobenzylacetate and triphenylphosphine were purchased from Merck.

2.2. Physical measurements

Melting points were measured on a SMPI apparatus. Elemental analyses for C, H and N were performed using a Perkin–Elmer 2400

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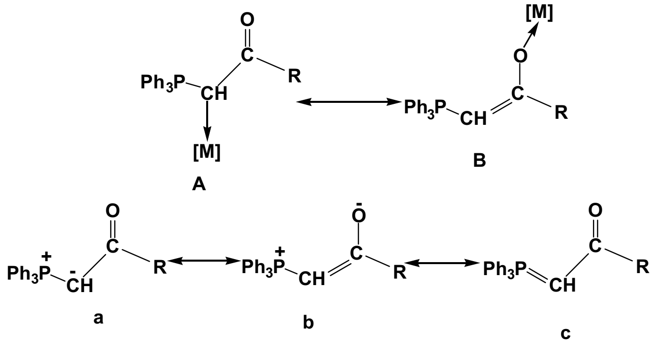


Scheme 1.

series analyzer. Fourier transform IR spectra were recorded on a Shimadzu 435-U-04 spectrophotometer and samples were prepared as KBr pellets. ^1H, ^{13}C and ^{31}P spectra were recorded on a 90 MHz Jeol spectrometer. X-ray analysis was performed on a STOE IPDS-II diffractometer.

2.3. Synthesis of the ligand and the metal complexes

2.3.1. Synthesis of BAPPY

A solution of triphenylphosphine (0.52 g, 2 mmol) and bromobenzylacetate (0.42 g, 2 mmol) in dry chloroform (15 mL) was stirred at room temperature for 10 h. The resulting white precipitate was filtered off, washed with diethyl ether and dried. Further treatment with an aqueous solution of NaOH (0.5 M, 50 mL) led to elimination of HBr, giving the free ligand. Yield: 0.66 g (89.3%), m.p. 118–120 °C. *Anal.* Calc. for for $C_{27}H_{20}O_2P$: C, 79.00; H, 5.64. Found: C, 78.44; H, 5.43%.

2.3.2. Synthesis of $[(BAPPY) \cdot HgCl_2]_2$ (**1**)

General procedure: To a magnetically stirred solution of $HgCl_2$ (0.135 g, 0.5 mmol) in methanol (10 mL), was added a methanolic solution (5 mL) of the ylide BAPPY (0.205 g 0.5 mmol). After 8 h the solvent was removed under reduced pressure to 3 mL. After addition of diethyl ether (30 mL) a white solid product was separated by filtration. Yield: 0.28 g (82.7%), m.p. 173–176 °C. *Anal.* Calc. for $C_{54}H_{40}Cl_4Hg_2O_4P_2$: C, 47.55; H, 3.39. Found: C, 46.26; H, 3.17%.

2.3.3. Synthesis of $[(BAPPY) \cdot HgBr_2]_2$ (**2**)

Yield: 0.35 g (85.2%), m.p. 177–179 °C. *Anal.* Calc. for $C_{54}H_{40}Br_4Hg_2O_4P_2$: C, 42.07; H, 3.00. C, 41.18; H, 2.83%.

2.3.4. Synthesis of $[(BAPPY) \cdot HgI_2]_2$ (**3**)

Yield: 0.36 g (81.8%), m.p. 167–170 °C. *Anal.* Calc. for $C_{54}H_{40}I_4Hg_2O_4P_2$: C, 37.49; H, 2.67. C, 37.10; H, 2.55%.

2.4. X-ray crystallography

Crystals were obtained from a dichloromethane/diethyl ether solution by solvent diffusion. A block colorless crystal of **3** 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 ($\lambda = 0.7107$ nm).

