

New mono and binuclear mercury(II) complexes of phosphorus ylides containing DMSO as ligand: Spectral and structural characterization

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Received 20 January 2008; received in revised form 19 February 2008; accepted 20 February 2008

Available online 4 March 2008

Abstract

Reaction of phosphorus ylides $\text{Ph}_3\text{PCHC}(\text{O})\text{C}_6\text{H}_4\text{NO}_2$ (Y') and (*p*-tolyl) $_3\text{PCHC}(\text{O})\text{C}_6\text{H}_4\text{Cl}$ (Y'') with HgX_2 ($X = \text{Cl}, \text{Br}$ and I) in equimolar ratios using methanol as solvent leads to binuclear products. The bridge-splitting reaction of binuclear complex $[(Y'') \cdot \text{HgI}_2]_2$ by DMSO yields the mononuclear complex $[(Y'') \cdot \text{HgI}_2 \cdot \text{DMSO}]$. This bridge-splitting reaction can be also a method for the synthesis of mononuclear products. C-coordination of ylides and O-coordination of DMSO are demonstrated by single crystal X-ray analyses of binuclear complexes of $[(Y') \cdot \text{HgI}_2]_2$ and $[(Y'') \cdot \text{HgI}_2]_2$ and mononuclear complex of $[(Y'') \cdot \text{HgI}_2 \cdot \text{DMSO}]$. Characterization of the obtained compounds was also performed by elemental analysis, IR, ^1H , ^{31}P , and ^{13}C NMR. Theoretical studies on Hg(II) complexes of Y' show that the cis-like isomers are about 4–12 kcal/mol less stable than the trans-like structures and the relative energy of cis- and trans-like isomers significantly depends on the size of the bridging halide. These studies on mercury complexes of Y'' 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.

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Keywords: Mercury(II) halide; Phosphorus ylide; DMSO; Triphenylphosphine; Triparatolylphosphine

1. Introduction

Phosphorus ylides are important reagents in organic chemistry, especially in the synthesis of naturally occurring products with biological and pharmacological activities [1]. These compounds have been used as reducing agents in coordination chemistry. The utility of metalated phosphorus ylides in synthetic chemistry has been well documented [2–5]. Synthesis of complexes derived from phosphorus ylides and Hg(II) halides was started in 1965 by Nesmeyanov et al. [6]. In 1975, Weleski et al. [7] proposed a symmetric

halide-bridged dimeric structure for Hg(II) halide complexes whereas Kalyanasundari et al. [8] reported an asymmetric halide-bridged dimeric structure in 1995. In 1985, Sanehi et al. [9] reported a mononuclear Hg(II) complex of phosphorus ylides without any structural characterization. We have recently focused on the synthesis of mononuclear, binuclear [10,11] and polynuclear [12] complexes derived from mercury(II) salts and phosphorus ylides. The α -keto-stabilized phosphorus ylides $\text{R}_3\text{P}=\text{C}(\text{R}')\text{COR}''$ show interesting properties such as their high stability and their ambidentate character as ligands (C- vs. O-coordination) [13–16]. This ambidentate character can be rationalized in terms of the resonance forms A–C, together with the isomeric form D (Chart 1).

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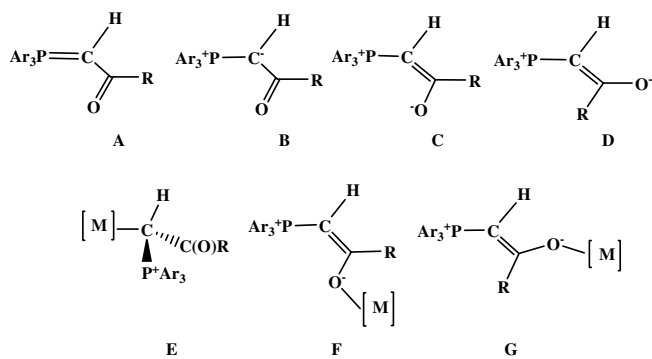


Chart 1.

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 [17], 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) [8,18–21], whereas, O-coordination dominates when the metals involved are hard, *e.g.*, Ti(IV), Zr(IV), and Hf(IV) [22]. Only W(0) complexes of the type $W(CO)_5L$ ($L = \text{ylide}$) [23] and Pd(II) complexes of stoichiometry $[Pd(C_6F_5)(L_2)(APPY)](ClO_4)$ [18] [$APPY = Ph_3PCHCOMe$; $L = PPh_3$ and PBu_3 ; $L_2 = \text{bipy}$] contain stable ylides O-linked to a soft metal centre.

The goals of this report are (i) to present a method for synthesis of mononuclear mercury(II) complexes of phosphonium ylides; (ii) to expand the knowledge in this field via synthesis, characterization and theoretical studies of new binuclear and mononuclear complexes. We believe that bridge-splitting reaction can be initiated for binuclear complexes by strong ligands leading to mononuclear products.

2. Experimental

2.1. Physical measurements and 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 and 2-bromo-4'-nitroacetophenone and concomitant elimination of HBr by NaOH [24]. Melting points were measured on a SMPI apparatus. Elemental analysis for C, H and N 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.

2.2. X-ray crystallography

The single crystal X-ray diffraction analyses for complexes $[(Y') \cdot HgI_2]_2$ and $[(Y'') \cdot HgI_2]_2$ were performed on a STOE IPDS-II two circle diffractometer at 293(2) K, using graphite monochromated Mo $K\alpha$ X-ray radiation ($\lambda = 0.7107$ nm). The data collection was performed at room temperature using the ω -scan technique and using the STOE X-AREA software package [25]. The crystal structures were solved by direct methods [26] and refined by using X-STEP32 crystallographic software package [27]. All of the non-hydrogen atoms were refined anisotropically. All of hydrogen atoms were located in ideal positions.

Single crystal X-ray diffraction data for $[(Y') \cdot HgI_2 \cdot DMSO]$ was measured on a Bruker SMART 4000 APEX II CCD diffractometer. Structure solution and refinement was carried out using SHELXS-97 and SHELXL-97, respectively [28,29]. The Structure was solved by direct methods and refined by full matrix least squares methods on F^2 . All non-hydrogen atoms were refined anisotropically. All hydrogens were included in calculated positions.

