

α -케토안정화된 일리드화 인의 수은(II) 및 은(I) 착물에 대한 X-선 및 분광학적 연구

K. Karami*, O. Büyükgüngör†, and H. Dalvand

Department of Chemistry, Isfahan University of Technology, Isfahan 84156/83111, Iran

†Department of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, 55139 Samsun, Turkey

(접수 2010. 3. 19; 수정 2010. 9. 30; 게재확정 2010. 12. 14)

X-ray and Spectroscopy Studies of Mercury (II) and Silver (I) Complexes of α -Ketostabilized Phosphorus Ylides

K. Karami*, O. Büyükgüngör†, and H. Dalvand

Department of Chemistry, Isfahan University of Technology, Isfahan 84156/83111, Iran. *E-mail: karami@cc.iut.ac.ir

†Department of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, 55139 Samsun, Turkey

(Received March 19, 2010; Revised September 30, 2010; Accepted December 14, 2010)

요 약. 전이금속 이온인 수은(II) 및 은(I)에 대한 α -케토안정화된 일리드화 인 $\text{Ph}_3\text{P}=\text{CHC}(\text{O})\text{C}_6\text{H}_4\text{-X}$ ($\text{X}=\text{Br}$, Ph)의 착물 반응 행동을 연구하였다. 수은(II) 착물 $\{\text{HgX}_2[\text{Y}]\}_2$ ($\text{Y}_1=4\text{-bromo benzoyl methylene triphenyl phosphorane}$; $\text{X}=\text{Cl}(1)$, $\text{Br}(2)$, $\text{I}(3)$, $\text{Y}_2=4\text{-phenyl benzoyl methylene triphenyl phosphorane}$; $\text{X}=\text{Cl}(4)$, $\text{Br}(5)$, $\text{I}(6)$)는 Y_1 및 Y_2 를 HgX_2 ($\text{X}=\text{Cl}$, Br , I)와 각각 반응시켜 제조하였다. α -케토안정화된 일리드화 인(Y_2)의 은(I) 착물 $[\text{Ag}(\text{Y}_2)_2]\text{X}$ ($\text{X}=\text{BF}_4(7)$, $\text{OTf}(8)$)는 이러한 일리드와 AgX ($\text{X}=\text{BF}_4$, OTf)를 아세톤에서 반응시켜 얻었다. 착물 (1)과 (4)의 결정구조를 고찰하였다. 일리드의 C-배위 이핵착물과 트랜스-구조의 착물 $[\text{Y}_1\text{HgCl}_2]_2$, CHCl_3 (1) 및 $[\text{Y}_2\text{HgCl}_2]_2$ (4)를 형성하는 이들 반응에 대해 단결정 X-선 분석을 통해 고찰하였다. 모든 착물(1-3)은 IR, ^1H 및 ^{31}P NMR 뿐만 아니라 ^{13}C NMR을 통하여 확인하였다.

주제어: α -케토안정화, 일리드화 인, 전이금속, 수은, 은

ABSTRACT. The complexation behavior of the α -ketostabilized phosphorus ylides $\text{Ph}_3\text{P}=\text{CHC}(\text{O})\text{C}_6\text{H}_4\text{-X}$ ($\text{X}=\text{Br}$, Ph) towards the transition metal ions mercury (II) and Silver (I) was investigated. The mercury(II) complex $\{\text{HgX}_2[\text{Y}]\}_2$ ($\text{Y}_1=4\text{-bromo benzoyl methylene triphenyl phosphorane}$; $\text{X}=\text{Cl}(1)$, $\text{Br}(2)$, $\text{I}(3)$, $\text{Y}_2=4\text{-phenyl benzoyl methylene triphenyl phosphorane}$; $\text{X}=\text{Cl}(4)$, $\text{Br}(5)$, $\text{I}(6)$) have been prepared from the reaction of Y_1 and Y_2 with HgX_2 ($\text{X}=\text{Cl}$, Br , I) respectively. Silver complexes $[\text{Ag}(\text{Y}_2)_2]\text{X}$ ($\text{X}=\text{BF}_4(7)$, $\text{OTf}(8)$) of the α -keto-stabilized phosphorus ylides (Y_2) were obtained by reacting this ylide with AgX ($\text{X}=\text{BF}_4$, OTf) in Me_2CO . The crystal structure of complexes (1) and (4) was discussed. These reactions led to binuclear complexes C-coordination of ylide and trans-like structure of complexes $[\text{Y}_1\text{HgCl}_2]_2$, CHCl_3 (1) and $[\text{Y}_2\text{HgCl}_2]_2$ (4) is demonstrated by single crystal X-ray analyses. Not only all of complexes have been studied by IR, ^1H and ^{31}P NMR spectroscopy, but also complexes 1-3 have been characterized by ^{13}C NMR.