The data were collected at 298 K to a maximum θ value of 26.78 ° and in a series of ω scans in 1 ° oscillations with 60 s exposures. Of the 33902 reflections that were collected, 11871 were unique ($R_{int} = 0.0442$), equivalent reflections were merged. Data were collected and integrated using the STOE X-AREA software package [8]. The refinement was performed using the X-STEP32 crystallographic software package [9]. The numerical absorption coefficient, μ, for Mo Kα radiation is 7.748 mm^{-1}. A numerical absorption correction was applied using X-RED [10] and X-SHAPE [11] software packages which resulted in transmission factors ranging from 0.212 and 0.083. The data were corrected for Lorentz and polarizing effects. The structure was solved by direct methods [12]. All of the non-hydrogen atoms were refined anisotropically. All of the hydrogen atoms were located in ideal positions. Anomalous dispersion effects were included in F_{calc} [13], the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley [14]. The values for the mass attenuation coefficient are those of Creagh and Hubbell [15].

2.5. Computational methods

The quantum chemical calculations were performed with GAUSSIAN03 [16]. The geometries were fully optimized using DFT at the B3LYP/LanL2MB level of theory [17]. This basis set includes effective core potentials (ECP) for both the mercury and phosphorus as well as halide (Cl, Br, and I) ions. The stability energy values for the complex and the energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of complex were calculated. Moreover, the HOMO–LUMO (H–L) energy gap, partial charges calculated from NBO analysis (natural bond orbital), structural parameters (such as bond lengths, bond angles), dipole and quadrupole moment were evaluated by DFT calculations. Atomic coordinates for the DFT calculations were obtained from the data of the X-ray crystal structure analyses for **3**.

3. Results and discussion

3.1. Synthesis

Reactions of HgX_2 (X = Cl, Br and I) with ylides in a 1:1 stoichiometry afforded halide-bridged dimeric structures **1–3** (Scheme 2) containing C-coordinated ylide ligands.

3.2. Infra-red spectra

The ν(CO) band, which is sensitive to complexation, occurs at 1610 cm^{-1} for the parent ylide, as in the case of other resonance stabilized ylides [18]. Coordination of the ylide through carbon causes an increase in ν(CO), while for O-coordination a lowering of ν(CO) is expected (Table 1).

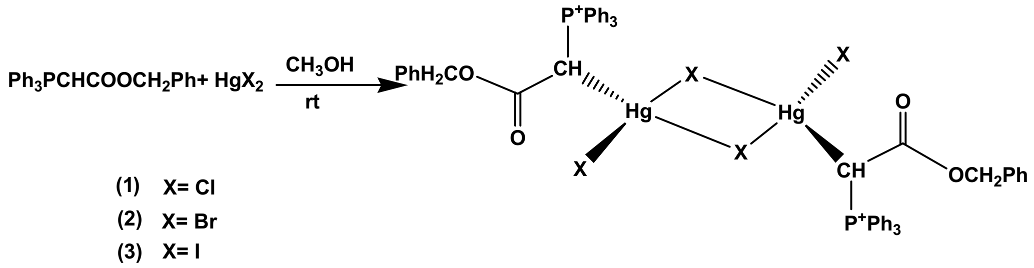
The infrared absorption bands observed for the three complexes at 1707, 1702 and 1688 cm^{-1} indicate coordination of the ylide through carbon. The ν(P^+–C^-) value, which is also diagnostic for the coordination, occurs at 958 cm^{-1} in Ph_3P^+–$^-CH_2$ and at 887 cm^{-1} in BAPPY. In the present study, the ν (P^+–C^-) values for all three complexes were shifted to lower frequencies and were observed at 839, 831 and 827 cm^{-1} for **1**, **2** and **3**, respectively, suggesting some removal of electron density from the P–C bond [19].

3.3. NMR spectral data

The ^1H NMR data for the mercury(II) complexes, along with those of the parent ylide, are listed in Table 2.

The signals due to the methine protons, when recorded in $CDCl_3$, were either broad or unobserved, probably due to the very low solubility of all the complexes in $CDCl_3$. Similar behavior was observed earlier in the case of ylide complexes of mercury(II) halides [20,21].

The expected downfield shifts of ^{31}P and ^1H signals for the PCH group upon complexation were observed in their corresponding



Scheme 2.

