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Structural, theoretical and multinuclear NMR study of mercury(II) complexes of phosphorus ylides: Mono and binuclear complexes

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ABSTRACT

Reaction of phosphorus ylide $Ph_3PCHC(O)C_6H_4Cl$ (**Y_1**) with HgX_2 (X = Cl, Br and I) and ylide (*p*-tolyl)$_3$PCH-C(O)CH_3 (**Y_2**) with HgI_2 in equimolar ratios using methanol as solvent leads to binuclear products. The bridge-splitting reaction of binuclear complex $[(Y_1) \cdot HgCl_2]_2$ by DMSO yields a mononuclear complex containing DMSO as ligand. O-coordination of DMSO is revealed by single crystal X-ray analysis in mononuclear complex of $[(Y_1) \cdot HgCl_2 \cdot DMSO]$. C-coordination of ylides is confirmed by X-ray structure of binuclear complex $[(Y_2) \cdot HgI_2]_2$. Characterization of the obtained compounds was also performed by elemental analysis, IR, ^1H, ^{31}P, and ^{13}C NMR. Theoretical studies on mercury(II) complexes of Y_1 show that formation of mononuclear complexes in DMSO solution in which DMSO acts as a ligand, energetically is more favorable than that of binuclear complexes.

1. Introduction

The utility of metalated phosphorus ylides in synthetic chemistry has been well documented [1,2]. Synthesis of complexes derived from phosphorus ylides and Hg(II) halides was started in 1965 by Nesmeyanov et al. [3]. In 1975, Weleski et al. [4] proposed a symmetric halide-bridged dimeric structure for Hg(II) halide complexes whereas Kalyanasundari et al. [5] reported an asymmetric halide-bridged dimeric structure in 1995. In 1985, Sanehi et al. [6] reported a mononuclear Hg(II) complex of phosphorus ylides without any structural characterization. We have recently focused on the synthesis of binuclear and polynuclear complexes derived from mercury(II) salts and phosphorus ylides [7–9]. The α-keto-stabilized phosphorus ylides $R_3P{=}C(R')COR''$ show interesting properties such as their high stability and their ambidentate character as ligands (C- versus O-coordination) [10]. This ambidentate character can be rationalized in terms of the resonance forms A–C, together with the isomeric form D (Chart 1).

Form B can be considered as leading to coordination by the carbon atom to give a complex of form E, whereas isomers C and D would both lead to coordination by the oxygen atom, affording structures F (*transoid*) and form G (*cisoid*), respectively. Although many coordination modes are possible for keto ylides [11], 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) [5,12–15], whereas, O-coordination dominates when the metals involved are hard, *e.g.*, Ti(IV), Zr(IV), and Hf(IV) [16]. Only W(0) complexes of the type $W(CO)_5L$ (L = ylide) [17] and Pd(II) complexes of stoichiometry $[Pd(C_6F_5)(L_2)(APPY)](ClO_4)$ [12] [APPY = Ph_3PCH-COMe; L = PPh_3 and PBu_3; L_2 = bipy] contain stable ylides O-linked to a soft metal centre.

2. Experimental

2.1. Materials

All reactions were performed in air. Starting materials were purchased from commercial sources and used without further purification. The ligands were synthesized by the reaction of related phosphine with 2-bromo-4′-chloroacetophenone or chloroacetone and concomitant elimination of HBr by NaOH [18].

2.2. Physical measurements

Melting points were measured on a SMPI apparatus. Elemental analysis for C and H atoms were performed using a Perkin–Elmer 2400 series analyzer. IR spectra were recorded on a Shimadzu 435-U-04 FT spectrophotometer from KBr pellets. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a 300 MHz Bruker spectrometer in DMSO-d_6 or $CDCl_3$ as solvent at 25 °C. Chemical shifts (ppm) are reported according to internal TMS and external 85% phosphoric acid. Coupling constants are given in Hz. The single crystal X-ray diffraction analyses were performed on a STOE IPDS-II two

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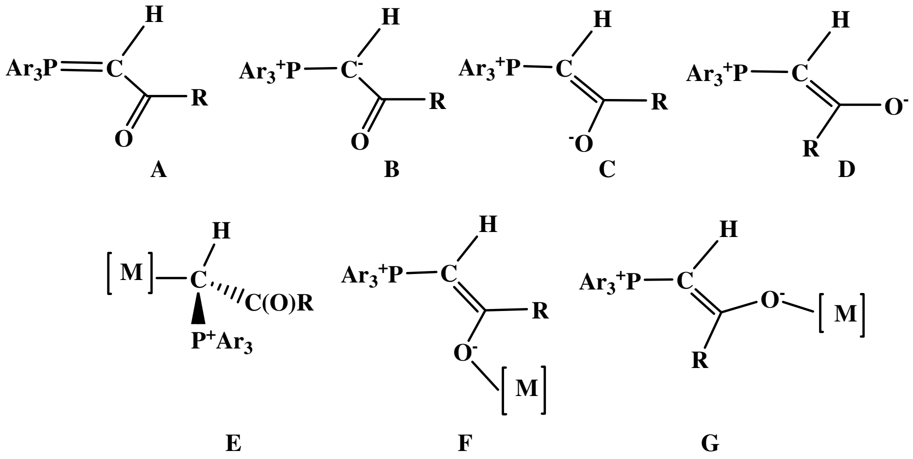


Chart 1.

circle diffractometer at 293(2) K, using graphite monochromated Mo Kα X-ray radiation ($\lambda = 0.7107$ nm). The data collection were performed at room temperature using the ω-scan technique and using the STOE X-AREA software package [19]. The crystal structures were solved by direct methods and refined by full-matrix least-squares on F^2 by SHELX [20] and using the X-STEP32 crystallographic software package [21]. All non-hydrogen atoms were refined anisotropically using reflections $I > 2\sigma(I)$. Hydrogen atoms were located in ideal positions.