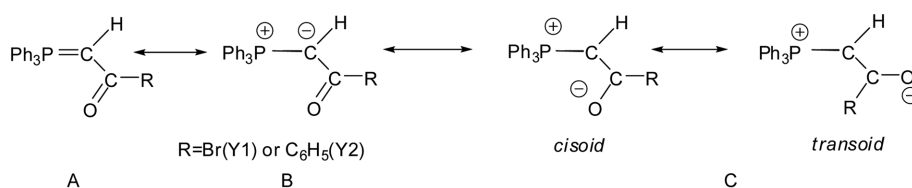
Keywords: α -keto-stabilization, Phosphorus ylides, Transition metals, Mercury, Silver

INTRODUCTION

α -ketostabilized phosphorus ylides are versatile ligands for heavy metal ions¹⁻⁵ and interesting ligands in organometallic chemistry and useful intermediates for organic synthesis.⁶⁻¹⁹ They are versatile ligands for catalysts in a very small number of catalytic reactions such as, for example, the hydrogenation of olefins²⁰ and the cyclotrimerization²¹ and polymerization of acetylenes,²² but the most important application is in the industrially used SHOP process.²³ The α -keto-stabilized phosphorus ylides are distinguishable from no stabilized ylides, since they can

be easily handled due to an additional stabilization from delocalization of the negative charge. The α -keto-stabilized phosphorus ylides was shown interesting properties such as their high stability and their ambidentate character as ligands (C- versus O-coordination).²⁴⁻³⁰ This ambidentate character can be rationalized in terms of the resonance forms A-C (Scheme 1).

We have been interested in investigating the different bonding modes have been adopted by ylides when coordinated to Hg (II), Ag (I) and Pd (II).²⁴⁻²⁷ The C and O-coordinated complexes of Hg (II) was formed.²⁸⁻³⁰ In this paper, we report the reactivity of the ligands 4-Bromo



Scheme 1.

benzoyl methylene triphenyl phosphorane (Y_1) and 4-Phenyl benzoyl methylene triphenyl phosphorane (Y_2), towards mercury (II) halides and silver (I) salts. One of the significance aspects of our work is to ascertain the preferred coordination modes of Y_1 and Y_2 to the Hg and Ag metals. In this study, we describe the preparation, spectroscopic characterization (IR and NMR) of mercury (II) and silver (I) complexes with the title ylides. By a comparison of the data collected and single crystal x-ray diffraction of 1 and 4, it demonstrates C-coordination of the ylides to the metals.