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

Compound	ν(CO) cm^{-1}	Ref.
$Ph_3PCHCON(CH_3)_2$	1530	[24]
$Ph_3PCHCOCH_3$ (APPY)	1530	[25]
$Ph_3PCHCOPh$ (BPPY)	1525	[26]
$(C_6H_4CH_3)_3PCHCOOCH_2C_6H_5$ (BAPPY)	1610	This work
C-coordination		
BAPPY · $HgCl_2$ (**1**)	1707	This work
BAPPY · $HgBr_2$ (**2**)	1702	This work
BAPPY · HgI_2 (**3**)	1688	This work
BPPY · $HgCl_2$	1635	[12]
BPPY · $HgBr_2$	1630	[12]
Au $[CH(PPh_3)CON(CH_3)_2]$	1605	[24]
O-coordination		
$[(Sn(CH_3)_3 \cdot BPPY]Cl$	1480	[27]
$[(SnPh_3).BPPY]Cl$	1470	[27]
$[Pd\{C_6F_5)(PPh_3\}_2(APPY)]ClO_4$	1513	[9]

APPY = acetylmethylenetriphenylphosphorane;
BPPY = benzoylmethylenephenylphosphorane.

Table 2
^1H and ^{31}P NMR data of BAPPY and its complexes with Hg(II) halides

Compound	δ (CH)	$^2J_{PH}$	δ (PPh_3)	δ (^{31}P)
BAPPY	2.93 (br)	–	7.16–7.88 (m)	15.04 (s)
BAPPY · $HgCl_2$	4.31 (br)	–	7.25–7.85 (m)	23.22 (s)
BAPPY · $HgBr_2$	4.17 (br)	–	7.26–7.95 (m)	21.85 (s)
BAPPY · HgI_2	4.19 (br)	–	7.35–8.05 (m)	20.24 (s)

(T = 298 K; J in Hz; TMS δ = 0.00 ppm). Recorded in $CDCl_3$, values (ppm) relative to internal TMS and external 85% phosphoric acid. s, singlet; m, multiplet; br, broad.

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

Possible assignments	BAPPY[a]	BAPPY · $HgCl_2$[b]	BAPPY · $HgBr_2$[b]	BAPPY · HgI_2[b]
CH	30.03 (d)	br	br	br
$^1J_{PC}$	124.89	–	–	–
CH_2	63.58 (s)	66.35 (s)	67.09 (s)	65.56 (s)
(CH_2Ph) (i)	138.32 (s)	135.50 (s)	135.50 (s)	135.78 (s)
(CH_2Ph) (o)	127.68 (s)	127.97 (s)	127.91 (s)	127.95 (s)
(CH_2Ph) (m)	127.36 (s)	127.79 (s)	127.74 (s)	128.75 (s)
(CH_2Ph) (p)	126.66 (s)	127.97 (s)	127.91 (s)	127.95 (s)
PPh_3 (i)	125.93 (d)	121.84 (d)	122.54 (d)	119.74 (d)
$^1J_{PC}$	63.19	88.69	89.32	92.72
PPh_3 (o)	132.55 (d)	132.54 (d)	132.97 (d)	133.04 (d)
$^2J_{PC}$	9.88	10.00	10.15	10.48
PPh_3 (m)	128.34 (d)	129.41 (d)	129.25 (d)	130.00 (d)
$^3J_{PC}$	12.25	12.34	12.29	11.78
PPh_3 (p)	131.64 (s)	133.86 (s)	133.63 (s)	133.20 (s)
CO	170.46 (s)	168.69 (s)	168.35 (s)	168.90 (s)

s, singlet; d, doublet; (o), ortho; (m), meta; (p), para; (i), ipso; br, broad.
[a] Recorded in $CDCl_3$.
[b] Recorded in DMSO-d_6.

spectra. The appearance of single signals for the PCH group in both the ^{31}P and ^1H NMR spectra 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 leads to the formation of *cis* and *trans* isomers which would give rise to two different signals in the ^{31}P and ^1H NMR spectra [6b]. The resonances in the ^{31}P NMR spectra of complexes **1**, **2** and **3** were observed to occur at a lower field with respect to the free ylide (Table 2). A comparison of the ^{31}P chemical shift of the three complexes at ambient temperature indicates a decrease in the order **1** > **2** > **3**. The ^{13}C NMR data of the complexes and the title ylide, along with possible assignments, are listed in Table 3.

