



Four-coordinate and pseudo five-coordinate Hg(II) complexes of a new bidentate phosphorus ylide: X-ray crystal structure and spectral characterization

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ABSTRACT

The reaction of $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (dppm) with $\text{BrCH}_2\text{C}(\text{O})\text{C}_6\text{H}_4\text{NO}_2$ in chloroform produces the new phosphonium salt $[\text{Ph}_2\text{PCH}_2\text{PPh}_2\text{CH}_2\text{C}(\text{O})\text{C}_6\text{H}_4\text{NO}_2]\text{Br}$ (**1**). Further, by reacting the phosphonium salt with appropriate base the bidentate phosphorus ylide, $\text{Ph}_2\text{PCH}_2\text{PPh}_2=\text{C}(\text{H})\text{C}(\text{O})\text{C}_6\text{H}_4\text{NO}_2$ (**2**) was obtained. The reaction of ligand **2** with mercury(II) halides in dry methanol led to the formation of the P, C-coordinated mononuclear complexes $[\text{HgX}_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2\text{C}(\text{H})\text{C}(\text{O})\text{C}_6\text{H}_4\text{NO}_2)]$ [$\text{X} = \text{Cl}$ (**3**), Br (**4**), I (**5**)]. Characterization of the obtained compounds was performed by elemental analysis, IR, ^1H , ^{31}P , and ^{13}C NMR. The X-ray crystal structure of **5** as well as the complex derived from crystallization of **4** in DMSO, $[\text{HgBr}_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2\text{C}(\text{H})\text{C}(\text{O})\text{C}_6\text{H}_4\text{NO}_2)(\text{DMSO})]$ (**6**), is reported. In both complexes **5** and **6** the title ylide is coordinated through the ylidic carbon and the phosphine atom. However, in compound **6** the Hg–C bond length is considerably weakened due to coordination of DMSO molecule to the metal ion and locating of ylidic carbon atom in the axial position of the resulting trigonal bipyramidal complex. Theoretical studies on ligand and all complexes at DFT (B3LYP) level of theory are also reported. The results show that the addition of DMSO molecule to the compound **4** and formation of compound **6** is energetically favored.

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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]. The α -keto stabilized ylides derived from bisphosphines, viz., $\text{Ph}_2\text{PCH}_2\text{PPh}_2=\text{C}(\text{H})\text{C}(\text{O})\text{R}$, $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2=\text{C}(\text{H})\text{C}(\text{O})\text{R}$ ($\text{R} = \text{Me}$, Ph or OMe) [6] and $\text{PhC}(\text{O})\text{C}(\text{H})=\text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2=\text{C}(\text{H})\text{C}(\text{O})\text{Ph}$ [7] form an important class of hybrid ligands containing both phosphine and ylide functionalities, and can exist in ylidic and enolate forms. These ligands can therefore engage in different kinds of bonding with metal ions [6–17].

Hg(II) forms C-coordinated complexes with $\text{X-C}_6\text{H}_4\text{C}(\text{O})\text{C}(\text{H})=\text{PAR}_3$ ($\text{X} = \text{Cl}$ and NO_2 ; $\text{Ar} = \text{phenyl}$ and p -tolyl) [18,19] and $\text{Ph}_3\text{P}=\text{C}(\text{H})\text{CO}(\text{OEt})$ [20]. On the other hand, regiospecific O-coordination of the acetyl oxygen has been observed for the reaction of Hg(II) halides with $\text{Ph}_3\text{P}=\text{C}(\text{COPh})(\text{COMe})$ [21]. The remarkable change in reactivity arises from a subtle variation in the molecu-

lar-electronic structure of the ylide due to the presence of additional keto stabilization. Coordination of ligands towards Hg(II) has assumed importance since, in nature's mercury detoxification process, the initial Hg–C bond cleavage involves the increase in the coordination number around Hg [22]. Furthermore, evidence for new classes of metal-binding motifs in enzymes, transcription factors, and regulatory proteins emphasize the need for structural insights about local Hg(II) coordination environments [23].

The investigation of the reactivity and coordination chemistry of carbonyl stabilized ylides is research field of our group [18–19,24]. We have now focused our attention to new bidentate phosphorus ylides. We aim to expand the scope of complexes with this type of bidentate phosphorus ylides, and to study the bonding properties of this type of ligands. In this context, we report the reactivity of **2** towards mercury(II) halides.

2. Experimental

2.1. Physical measurements and materials

All reactions were carried out under an atmosphere of dry nitrogen. Methanol was distilled over magnesium powder and diethyl ether (Et_2O) over a mixture of sodium and benzophenone just

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before use. All other solvents were reagent grade and used without further purifications. Melting points were measured on a SMP3 apparatus. 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 300 MHz Bruker and 90 MHz Jeol 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. Elemental analysis for C, H and N atoms were performed using a Perkin–Elmer 2400 series analyzer.

2.2. X-ray crystallography

The single crystal X-ray diffraction analyses for complexes **5** and **6** were performed on an Oxford Diffraction Xcalibur S Sapphire system at 150(2) K, using graphite monochromated Mo $\text{K}\alpha$ X-ray radiation ($\lambda = 0.7107 \text{ \AA}$). The crystal structures were solved by direct methods and refined by using SHELXS-97 and SHELXL-97 crystallographic software packages [25,26]. All non-hydrogen atoms were refined anisotropically using reflections $I > 2\sigma(I)$. Hydrogen atoms were located in ideal positions.

2.3. Computational details

The calculations were carried out at the density functional theory (DFT) level, using the B3LYP [27,28] exchange–correlation functional, with a LanL2DZ basis set [29] for compounds **5** and **6** and CEP-121G [30] for all compounds. The latter basis sets includes effective core potentials (ECP) for both the mercury and phosphorus atoms as well as halide (Br^- and I^-) ions. The program GAUSSIAN 03 was employed for all calculations [31]. The molecular structures of **2–8** in the ground state were fully optimized. Atomic coordinates for DFT calculations were obtained from the data of the X-ray crystal structure analyses of compounds **5** and **6**.

2.4. Synthesis of compounds

2.4.1. Synthesis of $[\text{Ph}_2\text{PCH}_2\text{PPh}_2\text{CH}_2\text{C}(\text{O})\text{C}_6\text{H}_4\text{NO}_2]\text{Br}$ (**1**)

A solution of bis(diphenylphosphino)methane (dppm) (0.192 g, 0.5 mmol) and 4-nitrophenacyl bromide (0.152 g, 0.5 mmol) in chloroform (17 ml) was stirred at room temperature for 2 h. The yellow solution was concentrated under reduced pressure to 5 ml, and diethyl ether (20 ml) was added. The orange solid formed was filtered, washed with diethyl ether (20 ml) and dried under reduced pressure. Yield: 0.276 g, 88%. M.p. 210–212 °C. Anal. Calc. for $\text{C}_{33}\text{H}_{28}\text{BrNO}_3\text{P}_2$: C, 63.07; H, 4.49; N, 2.23. Found: C, 62.98; H, 4.40; N, 2.39%.

2.4.2. Synthesis of $[\text{Ph}_2\text{PCH}_2\text{PPh}_2=\text{C}(\text{H})\text{C}(\text{O})\text{C}_6\text{H}_4\text{NO}_2]$ (**2**)

The resulting phosphonium salts (**1**) (0.314 g, 0.5 mmol) were treated with triethyl amine (0.5 ml) in toluene (15 ml). The triethyl amine hydrobromide was filtered off. Concentration of the toluene layer to 5 ml and subsequent addition of petroleum ether (25 ml) results in the precipitation of ligands as yellow solids. Yield: 0.222 g, 81%. M.p. 144–147 °C. Anal. Calc. for $\text{C}_{33}\text{H}_{27}\text{NO}_3\text{P}_2$: C, 72.39; H, 4.97; N, 2.56. Found: C, 72.57; H, 5.11; N, 2.78%.