2.3. Theoretical studies

The geometries of compounds were fully optimized at the Hartree–Fock (HF) level of theory using the GAUSSIAN98 program [22] on a Pentium-PC computer with 3600 MHz processor. The standard LanL2mb basis set was used for all complexes [23]. This basis set includes effective core potentials (ECP) for both the mercury and phosphorus as well as halide (Cl, Br and 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.

2.4. Preparation of $Ph_3PCHCOC_6H_4Cl$ (Y_1), general procedure for ylides [24]

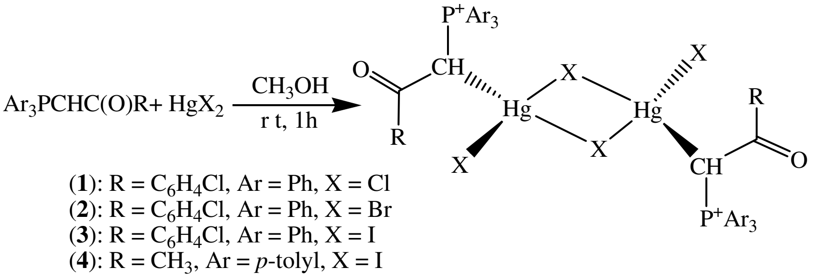
A solution of triphenylphosphine (0.131 g, 0.5 mmol) and 2-bromo-4′-chloroacetophenone (0.117 g, 0.5 mmol) in acetone (15 ml) was stirred at room temperature for 4 h. The resulting white precipitate was filtered off, washed with diethylether and dried. Further treatment with aqueous solution of NaOH (0.5 M, 50 ml) led to elimination of HBr, giving the free ligand Y_1. IR (KBr, cm^{-1}): ν 1579 (C=O), 1522, 1480, 1435, 1404, 1383, 1175, 1104, 1085, 1009, 882 (P–C), 848. ^1H NMR ($CDCl_3$) δ_H: 4.38 (d, $^2J_{PH} = 23.75$ Hz, 1H, CH); 7.25–7.94 (m, 19H, Ph). ^{31}P NMR ($CDCl_3$) δ_P: 14.19 (s). ^{13}C NMR ($CDCl_3$) δ_C: 50.65 (d, $^1J_{PC} = 110.3$ Hz, CH); 126.0 (d, $^1J_{PC} = 91.40$ Hz, PPh_3 (i)); 127.31 (COPh (m)); 128.03 (PPh_3 (p)); 128.48 (d, $^3J_{PC} = 12.41$ Hz, PPh_3 (m)); 131.80 (d, $^4J_{PC} = 2.73$ Hz, COPh (o)); 132.60 (d, $^2J_{PC} = 10.25$ Hz, PPh_3 (o)); 134.71 (COPh (p)); 139.15 (d, $^2J_{PC} = 14.69$ Hz, COPh (i)); 182.84 (d, $^2J_{PC} = 3.1$ Hz, CO).

2.5. $(p\text{-tolyl})_3PCHCOCH_3$ (Y_2)

Anal. Calc. for $C_{24}H_{25}OP$: C, 80.00; H, 7.00. Found: C, 79.51; H, 7.01%. Yield 0.364 g (92%). m.p., 100–102 °C. IR (KBr disk): ν (cm^{-1}) 1711, 1599 (C=O), 1502, 1448, 1425, 1402, 1363, 1313, 1193, 1156, 1111, 1038, 1002, 848 (P–C), 808 and 777. ^1H NMR ($CDCl_3$): δ (ppm) 2.04 (3H, s, $COCH_3$), 2.36 (9H, s, $3CH_3$), 3.65 (1H, d, $^2J_{PH} = 24.8$ Hz, CH); 7.24–7.52 (12H, m, Ph). ^{31}P NMR ($CDCl_3$) δ_P: 10.59 (s). ^{13}C NMR ($CDCl_3$) δ_c: 21.49 (s, $3CH_3$); 28.43 (d, $^3J_{PC} = 15.1$ Hz, $COCH_3$); 52.53 (d, $^1J_{PC} = 107.7$ Hz, CH); 124.29 (d, $^1J_{PC} = 92.7$ Hz, p-tolyl, (i)); 133.05 (d, $^2J_{PC} = 10.5$ Hz, p-tolyl, (o)); 129.51 (d, $^3J_{PC} = 12.3$ Hz, p-tolyl, (m)); 142.32 (p-tolyl, (p)); 190.38 (CO).