2.3. Theoretical studies

The geometries of compounds were fully optimized at the Hartree-Fock (HF) level of theory using the GAUSSIAN98 program [30] on a Pentium-PC computer with 3600 MHz processor. The standard LanL2mb basis set was used for all complexes [31]. This basis set includes effective core potentials (ECP) for both the mercury and phosphorus atoms 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. Sample preparation

2.4.1. Preparation of $Ph_3PCHCOC_6H_4NO_2$ (Y'), general procedure for ylides [32]

Triphenylphosphine (0.262 g, 1 mmol) and 2-bromo-4'-nitroacetophenone (0.243 g, 1 mmol) react in acetone as solvent to produce the related phosphonium salt. Further treatment with aqueous NaOH solution led to elimination of HBr, giving the free ligand Y' . IR (KBr disk): ν (cm^{-1}) 1529 (C=O), 884 (P-C). 1H NMR ($CDCl_3$): δ (ppm) 4.51 (1H, d, $^2J_{PH} = 22.9$ Hz, CH); 7.53–8.24 (19H, m, Ph). ^{31}P NMR ($CDCl_3$): δ (ppm) 14.19. ^{13}C NMR ($CDCl_3$): δ (ppm) 53.40 (d, $^1J_{PC} = 110.2$ Hz, CH) 122.89–148.11 (Ph); 181.79 (s, CO).

2.4.2. (*p*-tolyl)₃PCHCO(C₆H₄Cl) (Y'') [33]

IR (KBr, disk): ν (cm⁻¹) 1581 (C=O), 882 (P–C). ¹H NMR (CDCl₃) δ_{H} : 2.39 (s, 9H, 3CH₃); 4.34 (d, ²J_{PH} = 23.12 Hz, 1H, CH); 7.31–8.34 (m, 16H, Ph). ³¹P NMR (CDCl₃) δ_{P} : 13.15 (s). ¹³C NMR (CDCl₃) δ_{C} : 20.95 (s, 3CH₃); 51.19 (d, ¹J_{PC} = 112.1 Hz, CH); 123.33–142.00 (Ph); 182.31 (d, ²J_{PC} = 3.58 Hz, CO).

2.4.3. Synthesis of complexes

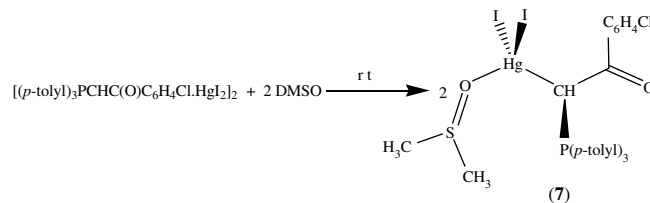
Binuclear complexes **1–6** were prepared based on a general procedure as follows (Scheme 1). The crystals of the complex **6** were obtained from the mother liquor methanol solution. X-ray quality crystals of the complex **3** and **7** (Schemes 1 and 2) were grown from a dimethylsulfoxide solution of compounds **3** and **6**, respectively. This was carried out by the slow evaporation of the solvent over several days.

2.4.3.1. Synthesis of [(Y') · HgCl₂]₂ (1), general procedure

for dimeric structures. To a methanolic solution (15 ml) of HgCl₂ (0.082 g, 0.3 mmol) was added a methanolic solution (10 ml) of Y' (0.128 g, 0.3 mmol). The mixture was stirred for 1 h. The separated solid was filtered and washed with diethyl ether. Anal. Calc. for C₅₂H₄₀Cl₄Hg₂N₂O₆P₂: C, 44.81; H, 2.89; N, 2.01. Found: C, 44.48; H, 2.86; N, 2.11%. Yield 0.163 g, 78%. M.p. 219–220 °C. IR (KBr disk): ν (cm⁻¹) 1639 (C=O), 1602, 1519, 1484, 1438, 1346, 1310, 1292, 1190, 1108, 1028, 1008, 998, 858 (P–C) and 827. ¹H NMR (DMSO-*d*₆): δ (ppm) 5.36 (1H, d, ²J_{PH} = 10.6 Hz, CH); 7.67–8.25 (19H, m, Ph). ³¹P NMR (DMSO-*d*₆): δ (ppm) 21.01 (s). ¹³C NMR (DMSO-*d*₆): δ (ppm) 48.45 (d, ¹J_{PC} = 81.0 Hz, CH); 123.05 (COPh (*m*)); 123.24 (d, ¹J_{PC} = 89.8 Hz, PPh₃ (*i*)); 129.16 (PPh₃ (*p*)); 129.43 (d, ³J_{PC} = 12.1 Hz, PPh₃ (*m*)); 133.24 (d, ²J_{PC} = 10.4 Hz, PPh₃ (*o*)); 133.5 (COPh (*o*)); 142.90 (d, ³J_{PC} = 9.6 Hz, COPh (*i*)); 149.14 (COPh (*p*)); 188.03 (s, CO).

2.4.3.2. [(Y') · HgBr₂]₂ (2). Anal. Calc. for C₅₂H₄₀Br₄-

Hg₂N₂O₆P₂: C, 39.74; H, 2.57; N, 1.78. Found: C, 39.29; H, 2.60; N, 1.74%. Yield 0.189 g, 80%. M.p. 226–227 °C. IR (KBr disk): ν (cm⁻¹) 1635 (C=O), 1599, 1522, 1482, 1434, 1347, 1317, 1289, 1193, 1106, 1034, 1011, 998, 885, 856 (P–C) and 811. ¹H NMR (DMSO-*d*₆): δ (ppm) 5.39 (1H, d, ²J_{PH} = 9.9 Hz, CH); 7.67–8.25 (19H, m, Ph). ³¹P



Scheme 2.

NMR (DMSO-*d*₆): δ (ppm) 20.99 (s). ¹³C NMR (DMSO-*d*₆): δ (ppm) 49.81 (d, ¹J_{PC} = 78.2 Hz, CH); 122.92 (COPh (*m*)); 123.82 (d, ¹J_{PC} = 89.8 Hz, PPh₃ (*i*)); 128.96 (PPh₃ (*p*)); 129.24 (d, ³J_{PC} = 12.6 Hz, PPh₃ (*m*)); 133.03 (d, ²J_{PC} = 9.8 Hz, PPh₃ (*o*)); 133.25 (COPh (*o*)); 144.11 (d, ³J_{PC} = 4.7 Hz, COPh (*i*)); 148.78 (COPh (*p*)); 186.13 (s, CO).