The ^{13}C shifts of the CO group in the complexes are around 168 ppm, which is higher field than the 170 ppm noted for the same carbon in the parent ylide, indicating much higher shielding of the carbon atom of the CO group in the complexes [21]. No coupling to Hg was observed at room temperature in the ^1H, ^{13}C and ^{31}P NMR spectra. Failure to observe satellites in the above spectra was previously noted in the ylide complexes of Hg(II) [22] and Ag(I) [23], which had been explained by fast exchange of the ylide with the metal.

3.4. Crystal structures analysis

Table 4 provides the crystallographic results and refinement information for complex **3**. The molecular structure of **3** is shown in Fig. 1. Fractional atomic coordinates and equivalent isotropic displacement coefficients (U_{eq}) for the non-hydrogen atoms of complex **3** and a view of the crystal packing are shown in Fig. S1. Table 5 lists key bond lengths and angles for complex **3**.

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 $Ph_3PCHCOPh$ [24], but is similar to the structure of the C-coordinated dinuclear mercury(II) halide complexes of $Ph_3PCHCOOEt$ (EPPY) [25a] and $Ph_3PCHCOPh$ (BPPY) [25b]. The C-coordination of BAPPY is in stark contrast to the O-coordination of the phosphorus ylide $Ph_3PC(COCH_3)(COC_6H_5)$ (ABPPY) to the Hg(II) center [26]. The difference in coordination mode between ABPPY and BAPPY 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 BAPPY; 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 [27]. These authors concluded that the preferred coordination mode is via the ylidic carbon, but that steric hindrance around the metal center or the ylidic carbon will necessitate O-coordination. Indeed, this trend is reflected here, both BPPY and BAPPY are slightly less sterically demanding than

ABPPY and are both C-coordinated to Hg(II). The Hg(II) in **3** is sp^3 hybridized and has a tetrahedral coordination environment with one short Hg–I bond, one Hg–C bond and two asymmetric bridging Hg–I bonds at distances of 2.841(9) and 3.129(8) Å. The significance of the Hg–C bond of length, 2.263(6) Å, compared to analogous distances in $[\mathrm{BPPY} \cdot \mathrm{HgI_2}]_2$ [25] and $[(C_6H_5)_3PC_5H_4 \cdot HgI_2]_2$ [22] (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 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

Table 4
Crystal data and refinement parameter for **3**

Empirical formula	$C_{54}H_{46}I_4Hg_2O_4P_2$
Formula weight	1729.63
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system, space group	monoclinic, $P2_1/c$
Unit cell dimensions	
a (Å)	20.493(4)
b (Å)	12.496(3)
c (Å)	23.293(5)
β (°)	109.52(3)
Volume (A^3)	5623(2)
Z, D_{calc} (Mg/m^3)	4, 2.043
Absorption coefficient (mm^{-1})	7.748
F(000)	32.16
Crystal size (mm)	0.35 × 0.30 × 0.20
Theta Range for data collection (°)	1.62–26.81
Limiting indices	$-25 \leqslant h \leqslant 23$, $-15 \leqslant k \leqslant 15$, $-29 \leqslant l \leqslant 29$
Reflections collected/unique	33 902/11 871 [R(int) = 0.0442]
Completeness to Theta = 23.78° (%)	98.60
Absorption correction	numerical
Maximum and minimum transmission	0.212 and 0.083
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	11 871/0/595
Goodness-of-fit on F^2	1.139
Final R_1, wR_2[a] (observation data)	0.0514, 0.0854
Final R_1, wR_2[a] (All data)	0.0755, 0.0928
Largest diffraction peak and hole (e A^{-3})	0.920 and −1.004

[a] $R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|, wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2}$.