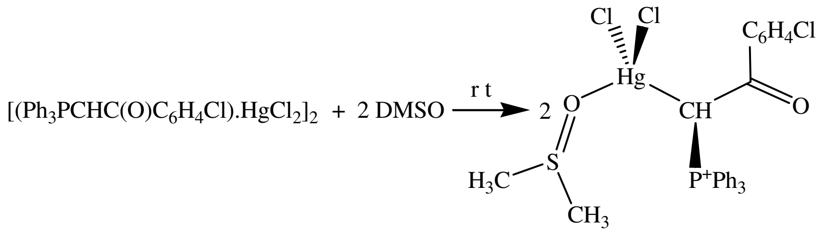
2.6. Synthesis of the complexes

The binuclear complexes **1**–**4** were prepared based on a general procedure as follows (Scheme 1). According to various papers [5,7,8,25], the binuclear structures are suggested for above compounds, as shown in Scheme 1. X-ray quality crystals of the complexes **4** and **5** (Schemes 1 and 2) were grown from a



(**1**): R = C_6H_4Cl, Ar = Ph, X = Cl
(**2**): R = C_6H_4Cl, Ar = Ph, X = Br
(**3**): R = C_6H_4Cl, Ar = Ph, X = I
(**4**): R = CH_3, Ar = p-tolyl, X = I

Scheme 1.



Scheme 2.

dimethylsulfoxide solution of compounds **4** and **1**, respectively. This was carried out by the slow evaporation of the solvent over several days.

2.6.1. Synthesis of $[(Y_1)\cdot HgCl_2]_2$ (**1**), general procedure for dimeric structures

To a methanolic solution (15 ml) of $HgCl_2$ (0.082 g, 0.3 mmol) was added a methanolic solution (10 ml) of Y_1 (0.124 g, 0.3 mmol). The mixture was stirred for 1 h. The separated solid was filtered and washed with diethyl ether. *Anal.* Calc. for $C_{26}H_{20}Cl_3HgOP$: C, 45.50; H, 2.94. Found: C, 44.41; H, 2.81%. Yield 0.115 g (56%). m.p. 215–217 °C. IR (KBr, cm^{-1}): ν 1635 (C=O), 1586, 1567, 1483, 1437, 1398, 1312, 1284, 1184, 1108, 1091, 1005, 823 (P–C). ^1H NMR (DMSO-d_6) δ_H: 5.46 (d, $^2J_{PH} = 6.36$ Hz, 1H, C*H*); 7.46–8.10 (m, 19H, Ph). ^{31}P NMR (DMSO-d_6) δ_p: 22.16 (s). ^{13}C NMR (DMSO-d_6) δ_c: 46.77 (d, $^1J_{PC} = 75.58$ Hz, *C*H); 123.33 (d, $^1J_{PC} = 89.46$ Hz, PPh_3 (*i*)); 127.81 (COPh (*m*)); 129.16 (d, $^3J_{PC} = 12.35$ Hz, PPh_3 (*m*)); 129.16 (COPh (*p*)); 129.74 (PPh_3 (*p*)); 133.10 (d, $^2J_{PC} = 9.46$ Hz, PPh_3 (*o*)); 136.22 (COPh (*o*)); 136.63 (COPh (*i*)); 188.82 (s, CO).

2.6.2. $[(Y_1)\cdot HgBr_2]_2$ (**2**)

Anal. Calc. for $C_{26}H_{20}Br_2ClHgOP$: C, 40.28; H, 2.60. Found: C, 40.13; H, 2.57%. Yield 0.193 g (83%). m.p. 195–197 °C. IR (KBr, cm^{-1}): ν 1625 (C=O), 1586, 1566, 1482, 1435, 1398, 1317, 1292, 1195, 1108, 1030, 1010, 997, 885, 819 (P–C) and 805. ^1H NMR (DMSO-d_6) δ_H: 5.38 (d, $^2J_{PH} = 7.62$ Hz, 1H, C*H*); 7.45–8.08 (m, 19H, Ph). ^{31}P NMR (DMSO-d_6) δ_p: 22.72 (s). ^{13}C NMR (DMSO-d_6) δ_c: 48.04 (d, $^1J_{PC} = 79.40$ Hz, *C*H); 124.13 (d, $^1J_{PC} = 89.97$ Hz, PPh_3 (*i*)); 128.52 (COPh (*m*)); 129.92 (d, $^3J_{PC} = 11.40$ Hz, PPh_3 (*m*)); 130.54 (PPH_3 (*p*)); 133.87 (d, $^2J_{PC} = 9.28$ Hz, PPh_3 (*o*)); 133.93 (COPh (*p*)); 136.96 (COPh (*o*)); 137.22 (COPh (*i*)); 189.41 (s, CO).