2.4.3.3. [(Y') · HgI₂]₂ (3). Anal. Calc. for C₅₂H₄₀Hg₂I₄-

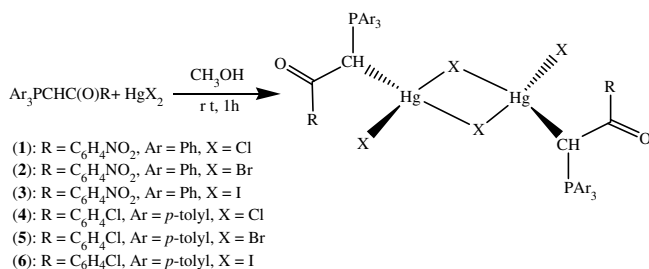
N₂O₆P₂: C, 35.49; H, 2.29; N, 1.59. Found: C, 35.87; H, 2.31; N, 1.59%. Yield 0.201 g, 76%. M.p. 206–207 °C. IR (KBr disk): ν (cm⁻¹) 1628 (C=O), 1595, 1520, 1481, 1435, 1347, 1316, 1290, 1191, 1107, 1035, 1011, 998, 879, 855 (P–C) and 809. ¹H NMR (DMSO-*d*₆): δ (ppm) 5.11 (1H, d, ²J_{PH} = 15.5 Hz, CH); 7.65–8.22 (19H, m, Ph). ³¹P NMR (DMSO-*d*₆): δ (ppm) 18.91 (s). ¹³C NMR (DMSO-*d*₆): δ (ppm) 50.72 (d, ¹J_{PC} = 92.9 Hz, CH); 122.80 (COPh (*m*)); 124.39 (d, ¹J_{PC} = 90.2 Hz, PPh₃ (*i*)); 128.41 (PPh₃ (*p*)); 129.04 (d, ³J_{PC} = 12.4 Hz, PPh₃ (*m*)); 132.85 (COPh (*o*)); 133.85 (d, ²J_{PC} = 10.1 Hz, PPh₃ (*o*)); 144.81 (d, ³J_{PC} = 13.0 Hz, COPh (*i*)); 148.35 (COPh (*p*)); 184.26 (s, CO).

2.4.3.4. [(Y'') · HgCl₂]₂ (4). Anal. Calc. for C₅₈H₅₂Cl₆-

Hg₂O₂P₂: C, 47.82; H, 3.60. Found: C, 47.65; H, 3.58%. Yield 0.148 g, 68%. M.p. 179–182 °C. IR (KBr disk): ν (cm⁻¹) 1642 (C=O), 1598, 1587, 1569, 1499, 1399, 1312, 1288, 1188, 1110, 1089, 1023, 1006, 821 (P–C) and 805. ¹H NMR (DMSO-*d*₆) δ_{H} : 2.45 (s, 9H, 3CH₃); 5.24 (br, 1H, CH); 7.38–8.12 (m, 16H, Ph). ³¹P NMR (DMSO-*d*₆) δ_{P} : 21.36 (s). ¹³C NMR (DMSO-*d*₆) δ_{C} : 21.59 (3CH₃); 121.10 (d, ¹J_{PC} = 92.46 Hz, *p*-tolyl (*i*)); 128.46 (COPh (*m*)); 130.44 (d, ³J_{PC} = 11.70 Hz, *p*-tolyl (*m*)); 130.52 (*p*-tolyl (*p*)); 133.74 (d, ²J_{PC} = 10.11 Hz, *p*-tolyl (*o*)); 137.08 (COPh (*p*)); 137.08 (COPh (*i*)); 144.28 (COPh (*o*)); (CO, was not seen or br).

2.4.3.5. [(Y'') · HgBr₂]₂ (5). Anal. Calc. for C₅₈H₅₂Br₄-

Cl₂Hg₂O₂P₂: C, 42.62; H, 3.21. Found: C, 42.38; H, 2.93%. Yield 0.174 g, 71%. M.p. 178–180 °C. IR (KBr disk): ν (cm⁻¹) 1624 (C=O), 1597, 1589, 1568, 1497, 1399, 1316, 1292, 1187, 1108, 1092, 1026, 1010, 824 (P–C), 808 and 794. ¹H NMR (CDCl₃) δ_{H} : 2.42 (s, 9H, 3CH₃); 5.32 (br, 1H, CH); 7.24–8.08 (m, 16H, Ph). ³¹P NMR (CDCl₃) δ_{P} : 24.04 (s). ¹³C NMR (CDCl₃) δ_{C} : 21.82 (3CH₃); 119.08 (d, ¹J_{PC} = 92.53 Hz, *p*-tolyl (*i*)); 128.97 (COPh (*m*)); 130.57 (*p*-tolyl (*p*)); 130.64 (d, ³J_{PC} = 11.34 Hz, *p*-tolyl (*m*));



Scheme 1.

133.71 (d, $^2J_{PC} = 9.43$ Hz, *p*-tolyl (*o*)); 134.52 (COPh (*p*)); 139.53 (COPh (*i*)); 144.97 (COPh (*o*)); 192.10 (s, CO).

2.4.3.6. $[(Y'') \cdot HgI_2]_2$ (**6**). Anal. Calc. for $C_{58}H_{52}Cl_2 \cdot Hg_2I_4O_2P_2$: C, 38.22; H, 2.88. Found: C, 37.79; H, 2.53%. Yield 0.205 g, 75%. M.p. 180–182 °C. IR (KBr disk): ν (cm^{-1}) 1708, 1625 (C=O), 1598, 1588, 1498, 1399, 1318, 1293, 1189, 1110, 1090, 1038, 1010, 820 (P–C) and 804. 1H NMR ($CDCl_3$) δ_H : 2.43 (s, 9H, 3CH₃); 4.97 (br d, $^2J_{PH} = 7.62$ Hz, 1H, CH); 7.34–7.97 (m, 16H, Ph). ^{31}P NMR ($CDCl_3$) δ_P : 19.51 (s). ^{13}C NMR ($DMSO-d_6$) δ_C : 21.14 (3CH₃); 120.83 (d, $^1J_{PC} = 91.78$ Hz, *p*-tolyl (*i*)); 127.91 (COPh (*m*)); 129.55 (*p*-tolyl (*p*)); 129.83 (d, $^3J_{PC} = 12.89$ Hz, *p*-tolyl (*m*)); 133.05 (d, $^2J_{PC} = 10.59$ Hz, *p*-tolyl (*o*)); 136.40 (COPh (*p*)); 136.93 (COPh (*i*)); 143.67 (COPh (*o*)); 187.44 (s, CO).