2.4.3. Synthesis of $[(\mathbf{2})\text{HgX}_2]$ [$\text{X} = \text{Cl}$ (**3**), Br (**4**), I (**5**)]

General procedure for complexes: To a solution of HgX_2 (0.3 mmol) in methanol (5 ml), a solution of **2** (0.164 g, 0.3 mmol) in the same solvent (5 ml) was added dropwise at -5°C and stirred for 2 h. The resulting solid was treated with dichloromethane (35 ml) and filtered through celite. Addition of excess methanol to the concentrated filtrate caused the precipitation of the products as pale yellow solids.

2.4.3.1. $[(\mathbf{2})\text{HgCl}_2]$ (**3**). Yield: 0.152 g, 62%. M.p. 185–187 °C. Anal. Calc. for $\text{C}_{33}\text{H}_{27}\text{Cl}_2\text{HgNO}_3\text{P}_2$: C, 48.39; H, 3.32; N, 1.71. Found: C, 47.98; H, 3.11; N, 1.92%.

2.4.3.2. $[(\mathbf{2})\text{HgBr}_2]$ (**4**). Yield: 0.184 g, 68%. M.p. 197–199 °C. Anal. Calc. for $\text{C}_{33}\text{H}_{27}\text{Br}_2\text{HgNO}_3\text{P}_2$: C, 43.66; H, 3.00; N, 1.54. Found: C, 43.21; H, 3.04; N, 1.40%.

2.4.3.3. $[(\mathbf{2})\text{HgI}_2]$ (**5**). Yield: 0.240 g, 80%. M.p. $>132^\circ\text{C}$ (decomposes). Anal. Calc. for $\text{C}_{33}\text{H}_{27}\text{I}_2\text{HgNO}_3\text{P}_2$: C, 39.56; H, 2.72; N, 1.40. Found: C, 39.28; H, 2.85; N, 1.65%.

2.4.3.4. $[(\mathbf{2})\text{HgBr}_2\text{DMSO}]$ (**6**). This compound was easily obtained from the crystallization of compound **4** (0.091 g, 0.1 mmol) in DMSO solution. The yellow crystals formed by the slow evaporation of the solvent over several days. Yield: 0.093 g, 95%. M.p. 180 °C (decomposes). Anal. Calc. for $\text{C}_{35}\text{H}_{33}\text{Br}_2\text{HgNO}_4\text{P}_2\text{S}$: C, 42.63; H, 3.34; N, 1.42. Found: C, 42.44; H, 3.41; N, 1.53%.

3. Results and discussion

3.1. Synthesis

The reaction of dppm with 4-nitrophenacyl bromide (prepared by reacting 4-nitroacetophenone with bromide in glacial acetic acid) for 2 h (1:1 molar ratio) in CHCl_3 gave the phosphonium salt (**1**) in good yield as a orange solid. Further treatment with triethyl amine led to elimination of $[\text{Et}_3\text{NH}]\text{Br}$, giving the free ligand (**2**) (Scheme 1). The reactions of Hg(II) halides with bidentate phosphorus ylide, $\text{Ph}_2\text{PCH}_2\text{PPh}_2=\text{C}(\text{H})\text{C}(\text{O})\text{C}_6\text{H}_4\text{NO}_2$ in 1:1 molar ratio yielded P, C-chelated complexes. The reaction of complex **4** by DMSO obtained complex **6** containing coordinated DMSO molecule (Scheme 2).

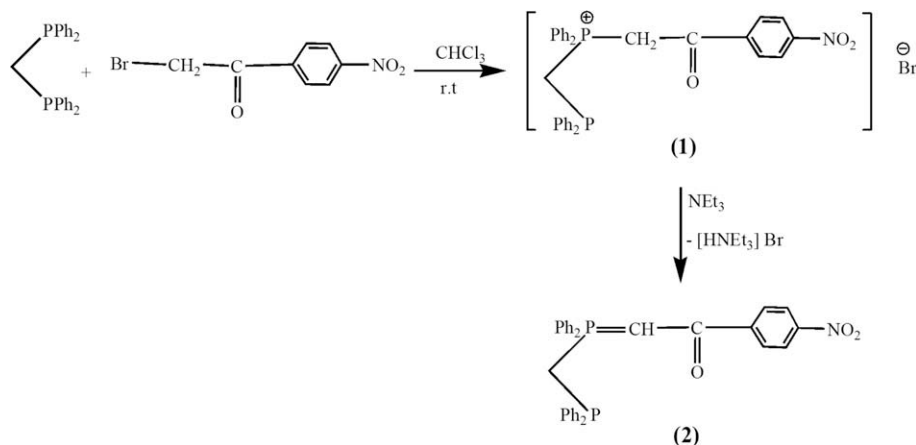
3.2. Spectroscopy

The IR data confirm the complete formation of the carbonylic ylide with the disappearance of the phosphonium CO band at 1684 cm^{-1} and the presence of a new strong CO band relative to a carbonyl stabilized ylide at 1524 cm^{-1} [14]. As noted previously [32], the coordination of the ylide through carbon or oxygen causes a significant increase or decrease, respectively, in the $\nu(\text{C}=\text{O})$ frequency. The infrared absorption bands observed for the three complexes around 1585 cm^{-1} indicate coordination of the ylide through ylidic carbon atom (Table 1). It should be noted that the appearance of a weak band probably associated to $\nu(\text{S}=\text{O})$ at 1016 cm^{-1} in the IR spectrum of compound **6** is unique difference between the IR spectra of compounds **4** and **6** [33].

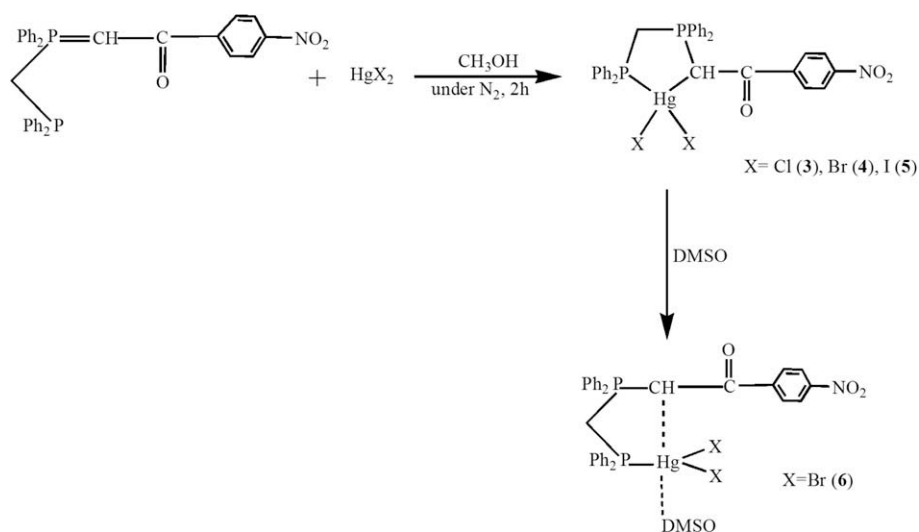
The ^{31}P NMR spectrum of **1** exhibits two doublets at 20.70 and -29.52 ppm , with a coupling constant $^2J_{\text{P-P}}$ of 64.5 Hz, attributable to PCH_2 and PPh_2 groups, respectively. The ^1H NMR spectrum exhibits a doublet at 6.10 ppm, with a $^2J_{\text{P-H}}$ of 12.81 Hz, related to a CH_2 group of a 4-nitrophenacyl bromide system bonded to a phosphonium moiety (Table 2) [14].