Table 5
A comparison between the selected calculated bond lengths (Å) and bond angles (°) for compound **3** with X-ray data

	X-ray	B3LYP/Lanl2mb
Bond lengths		
Hg(1)–C(1)	2.263(6)	2.341
Hg(1)–I(1)	2.6719(9)	3.042
Hg(1)–I(2)	2.8410(9)	3.197
Hg(1)–I(2)#1	3.1296(8)	3.316
P(1)–C(1)	1.783(6)	1.969
P(1)–C(10)	1.792(6)	1.949
P(1)–C(16)	1.808(7)	1.940
P(1)–C(22)	1.806(7)	1.961
Bond angles		
C(1)–Hg(1)–I(1)	129.12(15)	135.91
C(1)–Hg(1)–I(2)	113.42(16)	105.293
I(1)–Hg(1)–I(2)	111.88(3)	103.448
C(1)–Hg(1)–I(2)#1	96.84(15)	99.912
I(1)–Hg(1)–I(2)#1	102.57(3)	111.639
I(2)–Hg(1)–I(2)#1	93.22(3)	92.252
C(1)–P(1)–C(10)	115.4(3)	109.17
C(1)–P(1)–C(16)	108.4(3)	109.74
C(10)–P(1)–C(22)	106.8(3)	106.81
C(22)–P(1)–C(16)	107.4(3)	107.10
C(10)–P(1)–C(16)	108.3(3)	109.84
O(1)–C(2)–O(2)	123.4(6)	123.62
O(1)–C(2)–C(1)	126.4(6)	131.18
O(2)–C(3)–C(4)	114.0(6)	111.41
P(1)–C(1)–Hg(1)	113.1(3)	118.45

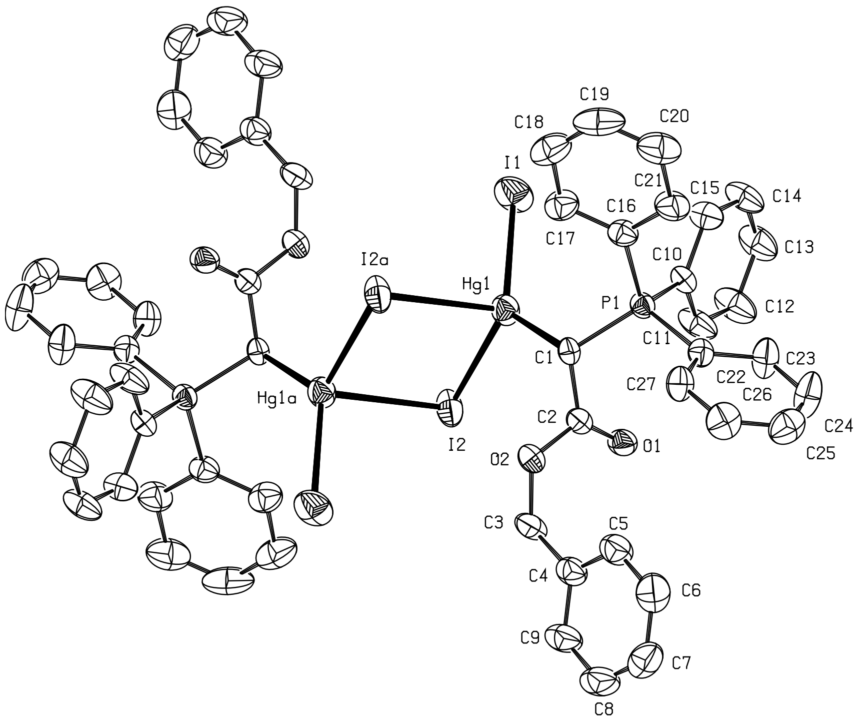


Fig. 1. Molecular structure of the complex $[(\mathrm{BAPPY}) \cdot \mathrm{HgI_2}]_2$. H atoms are omitted for clarity.

atom. The internuclear distances between mercury atoms were found to be 4.090(5), 4.014(1) and 3.810(2) Å in the structures **3**, $[BPPY \cdot HgI_2]_2$ and $[BPPY \cdot HgCl_2]_2$, respectively. These distances are much longer than the sum of the Van der Waals radii (1.5 Å) of the two mercury atoms [28] indicating the absence of significant bonding interactions between the mercury atoms in the molecular structures. The adaptation of dimeric structures in the 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).