2.4.3.7. $[(Y'') \cdot HgI_2 \cdot DMSO]$ (**7**). 0.182 g (0.1 mmol) of binuclear complex **6** was dissolved in DMSO (2 ml). The pale yellow crystals formed by the slow evaporation of the solvent over several days. Anal. Calc. for $C_{31}H_{31}ClHgI_2O_2PS$: C, 37.67; H, 3.16. Found: C, 37.52; H, 3.29%. Yield 0.186 g, 94%. Decomp. at 180 °C. IR (KBr disk): ν (cm^{-1}) 1621 (C=O), 1598, 1588, 1499, 1399, 1315, 1297, 1190, 1109, 1090, 1038, 1022, 1010, 827 (P–C) and 805. 1H NMR ($DMSO-d_6$) δ_H : 2.54 (s, 9H, 3CH₃); 5.07 (d, $^2J_{PH} = 10.75$ Hz, 1H, CH); 7.43–8.03 (m, 16H, Ph). ^{31}P NMR ($DMSO-d_6$) δ_P : 19.82 (s). ^{13}C NMR ($DMSO-d_6$) δ_C : 21.14 (3CH₃); 120.83 (d, $^1J_{PC} = 91.78$ Hz, *p*-tolyl (*i*)); 127.91 (COPh (*m*)); 129.55 (*p*-tolyl (*p*)); 129.83 (d, $^3J_{PC} = 12.89$ Hz, *p*-tolyl (*m*)); 133.05 (d, $^2J_{PC} = 10.59$ Hz, *p*-tolyl (*o*)); 136.40 (COPh (*p*)); 136.93 (COPh (*i*)); 143.67 (COPh (*o*)); 187.44 (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 [34]. The ν (P⁺–C[–]) band, which is also diagnostic of the coordination modes, occurs at lower frequencies for complexes in comparison to the parent ylides, consistent with some removal of electron density in the P–C bonds [10–12]. 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 [21]. It should be noted that there is not any significant difference in the IR absorption bands for binuclear and related mononuclear complexes.

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 [35]. The expected lower shielding of ^{31}P and 1H nuclei 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 18.91 and 21.36 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) [18]. The ^{31}P nuclei shielding of the complexes appeared to be lower by about 4.5–8 ppm with respect to the parent ylides also indicating that coordination of the ylide has occurred [8,10–12,36]. Satellites due to coupling to ^{199}Hg for ylidic complexes of Hg(II) are only observed at low temperature [10,36] or by solid-state ^{31}P NMR [36] and also in the case of $Hg(NO_3)_2 \cdot H_2O$ as metal source [12]. Failure to observe satellites in above spectra was previously noted in the ylide

Table 1
Crystallographic data summary for binuclear complexes **3** and **6**

Compound	3	6
Empirical formula	$C_{52}H_{40}Hg_2I_4N_2O_6P_2$	$C_{58}H_{52}Cl_2Hg_2I_4O_2P_2$
Fw	1759.58	1822.62
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P21/c$
<i>a</i> (Å)	10.0285(15)	11.9610(6)
<i>b</i> (Å)	12.1560(18)	11.3248(7)
<i>c</i> (Å)	12.8738(18)	22.7971(11)
α (°)	72.014(11)	90
β (°)	68.762(11)	95.251(4)
γ (°)	71.782(12)	90
Volume (Å ³)	1355.2(3)	3075.0(3)
<i>Z</i>	1	2
D_{calc} (Mg/m ³)	2.156	1.969
Absorption coefficient (mm ^{–1})	8.043	7.171
$F(000)$	10320	1704
Crystal size (mm)	0.60 × 0.30 × 0.22	0.3 × 0.2 × 0.1
θ Range for data collection (°)	1.81–26.79	1.79–29.22
Limiting indices	$-12 \leq h \leq 12,$ $-15 \leq k \leq 15,$ $-15 \leq l \leq 15$	$-16 \leq h \leq 13,$ $-14 \leq k \leq 15,$ $-31 \leq l \leq 31$
Reflections collected/unique (R_{int})	10320/5263 (0.0410)	19645/8069 (0.0334)
Completeness to θ	26.79, 90.7%	29.22, 96.6%
Absorption correction	Numerical	Numerical
Maximum and minimum transmission	0.175 and 0.070	0.485 and 0.195
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5263/0/307	8069/0/316
Goodness-of-fit on F^2	1.125	1.137
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0411,$ $wR_2 = 0.1067$	$R_1 = 0.0479,$ $wR_2 = 0.0827$
<i>R</i> indices (all data)	$R_1 = 0.0435,$ $wR_2 = 0.1086$	$R_1 = 0.0706,$ $wR_2 = 0.0894$
Largest difference in peak and hole (e Å ^{–3})	2.065 and –2.060	1.312 and –1.070

complexes of Hg(II) [37] and Ag(I) [21] 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 higher shielding of the ylidic carbon atoms. Such a higher shielding was observed in $[\text{PdCl}(\eta^3\text{-2-XC}_3\text{H}_4)(\text{C}_6\text{H}_5)_3\text{PCHCOR}]$ ($\text{X} = \text{H}, \text{CH}_3$; $\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$), and is due to the change in hybridization of the ylidic carbon atom on coordination [38]. Similar higher shielding of 2–3 ppm with reference to the parent ylide were also observed in the case of $[(\text{C}_6\text{H}_5)_3\text{PC}_5\text{H}_4\text{HgI}_2]_2$ [37]. The lower shielding of the carbonyl C atom in the complexes compared to the same carbon atom in the parent ylides was also observed.

3.2. X-ray crystallography

Table 1 provides the crystallographic results and refinement information for complexes **3** and **6**. The molecular structures are shown in Figs. 1 and 2. Pertinent bond distances and angles for **3** and **6** are given in Table 2. Packing diagrams, fractional atomic coordinates and equivalent isotropic displacement coefficients (U_{eq}) for the non-hydrogen atoms of the complexes are shown in Supplementary material.

The Hg(II) centre in complexes **3** and **6** is four-coordinate with sp^3 hybridization. This environment involves 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 **3**, (2.292(5) and 2.6846(7) Å, respectively) and in **6** (2.310(6) and 2.6999(6) Å, respectively) are

comparable to analogous distances in $(\text{Ph}_3\text{PCH-COPh} \cdot \text{HgI}_2)_2$ (2.312(13) and 2.705(1) Å, respectively) [8].