The ^{31}P NMR spectrum of **2** shows two doublets at 11.52 and -30.31 ppm , which are assigned to the $\text{PC}(\text{H})$ and PPh_2 groups, respectively. The ^1H NMR spectrum shows a doublet at 4.34 ppm attributable to the ylidic proton with a coupling constant $^2J_{\text{P-H}}$ of 22.94 Hz. The phosphonium atom of this compound shows upfield shifts compared to that of parent phosphonium salt (**1**), suggesting some increasing of electron density in the P–C bond (Table 2).

The ^{31}P chemical shift values for the complexes appear to be shifted downfield with respect to the parent ylide, also indicating that coordination of the ylide has occurred (Table 2). In the ^1H NMR spectra, the signals due to the methinic protons for com-



Scheme 1.



Scheme 2.

Table 1
IR data for compounds 1–6.

Compound	$\nu(\text{CO}) \text{ cm}^{-1}$	Reference
$\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\text{C}(\text{H})\text{C}(\text{O})\text{Ph}$	1521	[6]
$\text{Ph}_2\text{PCH}_2\text{PPh}_2\text{C}(\text{H})\text{C}(\text{O})\text{Ph}$	1523	[6]
1	1684	This work
2	1524	This work
<i>P</i> -coordinated		
$[\text{HgBr}_2(\text{PPh}_2(\text{CH}_2)_2\text{PPh}_2\text{C}(\text{H})\text{C}(\text{O})\text{Ph})_n]$	1511	[15]
$[\text{HgI}_2(\text{PPh}_2(\text{CH}_2)_2\text{PPh}_2\text{C}(\text{H})\text{C}(\text{O})\text{Ph})_n]$	1504	[15]
<i>P, C</i> -coordinated		
$[\text{HgCl}_2(\text{PPh}_2\text{CH}_2\text{PPh}_2\text{C}(\text{H})\text{C}(\text{O})\text{Ph})]$	1566	[13]
$[\text{HgBr}_2(\text{PPh}_2\text{CH}_2\text{PPh}_2\text{C}(\text{H})\text{C}(\text{O})\text{Ph})]$	1568	[13]
$[\text{HgCl}_2(\text{PPh}_2(\text{CH}_2)_2\text{PPh}_2\text{C}(\text{H})\text{C}(\text{O})\text{Ph})]$	1637	[15]
3	1584	This work
4	1586	This work
5	1585	This work
6	1585	This work

plexes are broad. Similar behavior was observed earlier in the case of ylide complexes of platinum(II) chloride [34]. The expected lower shielding of ^{31}P and ^1H nuclei for the $\text{PC}(\text{H})$ group upon complexation in the case of *C*-coordination were observed in their corresponding spectra.

Table 2
Selected ^1H and ^{31}P NMR spectral data for compounds 1–5 [δ (ppm), J (Hz)].

Compound	$\delta \text{ PCH}_2\text{CO}$ ($^2J_{\text{P-H}}$)	$\delta \text{ PCH}$ ($^2J_{\text{P-H}}$)	$\delta \text{ PPh}_2$ ($^2J_{\text{P-P}}$)	$\delta \text{ PCH}$ ($^2J_{\text{P-P}}$)
1 ^a	6.10 (12.81)	–	–29.52 (64.57)	20.70 (64.54)
2 ^a	–	4.34 (22.94)	–30.31 (62.47)	11.52 (65.63)
3 ^b	–	5.25 (12.18)	9.07 (br)	21.86 (35.13)
4 ^{b,c}	–	5.28 (10.57)	2.45 (br)	23.15 (43.29)
5 ^b	–	5.33 (9.49)	–1.93 (br)	24.45 (41.01)

br, broad.

^a Record in CDCl_3 .

^b Record in $\text{DMSO-}d_6$.

^c The same data was observed for compound **6** in DMSO solution.

The most interesting aspect of the ^{13}C spectra of the complexes is the upfield shift of the signals due to the ylidic carbon. Such an upfield shift observed in $[\text{PdCl}(\eta^3\text{-}2\text{-XC}_3\text{H}_4)(\text{C}_6\text{H}_5)_3\text{PCHCOR}]$ [$\text{X} = \text{H}, \text{CH}_3$; $\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$] was attributed to the change in hybridization of the ylidic carbon [35]. Similar upfield shifts of 2–3 ppm with reference to the parent ylide were also observed in the case of $[(\text{C}_6\text{H}_5)_3\text{PC}_5\text{H}_4\text{HgI}_2]_2$ [36]. The ^{13}C shifts of the CO group in the complexes are around 190 ppm (Table 3), relative to 184.05 ppm noted for the same carbon in the parent ylide, indicating much lower shielding of the carbon of the CO group in these complexes.

Table 3
¹³C NMR data for compounds 1–5.

Compound	1 ^a	2 ^a	3 ^b	4 ^{b,c}	5 ^b
PCH ₂ P	21.46(dd)	24.18(dd)	22.87(br)	22.10(br)	23.33(d)
¹ J _{P-C}	51.96, 51.96	58.19, 51.96	–	–	67.62
CH ₂	36.91(d)	–	–	–	–
¹ J _{P-C}	60.22	–	–	–	–
CH	–	52.78(d)	br	br	br
¹ J _{P-C}	–	112.64	–	–	–
CO	191.36(s)	181.99(s)	189.03(s)	186.95(s)	189.47(s)
Ph	117.27–150.65	122.99–148.15	123.48–149.36	119.07–151.16	123.06–149.45

dd, doublet of doublet; d, doublet; br, broad; and s, singlet

^a Record in CDCl₃.^b Record in DMSO-*d*₆.^c The same data was observed for compound 6 in DMSO solution.

It is clear that the NMR data for complexes 4 and 6 in DMSO solution should be the same, so an additional NMR data for compound 6 is not reported in Tables 2 and 3. No coupling to Hg was observed at room temperature in the ¹H, ¹³C and ³¹P NMR spectra for all these complexes. Failure to observe satellites in the above spectra was previously noted in the ylide complexes of Hg(II) [36] and Ag(I) [37], which had been explained by fast exchange of the ylide with the metal. Thus, the spectral data indicate the bidentate coordination of the ligand (2) through both phosphine group and ylidic carbon atom.

3.3. X-ray crystallography

Suitable crystals were obtained from dimethylsulfoxide solution by the slow evaporation of the solvent over several days. Table 4 provides the crystallographic results and refinement information for complexes 5 and 6. The molecular structures are shown in Figs. 1 and 2. Pertinent bond distances and angles for 5 and 6 are given in Table 5. Fractional atomic coordinates and equivalent isotropic displacement coefficients (*U*_{eq}) for the non-hydrogen atoms of the complexes are shown in Supplementary material.

The X-ray analysis in complex 5 reveals the P, C-chelate mode of coordination of the ligand (2) to Hg(II) atom in this complex. The Hg(II) center in complex 5 is four-coordinate with sp³ hybridization. The Hg atom is surrounded by one P atom of the PPh₂ unit, one ylidic C atom and two I atoms. The angles subtended by the ligand at the Hg(II) center in 5 vary from 89.65(17) to 116.17(5) indicating a distorted tetrahedral environment. The Hg–P bond length in 5 (2.5199(19) Å) is comparable to analogous distance in Hg(II)–phosphine complexes [13,38]. In known Hg(II) chelate complexes containing P, O and P, S donors, the Hg–P distances vary from 2.404(1) Å, as in *trans*-[Hg(Ph₂PNP(O)Ph₂)₂] [39], to 2.503(5) Å as in [HgI₂[Ph₂PCH₂P(S)Ph₂]] [40]. The Hg–C bond distance in 5 (2.446(8) Å) is longer than average of those found in a number of dinuclear or trinuclear Hg–phosphoylide compounds, 2.2 Å [20,32,36,41].