3.5. Theoretical studies

The optimized structure of this compound is shown in Fig. 2 and selected bond lengths and bond angles are given in Table 5.

As can be seen, the calculated bond lengths are slightly longer than the 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 the general formula $[BAPPY \cdot HgX_2]_2$ can be considered as both the observed *trans*-like or possible *cis*-like isomers. Table 5 shows the complete data collections for the X-ray results and theoretical calculation. In the *trans*-like structure of the compound, the internuclear distances between the mercury atoms were calculated to be 4.514 Å, indicating the absence of significant bonding interactions between the mercury atoms in the molecular structure. The Hg–C bond length in the trans structure is calculated to be 2.341 Å. A comparison of the bond lengths and bond angles from both methods (X-ray crystallography and quantum calculation) shows that the results of the calculation are the same as the X-ray crystallography results. For example the distances: P(1)–C(1), P(1)–C(10), P(1)–C(16), P(1)–C(22) have approximately equal values. These data show that the phenyl rings attached to phosphorus have little effect on the bond lengths between the phosphorus and carbon atoms. The stability energy values for this complex are reported in Table 6.

Furthermore, the energies of the HOMO and LUMO for the complex are summarized in Table 6. In this case, partial charge transfer will occur by a contribution from the mixing of the filled orbital of one component molecule with the vacant orbital of another. The most important terms in this kind of interaction are contributed from the partial charge transfer between the HOMO of one component and the LUMO of another. The HOMO–LUMO (H–L) energy gap is large in magnitude for this complex and corresponds to 4.161 eV. As listed in Table 6, the dipole moment of the trans complex in the *x*, *y* and *z* planes was only 0.0 De. This result shows that the complex has no polarity in the three planes. The structure of the HOMO and LUMO are shown in Figs. 3a and 3b.

Table 6
Energies, partial charges, dipole moment (De), quadrupole moment (De) and HOMO and LUMO energy of the B3LYP/lanl2mb optimized trans structure at the DFT/LanL2MB level of theory

Species		Values
E (eV)		−68048.41
HOMO (eV)		−4.403
LUMO (eV)		−0.242
H–L (eV)		4.161
Charge *s* (esu)		
Hg(1)		0.202
C(1)		−0.150
C(2)		0.228
C(3)		−0.043
C(4)		−0.008
P(1)		0.201
O(1)		−0.198
O(2)		−0.114
Dipole moment (De)		
X	*Y*	*Z*
0.00	0.00	0.00
Quadrupole moment (De)		
XX	*YY*	*ZZ*
−392.29	−399.01	−379.54
XY	*XZ*	*YZ*
−45.0531	104.66	−43.59