2.6.3. $[(Y_1)\cdot HgI_2]_2$ (**3**)

Anal. Calc. for $C_{26}H_{20}ClHgI_2OP$: C, 35.92; H, 2.32. Found: C, 35.86; H, 2.17%. Yield 0.170 g (82%). m.p. 192–194 °C. IR (KBr, cm^{-1}): ν 1620 (C=O), 1586, 1565, 1482, 1434, 1398, 1316, 1291, 1266, 1193, 1108, 1092, 1030, 1009, 998, 878, 820 (P–C) and 802. ^1H NMR (DMSO-d_6) δ_H: 5.12 (d, $^2J_{PH} = 12.46$ Hz, 1H, C*H*); 7.42–8.05 (m, 19H, Ph). ^{31}P NMR (DMSO-d_6) δ_p: 20.64 (s). ^{13}C NMR (DMSO-d_6) δ_c: 48.90 (d, $^1J_{PC} = 83.25$ Hz, *C*H); 124.71 (d, $^1J_{PC} = 89.74$ Hz, PPh_3 (*i*)); 128.45 (COPh (*m*)); 129.85 (d, $^3J_{PC} = 12.15$ Hz, PPh_3 (*m*)); 130.24 (PPh_3 (*p*)); 133.75 (d, $^2J_{PC} = 9.13$ Hz, PPh_3 (*o*)); 133.81 (COPh (*p*)); 136.66 (COPh (*o*)); 137.67 (d, $^3J_{PC} = 10.64$ Hz, COPh (*i*)); 187.81 (s, CO).

2.6.4. $[(Y_2)\cdot HgI_2]_2$ (**4**)

Anal. Calc. for $C_{24}H_{25}HgI_2OP$: C, 35.38; H, 3.09. Found: C, 35.24; H, 3.54%. Yield 0.218 g, 89%. m.p. 206–208 °C. IR (KBr, cm^{-1}): ν 1655 (C=O), 1596, 1497, 1399, 1350, 1289, 1192, 1149, 1106, 964, 902, 852 and 805. ^1H NMR (DMSO-d_6): δ (ppm) 2.14 (3H, s, COCH_3); 2.39 (9H, s, 3CH_3); 4.59 (1H, br, C*H*); 7.44–7.66 (12H, m, Ph). ^{31}P NMR (DMSO-d_6) δ_p: 20.63 (s). ^{13}C NMR (DMSO-d_6) δ_c: 21.03 (3*C*H_3); 30.54 (d, $^3J_{PC} = 11.2$ Hz, CO*C*H_3); 50.39 (d, $^1J_{PC} = 63.8$ Hz, *C*H); 119.97 (d, $^1J_{PC} = 92.6$ Hz, *p*-tolyl (*i*)); 129.84 (d, $^3J_{PC} = 12.6$ Hz, *p*-tolyl (*m*)); 133.09 (d, $^2J_{PC} = 10.2$ Hz, *p*-tolyl (*o*)); 143.81 ((*p*-tolyl) (*p*)); 197.91 (*C*O).

2.6.5. $[(Y_1)\cdot HgCl_2\cdot DMSO]$ (**5**)

0.137 g (0.1 mmol) of binuclear complex **1** was dissolved in DMSO (2 ml). The pale yellow crystals formed by the slow evaporation of the solvent over several days. Yield 0.147 g (96%). Decomposition at 180 °C. IR (KBr, cm^{-1}): ν 1635 (C=O), 1586, 1567, 1483, 1437, 1398, 1312, 1284, 1184, 1108, 1091, 1005, 823 (P–C). ^1H NMR (DMSO-d_6) δ_H: 5.46 (d, $^2J_{PH} = 6.36$ Hz, 1H, C*H*); 7.46–8.10 (m, 19H, Ph). ^{31}P NMR (DMSO-d_6) δ_p: 22.16 (s). ^{13}C NMR (DMSO-d_6) δ_c: 46.77 (d, $^1J_{PC} = 75.58$ Hz, *C*H); 123.33 (d, $^1J_{PC} = 89.46$ Hz, PPh_3 (*i*)); 127.81 (COPh (*m*)); 129.16 (d, $^3J_{PC} = 12.35$ Hz, PPh_3 (*m*)); 129.16 (COPh (*p*)); 129.74 (PPh_3 (*p*)); 133.10 (d, $^2J_{PC} = 9.46$ Hz, PPh_3 (*o*)); 136.22 (COPh (*o*)); 136.63 (COPh (*i*)); 188.82 (s, CO).

3. Results and discussion

3.1. Spectroscopy

The ν (CO) band, which is sensitive to complexation, is observed for complexes at higher frequencies compared to the parent ylides, indicating coordination of the ylide thorough carbon atom in each case [26]. The ν (P^+–C^-) band, (823, 819 and 820 cm^{-1} for complexes **1**–**3**, respectively) which is also diagnostic of the coordination modes, occurs at lower frequencies (882 cm^{-1}) in comparison to the parent ylide (Y_1), consistent with some removal of electron density in the P–C bonds [7–9]. C-coordination causes an increase in ν (CO) and decrease in ν (P^+–C^-) while for O-coordination a lowering for both frequencies is expected [15]. It should be noted that there is not any significant difference in the IR absorption bands for binuclear complex **1** and related mononuclear complex **5**.