The X-ray analysis in complex 6 reveals the P, C-coordination of the ligand to the mercury ion. However, in this compound due to coordination of DMSO molecule to the metal ion the Hg–C bond length, 2.872 Å, is considerably weakened in comparison with compound 5 (2.446(8) Å) and other complexes (an average of 2.4 Å) [13]. As can be seen in Fig. 2, the ylidic carbon and oxygen atom of the coordinated DMSO molecule are located in the

Table 4
Crystal data and refinement details for 5 and 6.

Compound	5	6
Empirical formula	C ₃₃ H ₂₇ HgI ₂ NO ₃ P ₂	C ₃₅ H ₃₃ Br ₂ HgNO ₄ P ₂ S
Formula weight	1001.89	986.03
Temperature (K)	150(2)	150(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	13.3138(3)	9.5319(2)
<i>b</i> (Å)	15.6912(3)	17.6760(4)
<i>c</i> (Å)	16.0974(3)	21.5859(7)
α (°)	90	90
β (°)	103.479(2)	99.039(3)
γ (°)	90	90
<i>Z</i>	4	4
Absorption coefficient (mm ⁻¹)	6.726	6.696
θ range for data collection (°)	3.00–25.05	2.99–25.00
Index ranges	–15 ≤ <i>h</i> ≤ 15 –13 ≤ <i>k</i> ≤ 18 –13 ≤ <i>l</i> ≤ 19	–10 ≤ <i>h</i> ≤ 11 –13 ≤ <i>k</i> ≤ 20 –25 ≤ <i>l</i> ≤ 14
Reflections collected	15 032	16 511
Independent reflections (<i>R</i> _{int})	5780 (0.0271)	6306 (0.0539)
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Maximum and minimum transmission	0.4319 and 0.3943	0.5263 and 0.2964
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Goodness-of-fit on <i>F</i> ²	1.047	0.923
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0427, <i>wR</i> ₂ = 0.1096	<i>R</i> ₁ = 0.0456, <i>wR</i> ₂ = 0.0752
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0565, <i>wR</i> ₂ = 0.1141	<i>R</i> ₁ = 0.0889, <i>wR</i> ₂ = 0.0821
Largest difference in peak and hole (e Å ⁻³)	1.491 and –2.910	1.879 and –1.400

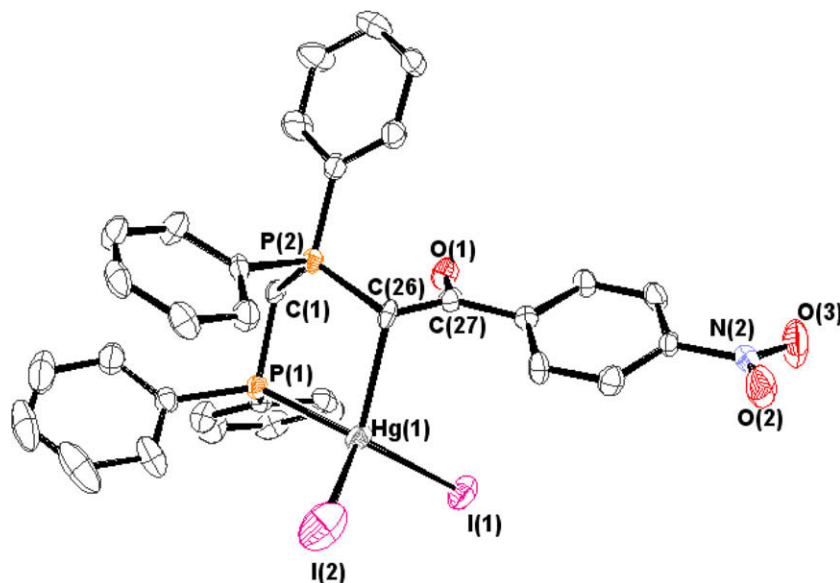


Fig. 1. ORTEP view of X-ray crystal structure of **5**. Hydrogen atoms are omitted for reasons of clarity.

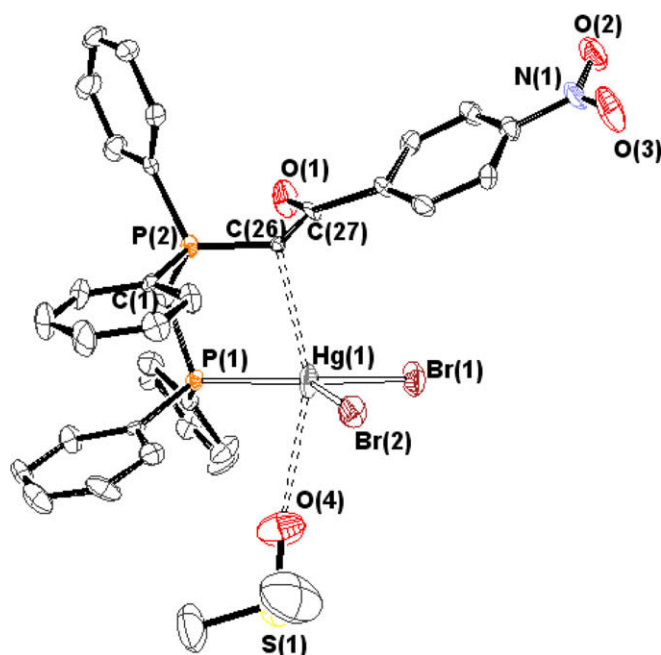


Fig. 2. ORTEP view of X-ray crystal structure of **6**. Hydrogen atoms are omitted for reasons of clarity.

axial positions of the resulting trigonal bipyramidal complex. Thus the Hg–O bond length, 3.060 Å, similar to Hg–C bond length is considerably elongated and is longer than expected value for coordinated DMSO molecule [18,42]. In the equatorial positions the Hg(II) atom is also surrounded by one phosphorous atom of the PPh₂ unit and two terminal Br atoms. Thus this compound can be considered as a pseudo five-coordinate complex. The C(26)–Hg–O(4) bond angle is 156.14 and the angles subtended by the ligand at the Hg(II) center in the equatorial positions are 104.17(3), 125.80(5) and 128.71(5), indicating a distorted trigonal bipyramidal environment. The Hg–P bond distance in **6**, 2.438(19) Å, is less than those found in complexes of [HgBr₂(PPh₃)₂] (2.540(16) and 2.535(15) Å) [43], [HgI₂(PPh₂(CH₂)₂PPh₂C(H)C(O)Ph)]_n (2.472(2) Å) [15] and **5**

Table 5
Selected bond lengths (Å) and bond angles (°) for **5** and **6**.