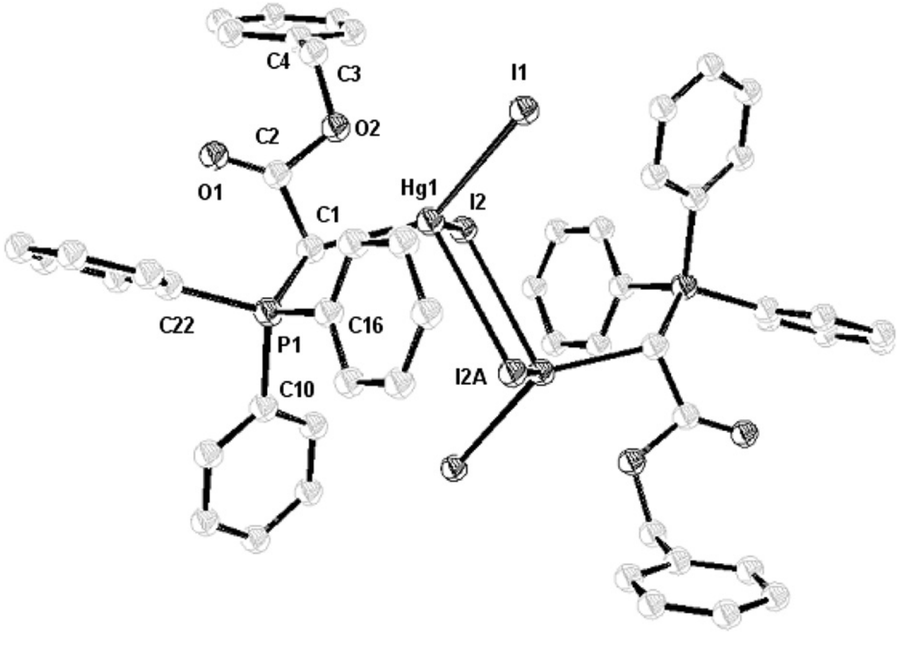


Fig. 2. Optimized structure of the complex $[(BAPPY) \cdot HgI_2]_2$.

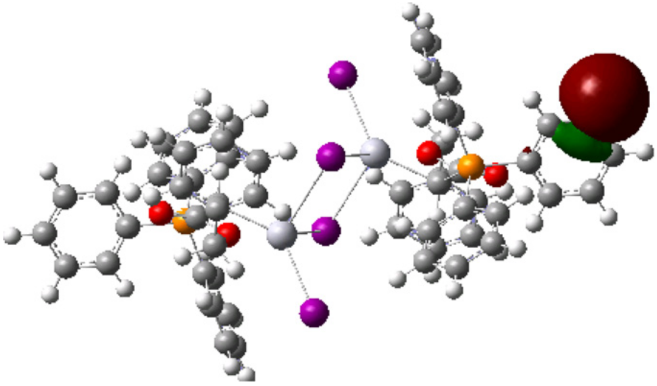


Fig. 3a. Structure of the HOMO of the complex $[(BAPPY) \cdot HgI_2]_2$.

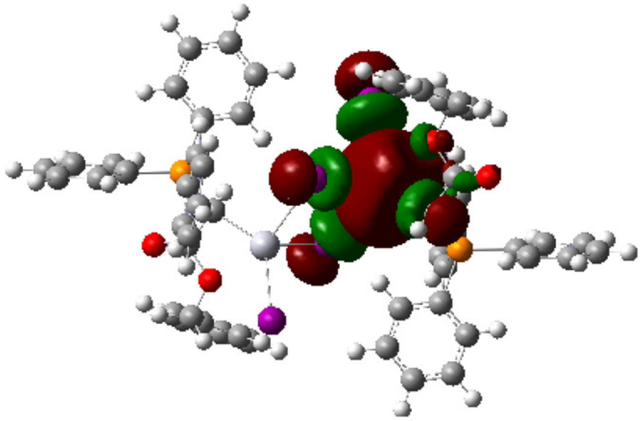


Fig. 3b. Structure of the LUMO of the complex $[(BAPPY) \cdot HgI_2]_2$.

4. Conclusions

The present study describes the synthesis and characterization of a new ylide (BAPPY) and its mercury(II) complexes of the general formula $[BAPPY.HgX_2]_2$ (X = Cl, Br, I). On the basis of the physico-chemical and spectroscopic data we propose that BAPPY herein exhibits monodentate C-coordination to the metal center. In addition theoretical studies on the gas phase structure of **3** confirms the *trans*-like dimeric structure for this compound, as obtained by X-ray crystal structure analyses.

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Appendix A. Supplementary data

CCDC 648218 contains the supplementary crystallographic data for **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.2008.03.010.

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