In the ^1H NMR spectra, the signals due to the methinic protons for complexes are doublet or broad. Similar behavior was observed earlier in the case of ylide complexes of platinum(II) chloride [27]. The expected downfield shifts of ^{31}P and ^1H signals for the PCH group upon complexation in the case of C-coordination were observed in their corresponding spectra. The proton decoupled ^{31}P NMR spectra show only one sharp singlet between 20.63 and 22.72 ppm in the complexes. The appearance of a single signal for the PCH group in each of the ^{31}P and ^1H NMR spectra indicates that all ligands are in the same environment in these complexes, as expected for C-coordination. It must be noted that O-coordination of the ylide generally leads to the formation of a mixture of *cisoid* and *transoid* isomers, giving rise to two different signals in ^{31}P and ^1H NMR spectra (Chart 1) [12]. The ^{31}P chemical shift values for the complexes appear to be shifted downfield by about 6.5–10 ppm with respect to the parent ylides also indicating that coordination of the ylide has occurred [5,7–9,25]. Satellites due to coupling to ^{199}Hg for ylidic complexes of Hg(II) are only observed at low temperature [7,25] or by solid-state ^{31}P NMR [25] and also in the case of $Hg(NO_3)_2\cdot H_2O$ as metal source [9]. Failure to observe satellites in above spectra was previously noted in the complexes of Hg(II) [28] and Ag(I) [15] and was assigned to fast exchange of the ylide with the metal at higher temperatures.

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 atoms. Such an upfield shift was 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), and is due to the change in hybridization of the ylidic carbon atom on coordination [29]. Similar up field shifts of 2–3 ppm with reference to the parent ylide were also observed in the case of $[(C_6H_5)_3PC_5H_4HgI_2]_2$ [28]. The downfield shifts of the carbonyl C atom in the complexes compared to the same carbon atom in the parent ylides, indicate a much lower shielding of the CO group in these complexes.

3.2. X-ray crystallography

Table 1 provides the crystallographic results and refinement information for complexes **4** and **5**. The molecular structures are shown in Figs. 1 and 2. Pertinent bond distances and angles for **4** and **5** are given in Tables 2 and 3, respectively. Packing diagrams, fractional atomic coordinates and equivalent isotropic displacement coefficients (Ueq) for the non-hydrogen atoms of complexes are shown in Supplementary materials.

The Hg(II) centre in complex **4** forms four-coordinate with sp^3 hybridization. This environment is contained of one short terminal Hg–I bond, one Hg–C bond and two asymmetric bridging Hg–I bonds. The Hg–C and terminal Hg–I bond lengths in **4** (2.279(8) and 2.7036(8) Å) are comparable to analogous distances in $[(Ph_3PCHCOPh)\cdot HgI_2]_2$ (2.312(13) and 2.705(1) Å, respectively) [5].

Table 1
Crystallographic data summary for complexes **4** and **5**

Compound	**4**	**5**
Empirical formula	$C_{48}H_{50}Hg_2I_4O_2P_2$	$C_{28}H_{26}Cl_3HgO_2PS$
F_w	1629.6	764.47
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	triclinic	orthorhombic
Space group	$P\bar{1}$	*Pbca*
a (Å)	11.697(2)	11.1014(11)
b (Å)	11.968(3)	18.7168(14)
c (Å)	11.933(2)	28.292(3)
α (°)	105.371(16)	90
β (°)	106.160(16)	90
γ (°)	115.223(15)	90
Volume (Å^3)	1302.4(5)	5878.5(9)
Z	1	8
D_{Calcd} (Mg/m^3)	2.078	1.727
Absorption coefficient (mm^{-1})	8.353	5.658
F(000)	752	2976
Crystal size (mm)	0.35 × 0.22 × 0.12	0.50 × 0.30 × 0.04
Theta range for data collection (°)	1.98–26.76	2.25–26.82
Limiting indices	$-14 \leqslant h \leqslant 14$, $-15 \leqslant k \leqslant 15$, $-15 \leqslant l \leqslant 15$	$-13 \leqslant h \leqslant 14$, $-23 \leqslant k \leqslant 20$, $-31 \leqslant l \leqslant 35$
Reflections collected/unique [*R*(int)]	7728/5006 [0.0304]	22647/6214 [0.0359]
Completeness to theta (%)	26.76, 90.5	26.82, 98.8
Absorption correction	numerical	numerical
Maximum and minimum transmission	0.370 and 0.131	0.800 and 0.145
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	5006/0/262	6214/0/327
Goodness-of-fit on F^2	1.113	1.161
Final *R* indices [$I > 2\text{sigma}(I)$]	$R_1 = 0.0375$, $wR_2 = 0.1240$	$R_1 = 0.0372$, $wR_2 = 0.0619$
R indices (all data)	$R_1 = 0.0456$, $wR_2 = 0.1362$	$R_1 = 0.0524$, $wR_2 = 0.0658$
Largest difference peak and hole (e Å^{-3})	0.891 and −1.003	0.870 and −0.597

The angles subtended by the ligands at the Hg(II) centre in **4** vary from 95.53(3) to 121.7(2) indicating a much distorted tetrahedral environment. The widening of the IHgC angle from the tetrahedral angle 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 halide-bridge between Hg atoms which requires the internal IHgI angle (95.53(3)) to be considerably smaller. The two mercury atoms and two bridging halides are perfectly coplanar. The internuclear distance between mercury atoms in complex **4** were found to be 3.926 Å, which is much longer than the sum of Van der Waals radii (3 Å) of the two mercury atoms [30], indicating the absence of significant bonding interactions between the mercury atoms in the molecular structures.