Complex 5	
Hg(1)–C(26)	2.446(8)
Hg(1)–P(1)	2.5199(19)
Hg(1)–I(1)	2.7070(7)
Hg(1)–I(2)	2.6946(9)
P(2)–C(26)	1.764(7)
O(1)–C(27)	1.231(9)
C(26)–Hg(1)–P(1)	89.65(17)
C(26)–Hg(1)–I(1)	112.69(17)
C(26)–Hg(1)–I(2)	108.68(18)
P(1)–Hg(1)–I(1)	114.17(5)
P(1)–Hg(1)–I(2)	116.17(5)
I(1)–Hg(1)–I(2)	113.12(3)
C(1)–P(1)–Hg(1)	101.1(2)
C(2)–P(1)–Hg(1)	116.8(3)
C(26)–P(2)–C(1)	111.7(4)
C(27)–C(26)–P(2)	112.1(5)
Complex 6	
Hg(1)–P(1)	2.4385(19)
Hg(1)–Br(1)	2.5664(9)
Hg(1)–Br(2)	2.5609(8)
P(2)–C(26)	1.737(7)
O(1)–C(27)	1.241(8)
O(4)–S(1)	1.531(6)
P(1)–Hg(1)–Br(1)	125.80(5)
P(1)–Hg(1)–Br(2)	128.71(5)
Br(1)–Hg(1)–Br(2)	104.17(3)
C(1)–P(1)–Hg(1)	107.1(2)
C(2)–P(1)–Hg(1)	115.5(2)
C(26)–P(2)–C(1)	112.0(3)
C(27)–C(26)–P(2)	115.2(5)

(2.519(19) Å), indicating relatively strong Hg–P bond in this complex. It is worth noting that in **6**, the S–O bond distance of 1.531(36) Å, is about 0.022 Å longer than the experimental reference value of 1.492(1) Å for free DMSO ligand [44].

The two terminal Hg–X distances in **5** (2.694(9) and 2.707(7) Å) and in **6** (2.560(8) and 2.566(4) Å) are comparable to analogous distances in [HgI₂(PPh₃)₂] (2.733(1) and 2.763(1) Å) [45] and [HgBr₂(PPh₃)₂] (2.626(8) and 2.633(6) Å) [43].

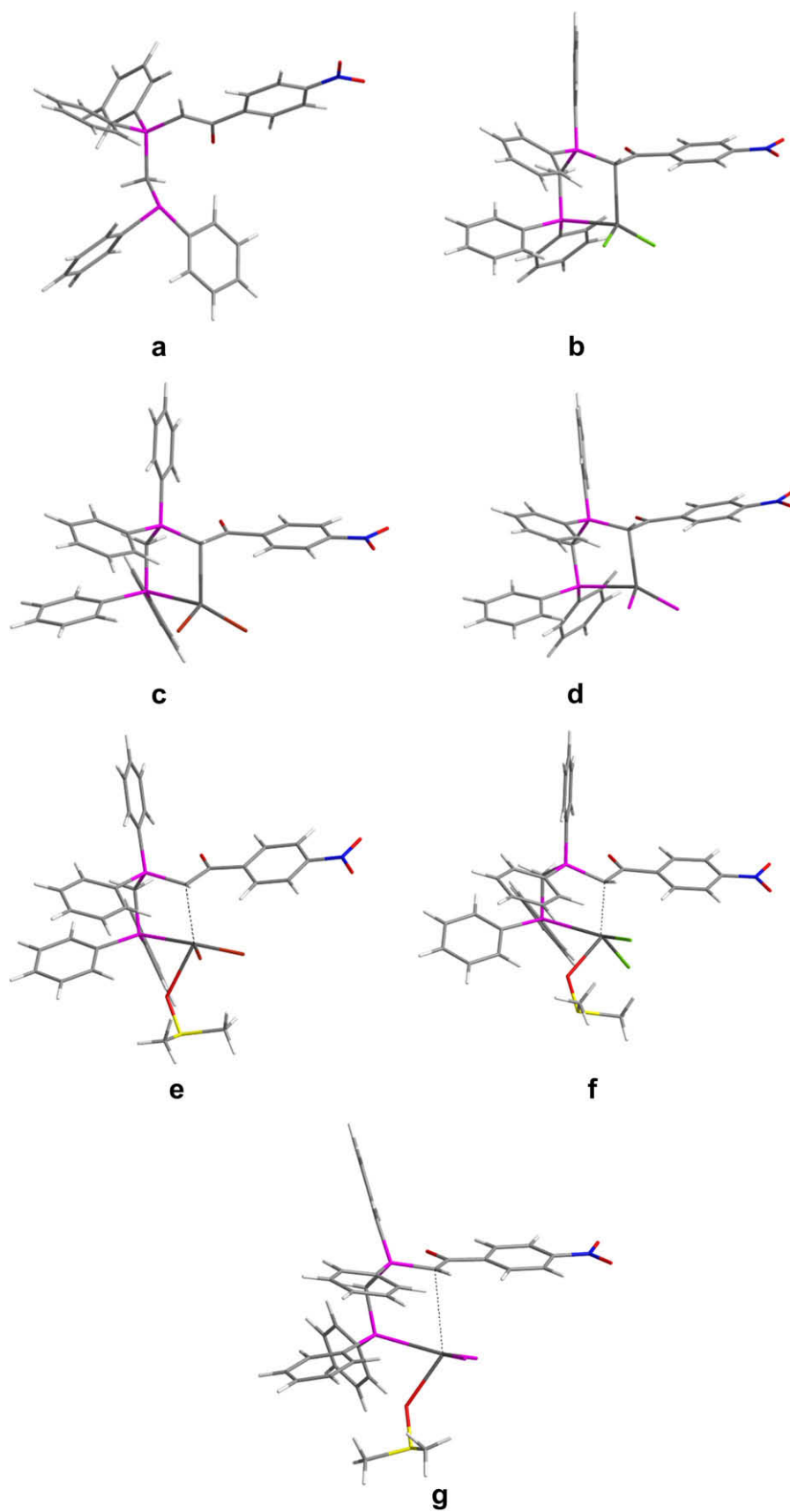


Fig. 3. Calculated molecular structures of (a) **2**, (b) **3**, (c) **4**, (d) **5**, (e) **6**, (f) **7**, and (g) **8**.

Table 6

A comparison between the selected calculated bond lengths (Å) and bond angles (°) for compounds **3**, **4** and **5** and corresponding experimental values for complex **5**.

	3		4		5	
	CEP-121G	LanL2DZ	CEP-121G	LanL2DZ	CEP-121G	X-ray
<i>Bond lengths</i>						
Hg(1)–C(26)	2.489	2.499	2.499	2.563	2.730	2.446
Hg(1)–P(1)	2.884	2.926	2.926	2.947	3.035	2.520
Hg(1)–X(1) ^a	2.537	2.617	2.617	2.817	2.839	2.707
Hg(1)–X(2) ^a	2.501	2.663	2.663	2.779	2.879	2.695
P(2)–C(26)	1.852	1.854	1.852	1.852	1.825	1.764
O(1)–C(27)	1.289	1.288	1.288	1.230	1.287	1.231
<i>Bond angles</i>						
C(26)–Hg(1)–P(1)	85.13	84.08	84.08	82.26	78.80	89.65
C(26)–Hg(1)–X(1) ^a	112.09	118.65	118.65	114.60	113.98	112.69
C(26)–Hg(1)–X(2) ^a	108.14	106.90	106.90	109.75	107.95	108.68
P(1)–Hg(1)–X(1) ^a	103.33	102.91	102.91	103.72	104.06	114.17
P(1)–Hg(1)–X(2) ^a	107.21	110.85	110.85	111.67	110.78	116.17
X(1) ^a –Hg(1)–X(2) ^a	130.78	125.18	125.18	125.85	129.43	113.12

^a X in the compounds **3**, **4** and **5** is Cl, Br and I, respectively.

Table 7

A comparison between the selected calculated bond lengths (Å) and bond angles (°) for compounds **6**, **7** and **8** and corresponding experimental values for complex **6**.