The angles subtended by the ligands at the Hg(II) centre in **3** and **6** vary from 91.402(17) to 125.42(11) (**3**) and 87.261(14) to 123.80(14) (**6**) 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 angles 91.402(17) (**3**) and 87.261(14) (**6**) to be considerably smaller. The two mercury atoms and two bridging halides in each case are perfectly coplanar. The internuclear distance between mercury atoms in these complexes were found to be 4.188 (**3**) and 4.0969 (**6**), that are much longer than the sum of van der Waals radii (1.5 Å) of the two mercury atoms [39], indicating the absence of significant bonding interactions between the mercury atoms in the molecular structures.

Table 3 provides the crystallographic results and refinement information for complex **7**. The molecular structure is shown in Fig. 3. Pertinent bond distances and angles for **7** are given in Table 4. Packing diagrams, fractional atomic coordinates and equivalent isotropic displacement coefficients (U_{eq}) for the non-hydrogen atoms are shown in Supplementary material.

The Hg(II) centre in complex **7** is coordinated by one carbon, one oxygen and two iodine atoms in a distorted tetrahedral geometry. The two different Hg–I distances in **7** (2.6701(5) and 2.7102(5) Å) are less than those of found in mononuclear complex of $[\text{HgI}_2(\text{PPh}_3)_2]$ (2.733(1) and

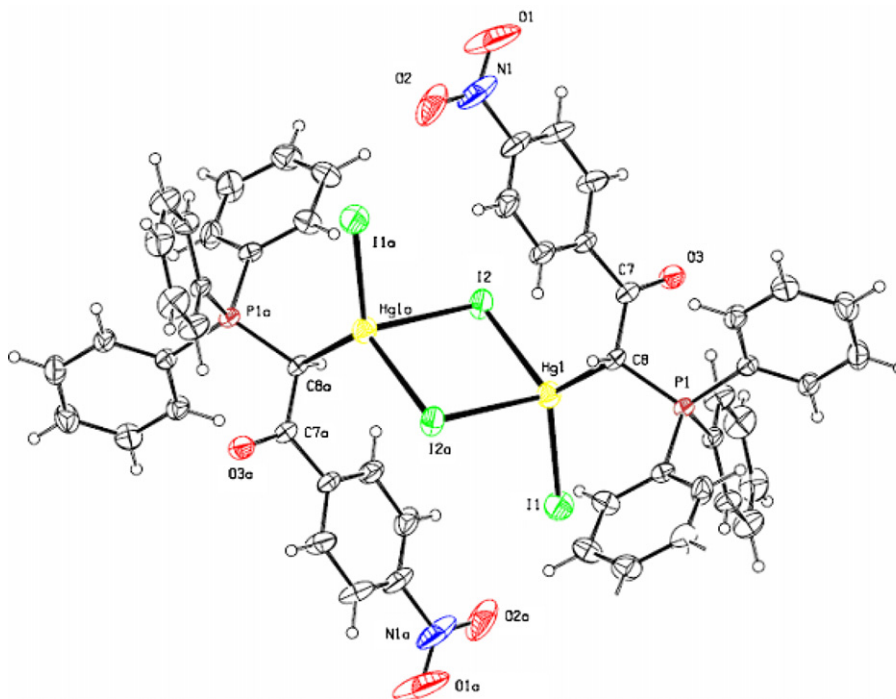
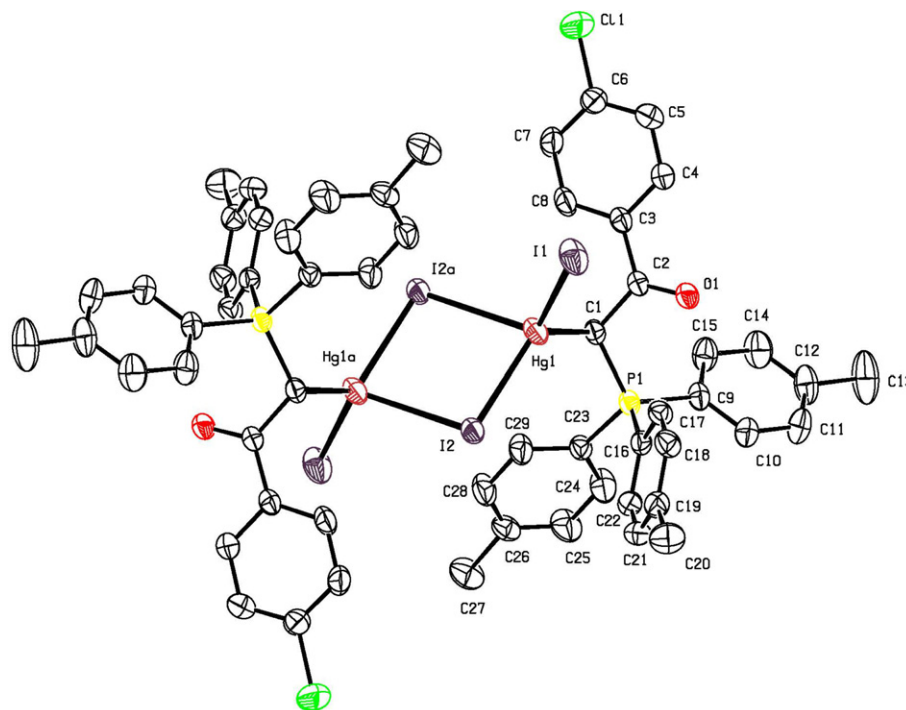


Fig. 1. ORTEP view of X-ray crystal structure of $[(\text{Y}') \cdot \text{HgI}_2]_2$ (**3**).