The Hg(II) centre in complex **5** is coordinated by one carbon, one oxygen and two chloro atoms in a distorted tetrahedral geometry. The two different Hg–Cl distances in **5** (2.3986(13) and 2.5106(12) Å) are less than those of found in mononuclear complex of $[HgCl_2(PPh_3)_2]$ [31] (2.559(2) and 2.545(3) Å), indicating relatively strong Hg–Cl bonds in **5**. Difference between two distances in these complexes might be arising from steric effects of the large ylidic groups. The angles around mercury in complex **5** vary from 87.39(13) to 139.45(11), indicating 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 steric effects of phosphine group needing the C–Hg–Cl angle to be larger.

The stabilized resonance structure for the parent ylides are destroyed by the complex formation, thus, the C(H)–C bond lengths, 1.473(12) Å (**4**) and 1.491(5) Å (**5**) are significantly longer than the corresponding distances found in the uncomplexed similar phosphoranes (1.407(8) Å [32] and 1.401(2) Å [33]). On the other hand, the bond length of P–C(H) in the similar ylide is 1.7194(17) Å [33] which shows that the corresponding bonds are considerably elongated to 1.786(8) Å (**4**) and 1.787(4) Å (**5**).

The C-coordination of the title ylides is in contrast to the O-coordination of the phosphorus ylide $Ph_3PC(COMe)(COPh)$ (ABPPY) in a different Hg(II) complex [34]. The difference in coordination mode between ABPPY and present ylides to Hg(II) can be rationalized in terms of the electronic properties, steric requirements and size and shape of the ligand in the final bonding mode. This may also explain by the electronic nature of the metal (Pd, Pt, Ru, Au, etc.) and even the position of the coordination site (*trans* to a C atom, *trans* to a N atom, *trans* to an O atom, and so on). The nucleophilicity of the carbanion in ABPPY is less than in our ylides; 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, these ylides are slightly less sterically demanding than ABPPY and are C-coordinated to Hg(II).

3.3. DMSO as ligand

Literature data show that the coordination mode of dimethylsulfoxide (DMSO) to relatively soft metal atoms depends on both electronic and steric factors deriving from the DMSO moderate π-acceptor properties and its greater steric demand in the case of S-bonding [36]. In the case of ruthenium(II) complexes, coordination through sulfur (DMSO–S) seems to be preferred over

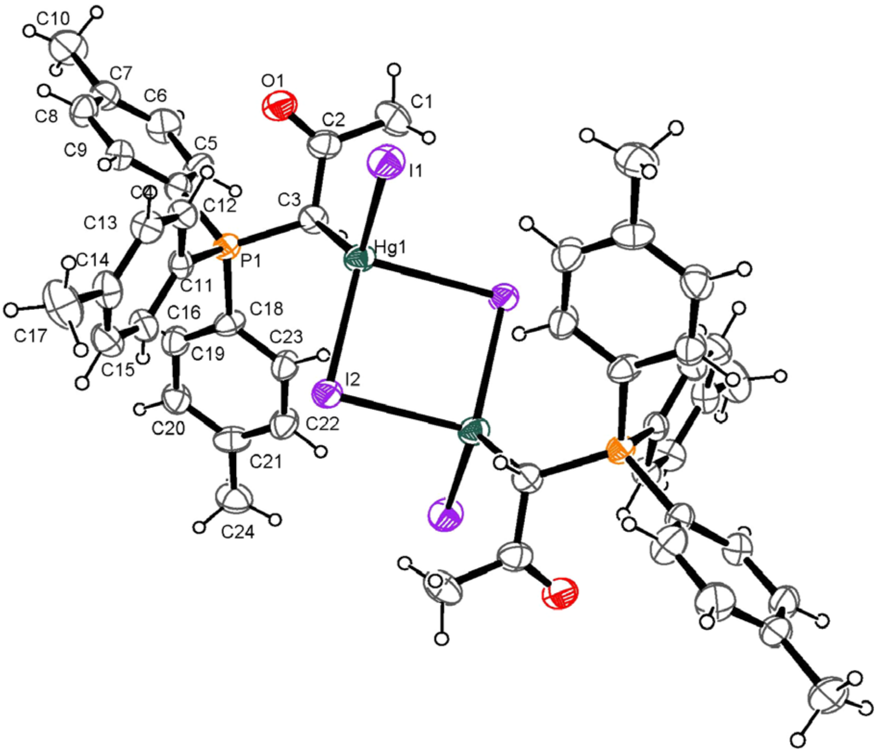


Fig. 1. ORTEP view of X-ray crystal structure of $[(Y_2) \cdot HgI_2]_2$ (**4**).