	6		7		8	
	CEP-121G	LanL2DZ	X-ray	CEP-121G	CEP-121G	
<i>Bond lengths</i>						
Hg(1)–P(1)	2.871	3.026	2.438	3.095	2.863	
Hg(1)–C(26)	2.576	2.750	2.872	2.392	3.488	
Hg(1)–O(4)	2.541	2.470	3.060	2.416	2.546	
Hg(1)–X(1) ^a	2.664	2.748	2.566	2.553	2.760	
Hg(1)–X(2) ^a	2.775	2.791	2.561	2.800	2.823	
P(2)–C(26)	1.843	1.817	1.737	1.860	1.807	
O(1)–C(27)	1.291	1.291	1.241	1.285	1.309	
O(4)–S(1)	1.739	1.720	1.531	1.737	1.730	
<i>Bond angles</i>						
P(1)–Hg(1)–C(26)	83.08	76.68	84.04	81.508	71.41	
P(1)–Hg(1)–X(1) ^a	106.74	100.54	125.80	99.88	109.66	
P(1)–Hg(1)–X(2) ^a	132.21	138.88	128.71	144.31	117.27	
P(1)–Hg(1)–O(4)	70.00	80.75	77.30	77.42	70.78	
C(26)–Hg(1)–O(4)	146.02	147.25	156.14	135.33	139.14	
C(26)–Hg(1)–X(2) ^a	91.66	88.79	90.79	86.20	84.53	
C(26)–Hg(1)–X(1) ^a	112.45	114.34	108.83	126.31	105.92	
X(1) ^a –Hg(1)–O(4)	95.34	92.79	94.22	96.06	100.484	
X(2) ^a –Hg(1)–O(4)	91.49	92.93	89.42	88.54	99.42	
X(1) ^a –Hg(1)–X(2) ^a	118.91	120.41	104.17	114.26	132.72	

^a X in the compounds **6**, **7** and **8** is Br, Cl and I, respectively.

3.4. Theoretical studies

As it discussed in previous section the compound **6** is product of the reaction of DMSO molecule with compound **4**. We were interested to study the latter reaction for compounds **3** and **5**. We can

assume that two new compounds, [(**2**)HgCl₂DMSO] (**7**) and [(**2**)HgI₂DMSO] (**8**), can be produced with the reaction of compounds **3** and **5** with DMSO molecule, respectively.

The optimized structures for compounds **2–8** are shown in Fig. 3. The optimized structure parameters for latter compounds calculated by DFT method listed in Tables 6–8 are in accordance with atom numbering scheme given in ORTEP views of compounds **5** and **6** (Figs. 1 and 2). Results of optimization energy for compound **5** (energy vs. optimization steps) were presented in Supplementary material (Fig. 1S).

A comparison between the selected calculated bond lengths (Å) and bond angles (°) for complexes **3–8** with corresponding experimental values for complexes **5** and **6** are presented in Tables 6 and 7. As it can be seen, the calculated structures using CEP-121G basis set for both complexes **5** and **6** in the gas-phase have better agreement with the structures determined by X-ray crystallography than those derived from LanL2DZ calculations. Thus for other complexes **3**, **4**, **7** and **8**, we reported only the results of CEP-121G calculations. In order to show the changes in the structure of ylide (**2**) upon coordination to metal ion, a comparison between the selected calculated bond lengths and bond angles for it and corresponding complexes **3–8** is also given in Table 8. As can be seen (Table 8), the stabilized resonance structure for the parent ylide (**2**) is destroyed by the complex formation, thus, the C(26)–C(27) bond lengths 1.466 Å (**3**), 1.467 Å (**4**), 1.461 Å (**5**), 1.460 Å (**6**), 1.476 Å (**7**) and 1.420 Å (**8**) are longer than the corresponding distance found in the parent ylide (**2**) [1.412 Å]. On the other hand, the C(26)–P(2) bond length in the free ylide is 1.799 Å and is elongated to 1.852, 1.854, 1.852, 1.843, 1.859, 1.807 Å and in compounds **3**, **4**,

Table 9

Calculated electronic energies for four-coordinate complexes, DMSO and pseudo five-coordinate complexes involved in Eq. (1).

Compound	[(2)HgX ₂] (hartree)	DMSO (hartree)	[(2)HgX ₂ DMSO] (hartree)	ΔE (kcal mol ⁻¹)
X = Cl	–456.707	–40.891	–497.624	16.47
X = Br	–453.635	–40.8901	–494.549	14.54
X = I	–449.769	–40.891	–490.672	7.42

Table 10

HOMO, LUMO and gap energy of the optimized structure of compound **2–5** at the B3LYP/CEP-121G level of theory.

Species	Value			
	2	3	4	5
HOMO (eV)	–5.667	–6.553	–6.332	–6.010
LUMO (eV)	–2.941	–3.251	–3.271	–3.259
H–L (eV)	2.726	3.302	3.061	2.751

Table 8

A comparison between the selected calculated bond lengths (Å) and bond angles (°) for ligand **2** and corresponding complexes (**3–8**).

	2	3	4	5	6	7	8
<i>Bond lengths</i>							
C(26)–C(27)	1.412	1.466	1.467	1.461	1.460	1.476	1.420
P(2)–C(26)	1.799	1.852	1.854	1.852	1.843	1.859	1.807
P(2)–C(1)	1.902	1.893	1.893	1.890	1.897	1.892	1.901
P(1)–C(1)	1.941	1.927	1.926	1.927	1.916	1.929	1.919
O(1)–C(27)	1.311	1.289	1.288	1.291	1.291	1.285	1.309
<i>Bond angles</i>							
C(1)–P(2)–C(26)	115.22	111.15	111.16	111.83	110.36	111.10	112.17
P(2)–C(26)–C(27)	116.75	110.32	110.62	110.37	110.91	111.13	113.52
P(1)–C(1)–P(2)	113.70	112.54	112.70	112.45	110.55	111.38	115.31

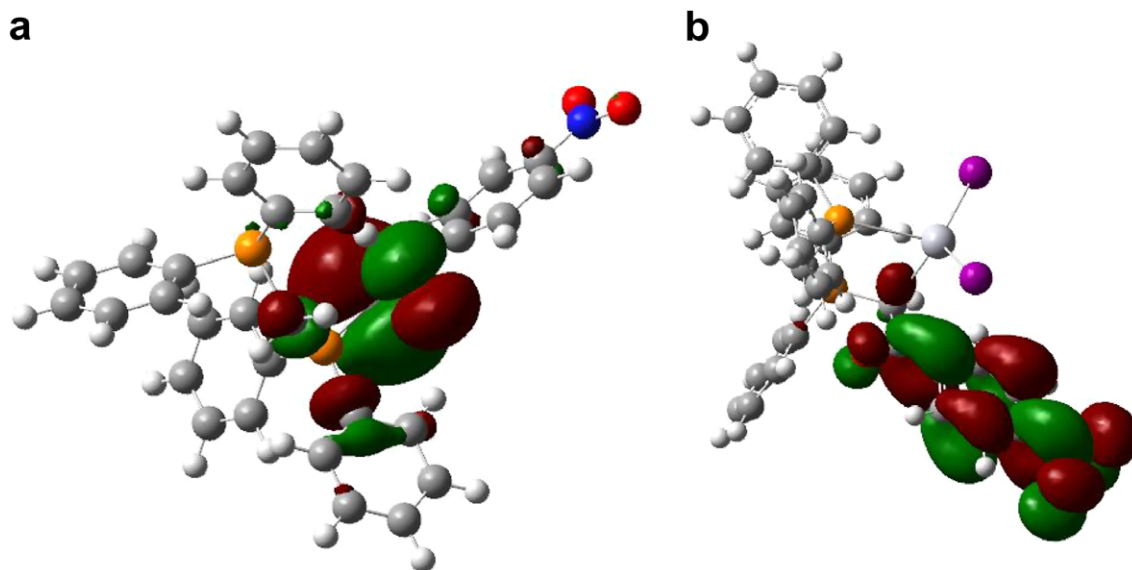


Fig. 4. Illustration of calculated (a) HOMO and (b) LUMO for compound 5.