Fig. 2. ORTEP view of X-ray crystal structure of $[(Y'') \cdot \text{HgI}_2]_2$ (**6**).Table 2
Selected bond lengths (Å) and angles (°) for **3** and **6**

	3	6
<i>Bond lengths</i>		
C(H)–C	1.475(7)	1.488(7)
C(H)–P	1.793(4)	1.774(6)
C(H)–Hg	2.292(5)	2.310(6)
C–O	1.220(7)	1.225(6)
I(1)–Hg(1)	2.6846(7)	2.6999(6)
I(2)–Hg(1)	2.7900(6)	2.7902(5)
I(2)–Hg(1a)	3.1924(6)	3.1362(5)
<i>Bond angles</i>		
C(O)–C(H)–Hg	105.5(3)	101.6(4)
P–C(1)–Hg	111.5(2)	112.0(3)
Hg(1)–I(2)–Hg(1a)	88.598(17)	92.739(14)
C(H)–Hg–I(1)	125.42(11)	114.25(13)
C(H)–Hg–I(2)	116.89(11)	123.80(14)
I(1)–Hg–I(2)	114.00(2)	114.54(2)
C(1)–Hg(1)–I(2a)	95.78(12)	96.26(15)
I(1)–Hg(1)–I(2a)	101.47(2)	114.89(2)
I(2)–Hg(1)–I(2a)	91.402(17)	87.261(14)

2.763(1) Å [40], indicating relatively strong Hg–I bonds in **7**. Above distances are comparable to 2.693(2) and 2.727(2) Å found in $[\text{HgI}_2\{\text{Ph}_2\text{P}(\text{S})\text{CH}_2\text{PPh}_2\}]$ [41] and terminal Hg–I distance of 2.6999(6) Å noted for dimeric complex **6**. The difference between two distances in these complexes might be arising from steric effects of the large ylidic groups. The angles around mercury vary from 85.00(15) to 120.87(12), 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 causing the CHgI angle to be larger.

The stabilized resonance structure for the parent ylides is destroyed by the complex formation, thus, the C(H)–C bond lengths 1.475(7) Å (**3**), 1.488(7) Å (**6**) and 1.478(7) Å (**7**) are significantly longer than the corresponding distances found in the similar uncomplexed phosphoranes (1.407(8) Å [42] and 1.401(2) Å [43]). On the other hand, the bond length of P–C(H) in the similar ylide is 1.7194(17) Å [43] which shows that the corresponding bonds are considerably elongated to 1.793(4) Å (**3**), 1.774(6) Å (**6**) and 1.785(5) Å (**7**). The Hg–I(1), Hg–I(2) and Hg–C bond lengths in **7** (2.6701, 2.71 and 2.261 Å, respectively) are shorter than those of found in the parent binuclear complex **6** (2.6999, 2.79 and 2.310 Å, respectively) indicating relatively strong bonds in mononuclear complexes compared to binuclears.

The C-coordination of the title ylides is in contrast to the O-coordination of the phosphorus ylide $\text{Ph}_3\text{PC}(\text{CO-Me})(\text{COPh})$ (ABPPY) in a different Hg(II) complex [44]. The difference in coordination mode between ABPPY and these ylides to Hg(II) can be rationalized in terms of the electronic properties and steric requirements of the ylides. The lower electronic density at the ylidic C atom in doubly stabilized ylides compared to simple stabilized ylides has been calculated by DFT (density functional theory) methods recently [45]. It was also demonstrated in the same paper that these factors are not solely responsible for the bonding properties of doubly stabilized ylides. For “simple” stabilized ylides, the C- vs. O-bonding is also a very delicate balance of steric and electronic properties

Table 3
Crystallographic data summary for mononuclear complex 7

Compound	7
Empirical formula	C ₃₁ H ₃₂ ClHgI ₂ O ₂ PS
Fw	989.44
Temperature (K)	150(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2(1)/n
a (Å)	11.4861(6)
b (Å)	14.1632(7)
c (Å)	20.9956(11)
α (°)	90
β (°)	104.233(3)
γ (°)	90
Volume (Å ³)	3310.7(3)
Z	4
D _{calc} (Mg/m ³)	1.985
Absorption coefficient (mm ⁻¹)	6.732
F(000)	1872
Crystal size (mm)	0.32 × 0.21 × 0.14
θ Range for data collection (°)	1.75–27.50
Limiting indices	−14 ≤ h ≤ 14, −18 ≤ k ≤ 18, −27 ≤ l ≤ 27
Reflections collected	105375
Independent reflections (R _{int})	7601 (0.0375)
Completeness to θ = 25.00°	100.0%
Absorption correction	Semi-empirical from equivalents
Maximum and minimum transmission	0.4525 and 0.2219
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	7601/236/357
Goodness-of-fit on F ²	1.098
Final R indices [I > 2σ(I)]	R ₁ = 0.0351, wR ₂ = 0.1016
R indices (all data)	R ₁ = 0.0397, wR ₂ = 0.1068
Largest difference in peak and hole (e Å ⁻³)	1.872 and −3.022

[46]. In this balance it is necessary to consider not only the size and shape of the ligand in the final bonding mode, but also the electronic nature of the metal (Pd, Pt, Ru, Au, etc.) and the donor atoms (C, O, N, 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). All these facts must be considered as a whole in order to account for the final bonding mode of a given ylide. 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 [47]. 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).

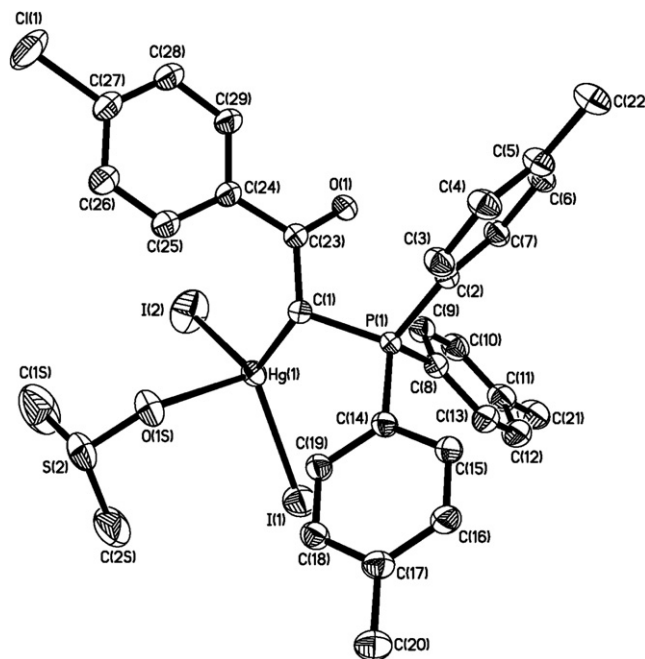


Fig. 3. ORTEP view of X-ray crystal structure of [(Y'') · HgI₂ · DMSO] (7).