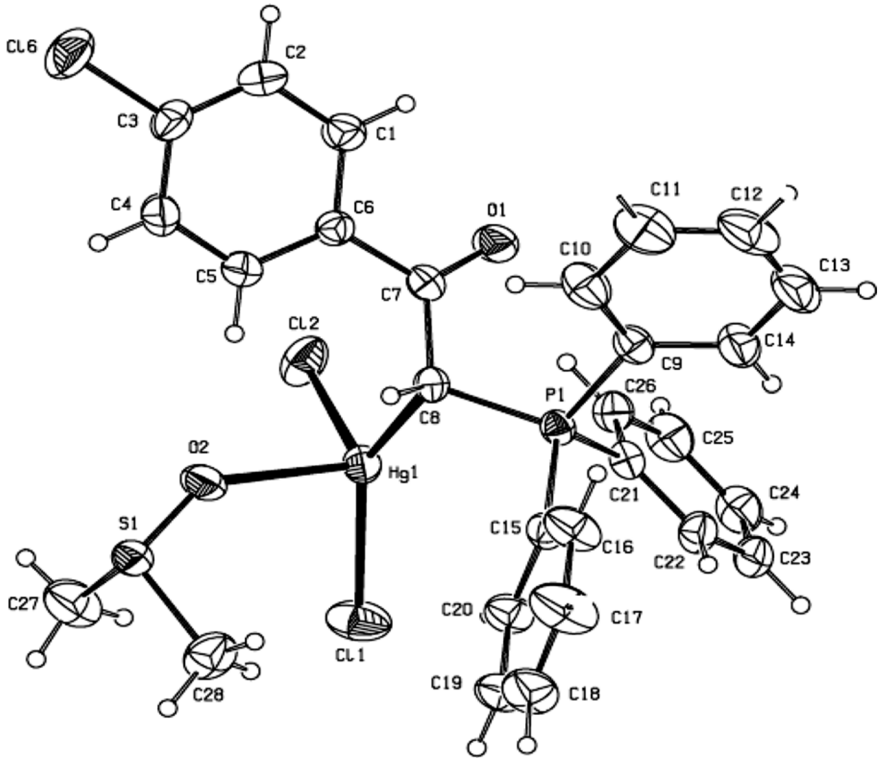


Fig. 2. ORTEP view of X-ray crystal structure of $[(Y_1) \cdot HgCl_2 \cdot DMSO]$ (**5**).

coordination through oxygen (DMSO–O) to get stable species, unless ligand overcrowding occurs [37] or DMSO is trans to strong π-acceptors like CO [38] and NO [39,40]. A similar overestimate is found for the calculated S–O distance in 'free' DMSO (1.509 Å), which results 0.018 Å longer than the experimental reference value of 1.492(1) Å [41]. The significant elongation of the S–O distance upon O-coordination is further confirmed by the recent X-ray structure determination of a disulfoxide and related copper(II) complexes, where the average S–O distances are of 1.487(4) Å (free) and 1.520(3) Å (O-bonded) [42]. This work reports the example of

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

Bond lengths	**4**
C(3)–C(2)	1.473(12)
C(3)–P(1)	1.786(8)
C(3)–Hg(1)	2.279(8)
C(2)–O(1)	1.214(12)
I(1)–Hg(1)	2.7036(8)
I(2)–Hg(1)	2.7795(9)
I(2)–Hg(1)#1	3.0544(12)
Bond angles	
C(2)–C(3)–Hg(1)	101.3(6)
P(1)–C(3)–Hg(1)	111.2(4)
Hg(1)–I(2)–Hg(1)#1	84.47(3)
C(2)–Hg(1)–I(1)	119.1(2)
C(2)–Hg(1)–I(2)	121.7(2)
I(1)–Hg(1)–I(2)	111.08(3)
C(3)–Hg(1)–I(2)#1	98.4(2)
I(1)–Hg(1)–I(2)#1	104.96(3)
I(2)–Hg(1)–I(2)#1	95.53(3)

Table 3
Selected bond lengths (Å) and angles (°) for **5**

Bond lengths	**5**
Hg(1)–C(8)	2.208(4)
Hg(1)–Cl(1)	2.3986(13)
Hg(1)–Cl(2)	2.5106(12)
Hg(1)–O(2)	2.548(3)
P(1)–C(8)	1.787(4)
O(1)–C(7)	1.220(5)
C(8)–C(7)	1.491(5)
O(2)–S(1)	1.507(3)
Bond angles	
Cl(2)–Hg(1)–Cl(1)	105.46(6)
C(8)–Hg(1)–Cl(2)	112.91(11)
C(8)–Hg(1)–Cl(1)	139.45(11)
C(8)–Hg(1)–O(2)	87.39(13)
O(2)–Hg(1)–Cl(2)	104.32(9)
O(2)–Hg(1)–Cl(1)	95.67(8)
C(7)–C(8)–P(1)	114.4(3)
C(7)–C(8)–Hg(1)	108.5(3)
P(1)–C(8)–Hg(1)	109.29(19)

a mercury(II) complex containing DMSO as ligand with an O-coordination mode. It is worth noting that in **5**, the S–O bond distance of 1.507(3) Å, is about 0.015 Å longer than the experimental reference value of 1.492(1) Å for free DMSO ligand [41].

3.4. Theoretical studies

We were interested to determine whether the formation of mononuclear complexes in the gas phase in which DMSO acts as ligand, energetically is more favorable than those of binuclear complexes. The analytical and spectroscopic data for compound **5** can be similar to those of the other complexes synthesized here containing ylide Y_1. Thus the observed geometry of compound **5** was considered for ab initio calculations. The optimized structure of compounds **5** is shown in Fig. 3. A comparison between the calculated bond lengths (Å) and bond angles (°) for this compound with corresponding experimental values are presented in Table 4. A list of calculated key bond lengths and bond angles and the optimized structure of compounds $[(Y_1) \cdot HgX_2 \cdot DMSO]$ (where X = Br and I) are presented in Supplementary materials.