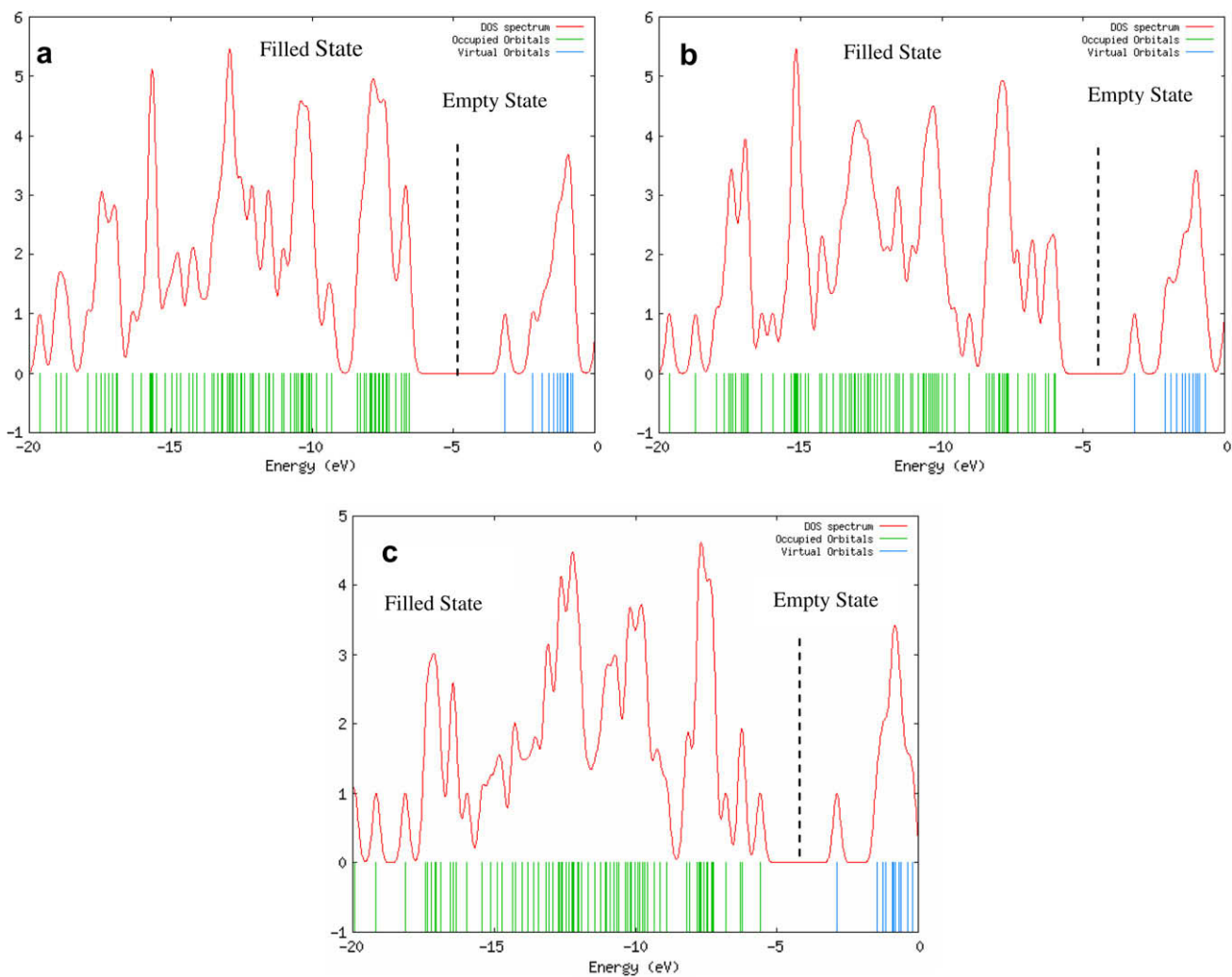


Fig. 5. Electronic density of states (EDOS) of (a) 4, (b) 5, and (c) 2. Blue lines represent virtual orbitals, green lines represent occupied orbitals and a red line represents DOS spectra. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

5, **6**, **7** and **8**, respectively. Obviously, the significant changes in the bond lengths and bond angles of the parent ylide due to complexation must be found around the coordinated part of the ligand (i.e. C(26)–P(2)–C(1)–P(1) moiety). The changes in bond lengths and bond angles calculated here are very similar to those observed for the complexes of similar ylides [13,18].

As we explained in previous sections the complex **6** is the product of the crystallization of the compound **4** in DMSO solution. The results of present calculations show that the product of the following proposed reaction (Eq. (1)) is about 16.47, 14.54 and 7.42 kcal/mol more stable than reactants for compounds **3**, **4** and **5**, respectively (see Table 9).



Thus, it is clear that for all compounds synthesized here, the gas-phase reaction shown in Eq. (1) is an exothermic reaction. Therefore the coordination of the DMSO molecule to the central Hg(II) metal ion and weakening of the Hg–C bond length is energetically favored for all compounds **3**, **4** and **5**. However, we could not isolate the products of latter reaction in the case of compounds **3** and **5**.

The energies of the HOMO and LUMO for ligand (**2**) and complexes (**3–5**) are summarized in Table 10. Comparing HOMO–LUMO (H–L) gap energies of ligand and complexes show that the values of gap energies of all complexes are slightly higher than ligand. As can be seen in Table 10, the calculated energy gap between the latter orbitals for complexes **3**, **4** and **5** is 3.302, 3.061, 2.751 (eV), respectively. Thus, as expected the complex including iodine as a ligand is softest compound and that including chlorine ligand is hardest one. This is completely consistent with this fact that a hard group makes molecule hard and a soft groups makes it soft. However, it is interesting that the energy of LUMO, the target orbital for nucleophilic attack of DMSO molecule, is lowest for compound **4**. Thus it can be probably a reason for this fact that we have observed the DMSO reaction only for latter compound. But as we mentioned above it seems that the reaction of DMSO molecule with all compounds **3**, **4** and **5** is potentially possible. Three-dimensional pictures of the HOMO and LUMO for **5** are presented in Fig. 4.

The total density of states (DOS) was also calculated from the eigenvalues generated by B3LYP/LanL2DZ level of theory (see Fig. 5). The DOS of a system describes the number of states at each energy level that are available to be occupied. A high DOS at a specific energy level means that there are many states available for occupation. A DOS of zero means that no states can be occupied at that energy level [46]. Fig. 5 shows a DOS spectrum, in which the sharp peaks originating were clearly observed. We defined the gap between the first peaks of the empty and filled state as the energy gap (E_g). The fermi level (E_f) was located at the center of E_g , indicating that the charge transfer was occurred. Compared DOS of complexes **4** and **5** with ligand show that significantly change in Fermi level and position of the sharp peaks were occurred.

4. Conclusions

In this paper, we have shown that mercury(II) halides react with a new bidentate phosphorus ylide, $\text{Ph}_2\text{PCH}_2\text{PPh}_2=\text{C}(\text{H})\text{C}(\text{O})\text{C}_6\text{H}_4\text{NO}_2$, to form P, C-chelated complexes. Two type of complexes were characterized by X-ray crystal structure analysis: $[\text{HgI}_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2\text{C}(\text{H})\text{C}(\text{O})\text{C}_6\text{H}_4\text{NO}_2)]$ vs. $[\text{HgBr}_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2\text{C}(\text{H})\text{C}(\text{O})\text{C}_6\text{H}_4\text{NO}_2)\text{DMSO}]$. It was shown that the coordination of DMSO molecule to the central Hg(II) ion considerably increases the Hg–C bond length and slightly decreases the Hg–P bond length. The theoretical calculations confirmed that the reaction of DMSO

molecule with complex (**4**) and formation of a pseudo five-coordinated complex (**6**) is an exothermic reaction and is potentially possible for present complexes.