Table 4
Selected bond lengths (Å) and angles (°) for 7

7	
<i>Bond lengths</i>	
Hg(1)–C(1)	2.261(5)
Hg(1)–I(1)	2.6701(5)
Hg(1)–I(2)	2.7102(5)
Hg(1)–O(1S)	2.621(4)
P(1)–C(1)	1.785(5)
O(1)–C(23)	1.221(6)
C(1)–C(23)	1.478(7)
S(2)–O(1S)	1.515(4)
<i>Bond angles</i>	
I(2)–Hg(1)–I(1)	117.063(19)
C(1)–Hg(1)–I(2)	120.87(12)
C(1)–Hg(1)–I(1)	119.64(12)
C(1)–Hg(1)–O(1S)	85.00(15)
O(1S)–Hg(1)–I(2)	102.69(10)
O(1S)–Hg(1)–I(1)	97.99(10)
C(23)–C(1)–P(1)	114.2(3)
C(23)–C(1)–Hg(1)	106.8(3)
P(1)–C(1)–Hg(1)	109.8(2)

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 [48]. In the case of ruthenium(II) complexes, coordination through sulfur (DMSO–S) seems to be preferred over coordination through oxygen (DMSO–O) to get stable species, unless

ligand overcrowding occurs [49] or DMSO is trans to strong π -acceptors like CO [50] and NO [51,52]. Although on the basis of the Hard-Soft-Acid-Base principle, S-bonding is preferred by 'soft' metal ions but with bulky ligands like present phosphorus ylides, steric effects can induce O-bonding. It may also be seen that for 'soft' metal ions, such as Ag(I), Cd(II), and Hg(II), there is evidence of a prevalence of O-bonded species, even in the absence of π -accepting or bulky ligands. This suggests that a particular electronic structure is required in order to favor the metal–sulfur bond over the metal–oxygen one [48]. Bulkiness of present ylides and the absence of above influences in the structure shown in Fig. 3 lead to preferring of O-bonding. An 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 [53]. 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) [54]. It is worth noting that in **7** the S–O bond distance of 1.515(4) Å, is about 0.023 Å longer than the experimental reference value of 1.492(1) Å for free DMSO ligand [53].

3.4. Theoretical studies

We were interested to (i) determine the amount of the energy difference between the observed trans-like structures and the alternative possible cis-like isomers; (ii) determine whether the formation of mononuclear complexes in the gas-phase in which DMSO acts as ligand, energetically are more favorable than those of binuclear complexes.

The observed geometry of compound **3** was used as a basis of ab initio calculations for compounds **1–3**. The optimized cis and trans structures of **3** are shown in Fig. 4. A

comparison between the calculated bond lengths (Å) and bond angles (°) with corresponding experimental values for compound **3** is presented in Table 5. A list of calculated key bond lengths and bond angles and the optimized structures of compounds **1** and **2** are presented in Supplementary material.

The calculated structure of **3** in the gas-phase agrees well with the structure observed by X-ray crystallography, although the calculated bond lengths are slightly longer than measured ones. We then changed the geometrical structure of compound **3** by replacement of position of one terminal halide atom with one coordinated ylide group

Table 5

A comparison between the calculated bond lengths (Å) and bond angles (°) with corresponding experimental values for compound **3**

[(Y') · HgI ₂] ₂ (3)	X-ray	HF/LanI2mb
<i>Bond lengths</i>		
I(2)–Hg(1)	3.192(6)	3.217
I(1)–Hg(1)	2.685(7)	2.964
I(2a)–Hg(1)	2.790(6)	3.172
P(1)–C(15)	1.805(5)	1.918
P(1)–C(8)	1.793(4)	1.976
C(9)–P(1)	1.805(5)	1.932
C(21)–P(1)	1.804(5)	1.929
Hg(1)–C(8)	2.292(5)	2.263
<i>Bond angles</i>		
Hg(1)–I(2)–Hg(1a)	88.599	89.315
I(2)–Hg(1)–I(2a)	91.401	90.683
I(2a)–Hg(1)–I(1)	101.467	107.523
I(2)–Hg(1)–C(8)	95.797	107.475
I(2)–Hg(1)–I(1)	114.000	104.439
I(2a)–Hg(1)–C(8)	116.881	109.253
I(1)–Hg(1)–C(8)	125.427	130.200
O(3)–C(7)–C(6)	119.502	120.823
O(3)–C(7)–C(8)	122.024	120.919
Hg(1)–C(8)–P(1)	111.494	111.892

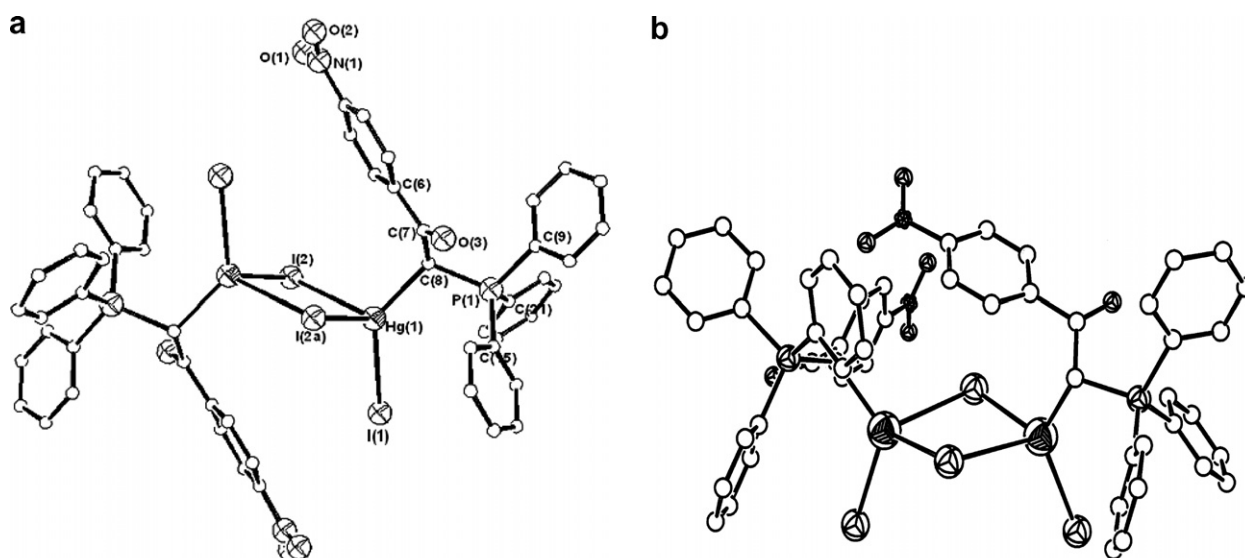


Fig. 4. Calculated molecular structures of (a) *trans*-[(Y') · HgI₂]₂ and (b) *cis*-[(Y') · HgI₂]₂.