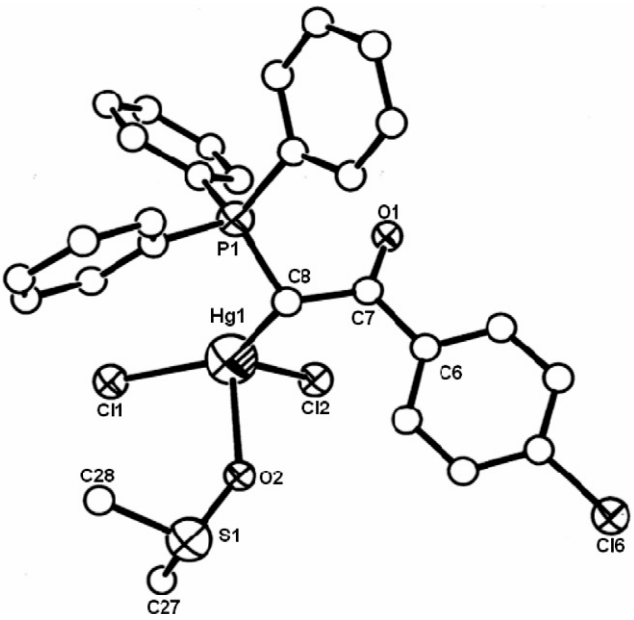


Fig. 3. The optimized structure of compound **5**.

Table 4
A comparison between the calculated bond lengths (Å) and bond angles (°) for compound **5** with corresponding experimental values

$[(Y_1) \cdot HgCl_2 \cdot DMSO]$ (**5**)	X-ray	HF/Lanl2mb
Bond lengths		
Hg(1)–Cl(2)	2.511(12)	2.676
Hg(1)–Cl(1)	2.399(13)	2.688
Hg(1)–O(2)	2.548(3)	2.301
C(8)–Hg(1)	2.207(4)	2.272
P(1)–C(8)	1.788(4)	1.919
C(8)–C(7)	1.491(5)	1.538
C(7)–O(1)	1.220(5)	1.222
Bond angles		
C(8)–Hg(1)–Cl(1)	139.451	121.872
C(8)–Hg(1)–Cl(2)	112.912	106.614
Cl(1)–Hg(1)–Cl(2)	105.452	120.035
Cl(1)–Hg(1)–O(2)	95.677	95.351
Cl(2)–Hg(1)–O(2)	104.327	99.840
C(8)–C(7)–O(1)	121.186	122.329
Hg(1)–O(2)–S(1)	139.574	117.325

As can be seen, the calculated bond lengths are slightly longer than measured ones but the similarity of calculated and measured bond angles reflects the similar geometrical structures for these compounds in both the solid state and gas-phase. The results of calculations (Table 5) show that the products of following proposed reaction (Eq. (1)) are more stable than reactants. These stabilities are about 32, 34 and 40 kcal/mol where X is Cl, Br and I, respectively.

$$[(Y_1) \cdot HgX_2]_2 + 2DMSO \xrightarrow{rt} 2[(Y_1) \cdot HgX_2 \cdot DMSO] \qquad (1)$$

The similarity of calculated energies for latter reaction of Y_1 complexes indicate that the reaction energy mainly depends on the bridging halide atom. Therefore it is clear that for all compounds synthesized here, the gas-phase reaction shown in Eq. (1) is an exothermic reaction, thus it seems that the bridge-splitting reaction in

Table 5
Calculated electronic energies for binuclear complexes, DMSO and mononuclear complexes involved in Eq. (1)

Compounds	$[(Y) \cdot HgX_2]_2$ (hartree)	DMSO (hartree)	$[(Y) \cdot HgX_2 \cdot DMSO]$ (hartree)	ΔE (kcal.mol^{-1})
X = Cl	−2299.4410769	−161.8305649	−1311.5770188	32.524
X = Br	−2292.3597909	−161.8305649	−1308.0376782	34.159
X = I	−2285.2766229	−161.8305649	−1304.5010169	40.337

DMSO solution is potentially possible for all dimeric complexes of Y_1 in which DMSO acts as a ligand. The data show that in the case of iodine complex, the formation of mononuclear complexes is relatively more favorable than corresponding chlorine and bromine complexes (Table 5).

4. Conclusions

Present study describes the synthesis and characterization of mononuclear and binuclear Hg(II) complexes of phosphorus ylides. On the basis of the physico-chemical and spectroscopic data we propose that ligands herein exhibit monodentate C-coordination to the metal centre, which is further confirmed by the X-ray crystal structure of the complexes. This study also presents a method for synthesis of mononuclear Hg(II) complexes of phosphorus ylides via bridge-splitting reaction using DMSO as ligand. Theoretical studies on the gas-phase structure of the complexes, confirm that, the bridge-splitting reaction in DMSO solution is potentially possible for all dimeric complexes in which DMSO acts as a ligand.

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Appendix A. Supplementary data

CCDC 648212 and 648213 contain the supplementary crystallographic data for $[(Y_1)\cdot HgCl_2\cdot DMSO]$ and $[(Y_2)\cdot HgI_2]_2$. 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.poly.2008.03.009.

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