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Appendix A. Supplementary material

CCDC 703481 and 717739 contain the supplementary crystallographic data for complexes **5** and **6**. 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.2010.02.029](https://doi.org/10.1016/j.jorganchem.2010.02.029).

References

- [1] G. Wittig, *Angew. Chem.* 92 (1980) 671–675.
- [2] G. Wagner, T.B. Pakhomova, N.A. Bokach, *Inorg. Chem.* 40 (2001) 1683–1689.
- [3] N.A. Bokach, V.Y. Kukushkin, M. Haukka, *Inorg. Chem.* 42 (2003) 3602–3608.
- [4] H.J. Christau, *Chem. Rev.* 94 (1994) 1299–1313.
- [5] O.I. Kolodiazny, *Tetrahedron* 52 (1996) 1855–1929.
- [6] Y. Oosawa, H. Urabe, T. Saito, Y. Sasaki, *J. Organomet. Chem.* 122 (1976) 113–121.
- [7] A. Spannenberg, W. Baumann, U. Rosenthal, *Organometallics* 19 (2000) 3991–3993.
- [8] R. Uson, J. Fornies, R. Navarro, A.M. Ortega, *J. Organomet. Chem.* 334 (1987) 389–397.
- [9] I.J.B. Lin, H.C. Shy, C.W. Liu, L.-K. Liu, S.-K. Yeh, *J. Chem. Soc., Dalton Trans.* (1990) 2509–2514.
- [10] D. Saravanabharathi, T.S. Venkatakrishnan, M. Nethaji, S.S. Krishnamurthy, *Proc. Ind. Acad. Sci. (Chem. Sci.)* 115 (2003) 741–749.
- [11] L.R. Falvello, S. Fernandez, R. Navarro, E.P. Urriolabeitia, *Inorg. Chem.* 39 (2000) 2957–2960.
- [12] H. Takahashi, Y. Oosawa, A. Kobayashi, T. Saito, Y. Sasaki, *Bull. Chem. Soc. Jpn.* 50 (1977) 1771–1775.
- [13] M.M. Ebrahimia, K. Panchanatheswaran, A. Neels, *J. Organomet. Chem.* 694 (2009) 643–648.
- [14] S.M. Sbovata, A. Tassan, G. Facchin, *Inorg. Chim. Acta* 361 (2008) 3177–3183.
- [15] M.M. Ebrahim, *Polyhedron* 26 (2007) 3491–3495.
- [16] H. Takahashi, Y. Oosawa, A. Kobayashi, T. Saito, Y. Sasaki, *Chem. Lett.* 1 (1976) 15–16.
- [17] L.R. Falvello, M.E. Margalejo, R. Navarro, E.P. Urriolabeitia, *Inorg. Chim. Acta* 347 (2003) 75–85.
- [18] S.J. Sabounchei, H. Nemattalab, S. Salehzadeh, M. Bayat, H.R. Khavasi, H. Adams, *J. Organomet. Chem.* 693 (2008) 1975–1985.
- [19] S.J. Sabounchei, H. Nemattalab, S. Salehzadeh, S. Khani, M. Bayat, H. Adams, M.D. Ward, *Inorg. Chim. Acta* 362 (2009) 105–112.
- [20] E.C. Spencer, M.B. Mariyatra, J.A.K. Howard, A.M. Kenwright, *J. Organomet. Chem.* 692 (2007) 1081–1086.
- [21] P. Laavanya, U. Venkatasubramanian, K. Panchanatheswaran, J.A.K. Bauer, *Chem. Commun.* (2001) 1660–1661.
- [22] P. Barbaro, F. Ceconi, C.A. Ghilardi, S. Midollini, A. Orlandini, A. Vacca, *Inorg. Chem.* 33 (1994) 6163–6170.
- [23] D.C. Bebout, A.E. DeLanoy, D.E. Ehmman, M.E. Kastner, D.A. Parrish, R.J. Butcher, *Inorg. Chem.* 37 (1998) 2952–2959.
- [24] S.J. Sabounchei, H. Nemattalab, H.R. Khavasi, *J. Organomet. Chem.* 692 (2007) 5440–5446.
- [25] G.M. Sheldrick, *SHELXS-97*, A Program for Automatic Solution of Crystal Structures, University of Göttingen, Germany, 1997.
- [26] G.M. Sheldrick, *SHELX-97*, A Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.
- [27] A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648–5652.
- [28] C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B* 37 (1988) 785–789.
- [29] J.B. Collins, P.V.R. Schleyer, J.S. Binkley, J.A. Pople, *J. Chem. Phys.* 64 (1976) 5142–5151.
- [30] T.R. Cundari, W.J. Stevens, *J. Chem. Phys.* 98 (1993) 5555–5565.
- [31] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, J.T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A.

- Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, revision B.03; Inc., Pittsburg, PA, 2003.
- [32] M. Kalyanasundari, K. Panchanatheswaran, W.T. Robinson, H. Wen, *J. Organomet. Chem.* 491 (1995) 103–109.
- [33] J.A. Davies, *Adv. Inorg. Chem. Radiochem.* 24 (1981) 123–131.
- [34] J.A. Teagle, J.L. Burmeister, *Inorg. Chim. Acta* 118 (1986) 65–72.
- [35] G. Facchin, R. Bertani, M. Calligaris, G. Nardin, M. Mari, *J. Chem. Soc., Dalton Trans.* (1987) 1381–1387.
- [36] N.L. Holy, N.C. Baenziger, R.M. Flynn, D.C. Swenson, *J. Am. Chem. Soc.* 98 (1976) 7823–7824.
- [37] J. Vicente, M.T. Chicote, J. Baeza, J. Martin, I. Hamas, J. Iurpin, P.G. Jones, *J. Organomet. Chem.* 331 (1987) 409–421.
- [38] M. Kubicki, S.K. Hadjikakou, M.N. Xanthopoulou, *Polyhedron* 20 (2001) 2179–2185.
- [39] R. Haid, R. Gutmann, G. Czermak, C. Langes, W. Oberhauser, H. Kopacka, K.H. Ongania, P. Bruggeller, *Inorg. Chem. Commun.* 6 (2003) 61–67.
- [40] T.S. Lobana, M.K. Sandhu, M.J. Liddell, E.R.T. Tiekink, *J. Chem. Soc., Dalton Trans.* (1990) 691–694.
- [41] B. Kalyanasundari, K. Panchanatheswaran, V. Parthasarathi, W.T. Robinson, *Bull. Chem. Soc. Jpn.* 72 (1999) 33–36.
- [42] M.M. Ebrahim, A. Neels, *Polyhedron* 26 (2007) 1277–1284.
- [43] N.A. Bell, T.D. Dee, *Inorg. Chim. Acta* 71 (1983) 135–140.
- [44] M. Calligaris, N.S. Panina, *J. Mol. Struct.* 646 (2003) 61–66.
- [45] L. Fälth, *Chem. Scripta* 9 (1976) 71–73.
- [46] S. Inoue, H. Suto, W. Wongwiriyanpan, T. Kimura, Y. Murata, S.I. Honda, M. Katayama, *Appl. Phys. Exp.* 2 (2009) 035005.