Table 6
A comparison between energies of cis- and trans-like isomers for compounds 1–3

Compound	Cis (hartree)	Trans (hartree)	ΔE (kcal mol ⁻¹) ^a	
1	[(Y') · HgCl ₂] ₂	-2672.5879487	-2672.6077282	12.41
2	[(Y') · HgBr ₂] ₂	-2665.5202294	-2665.5266673	4.04
3	[(Y') · HgI ₂] ₂	-2658.4301041	-2658.436498	4.01

^a The energy of cis-like isomer relative to trans-like isomer.

to obtain cis-like isomers which were used as the basis for additional calculations. The minimization of these isomers at the same level of theory gave the desired cis-like isomers for complexes 1–3. As can be seen in Table 6 the latter cis-like isomers are about 4–12 kcal/mol less stable than trans-like structures. It is clear therefore that the dimeric structure with the general formula [Ylide · HgX₂]₂ may occur as either the observed trans-like isomer or the alternative higher-energy cis-like isomer.

It is interesting that when the ylide is bulky such as Y', the relative energy of cis- and trans-like isomers significantly depends on the size of the bridging halide. Note that the cis-like isomer in the case of compounds 2 and 3 is only about 4 kcal less stable than the trans-like isomer, but in the case of compound 1 the cis-like isomer is more than 12 kcal less stable than trans-like isomer (Table 6).

In the trans-like structures of compounds 1–3, the inter-nuclear distances between mercury atoms were calculated to be 4.11, 4.28 and 4.49 Å, respectively, indicating the absence of significant bonding interactions between the mercury atoms. These distances are also increased by increasing the size of the bridging halides (Cl, Br and I).

The analytical and spectroscopic data for compound 7 can be similar to those of the other complexes synthesized here containing ylide Y''. Thus the observed geometry of compound 7 was considered for ab initio calculations. The optimized structure of compound 7 is shown in Fig. 5. A comparison between the calculated bond lengths (Å) and bond angles (°) for these compounds with corresponding experimental values are presented in Table 7. A

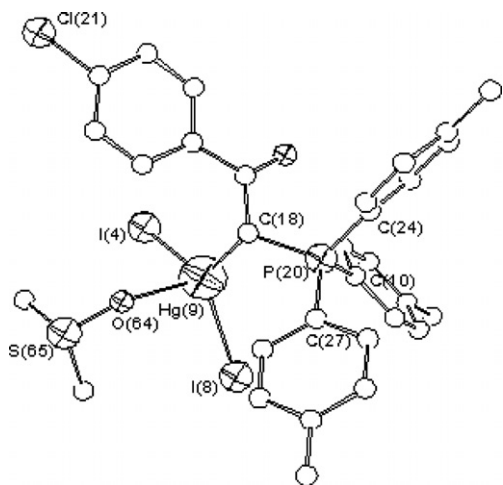


Fig. 5. Calculated molecular structure of [(Y'') · HgI₂ · DMSO].

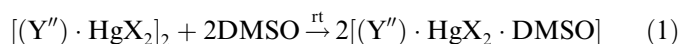
Table 7

A comparison between the calculated bond lengths (Å) and bond angles (°) for compound [(Y'') · HgI₂ · DMSO] (7) with corresponding experimental values

[(Y'') · HgI ₂ · DMSO](7)	X-ray	HF/Lan12mb
<i>Bond lengths</i>		
Hg(9)–I(8)	2.710	3.069
Hg(9)–I(4)	2.670	3.028
Hg(9)–C(18)	2.261	2.283
Hg(9)–O(64)	2.621	2.309
P(20)–C(10)	1.803	1.917
P(20)–C(24)	1.789	1.932
P(20)–C(27)	1.797	1.924
P(20)–C(18)	1.784	1.965
<i>Bond angles</i>		
I(4)–Hg(9)–I(8)	117.066	114.128
I(4)–Hg(9)–C(18)	120.882	119.012
I(4)–Hg(9)–O(64)	102.683	99.468
I(8)–Hg(9)–C(18)	119.633	119.012
I(8)–Hg(9)–O(64)	97.991	102.462
O(7)–C(14)–C(15)	120.444	120.734
O(7)–C(14)–C(18)	121.345	122.713
C(10)–P(20)–C(18)	113.827	110.479
C(10)–P(20)–C(24)	107.439	109.639
C(10)–P(20)–C(27)	109.304	109.926
C(18)–P(20)–C(24)	111.953	111.299
C(18)–P(20)–C(27)	106.801	110.191
C(24)–P(20)–C(27)	107.320	105.179
Hg(9)–C(18)–P(20)	109.792	113.010

list of calculated key bond lengths and bond angles and the optimized structures of compounds [(Y'') · HgX₂ · DMSO] (where X = Cl and Br) are presented in Supplementary material.

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 8) show that the products of the following proposed reaction (Eq. (1)) are more stable than reactants. These stabilities are about 29, 34 and 40 kcal/mol where X is Cl, Br and I, respectively.



The similarity of calculated energies for latter reaction indicates 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 DMSO solution is potentially

Table 8

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	-2530.9594524	-161.8305649	-1427.3332829	28.86
X = Br	-2523.8733023	-161.8305649	-1423.7940979	33.74
X = I	-2516.7904538	-161.8305649	-1420.2577546	40.11

possible for all dimeric complexes 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 8).

4. Conclusions

Present study describes the synthesis and characterization of a series of binuclear and mononuclear 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 some of ligands like DMSO. Theoretical studies on the gas-phase structure of the complexes, confirm that, the bridge-splitting reaction in DMSO solution is potentially possible for dimeric complexes in which DMSO acts as a ligand.

Acknowledgements

We are grateful to the Bu-Ali Sina University for a grant and Mr. Zebarjadian for recording the NMR spectra. The authors thank Prof. Michael D. Ward (Department of Chemistry, University of Sheffield, Sheffield S3 7HF, UK) for his invaluable support in one of X-ray experiments.

Appendix A. Supplementary material

CCDC 648211, 663328 and 648218 contain the supplementary crystallographic data for complexes **3**, **6** and **7**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2008.02.025](https://doi.org/10.1016/j.jorganchem.2008.02.025).

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