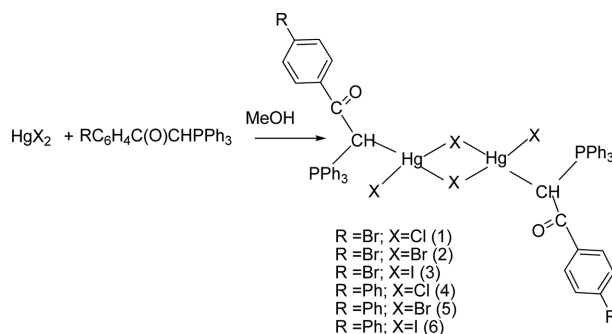
RESULTS AND DISCUSSION

Spectroscopy

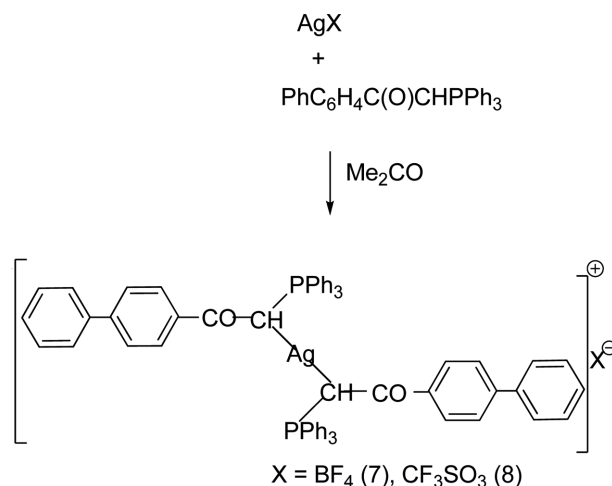
IR and NMR spectroscopy are suitable indicators for judging the bonding mode of the α -keto ylides. The IR spectra of 1-8 (Table 1) show that ν (CO) absorption at between 1600-1645 cm^{-1} in the region typical for the C-bonded phosphorus ylides.¹⁶ The increasing carbonyl stretching frequency in the IR spectra of these complexes, confirm that the ligand is bound through the carbon of ylide to Hg (II) and Ag (I) center (Table 1, Scheme 2). Similarly, in the ^1H and ^{31}P NMR spectra of complexes 1-6 the downfield shift of the signal due to the PCH group are ascribed to C-coordination of the ylide (Table 1). In the ^1H NMR spectra of 7 and 8, the singlet at 5.35 and 5.40 ppm, respectively due to the methine proton appear in the downfield. These downfield shifts of the signal due to C-

Table 1. Selected IR (cm^{-1}), ^1H and ^{31}P NMR spectral data [δ (ppm), J (Hz)]

	$\nu(\text{C}=\text{O})$	δ_{PCH}	$^2J_{\text{P-H}}$	δ_{PPh_3}
Y_1	1518	4.2(d)	24.02	16.5
Y_2	1507	4.52(d)	24	17.2
1	1635	5.22(br)	-	25.2
2	1621	5.06(br)	-	24.52
3	1618	4.96(br)	-	23.49
4	1645	5.5(br)	-	27.45
5	1628	5.1(br)	--	25.6
6	1623	5.06(br)	-	20.54
7	1601	5.35(br)	-	24.80
8	1601	5.4(br)	-	24.48



Scheme 2.



Scheme 3.

coordination of the ylide (Table 1, Scheme 3). The resonances of the ^{31}P NMR complexes 1-8 have been observed to occur at a lower field with respect to the free ylide (Table 1, Scheme 2 and 3). The expected downfield shifts of ^{31}P and ^1H signals for the PCH group upon complexation were observed in their corresponding spectra. The appearance of single signals for the PCH group in both the ^{31}P and ^1H NMR at ambient temperature indicates the presence of only one molecule for all the complexes as expected for C-coordination.³¹ That the bonding of the ylide to Hg (II) in the chloride complex is much weaker than in the bromide and the iodide complexes is indicative in the ^1H NMR spectra in which the methine group resonances appear at δ 4.2, 4.52, 5.22, 5.06, 4.96, 5.5, 5.1, 5.06 and for the free ylides (Y_1 and Y_2) and complexes 1-

6, respectively (Table 1).

Although two diastereoisomer (RR/SS and RS) are possible for each complex (because the methine carbons are chiral) NMR spectroscopy dose not distinguish them at room temperature. The methine resonances of complexes (1-8) are intermediate between those in the free ylides and phosphonium salts; this was observed for other C-coordinated carbonyl-stabilized phosphorus ylide complexes and $^2J_{PH}$ values smaller than the free ylides and phosphonium salts: because the hybridization changes in the ylidic carbon (SP²-SP³) in the C-coordination mode.³² Values of $^2J_{PH}$ much larger (ca. 20 Hz) have been observed in complexes where coordination is through the oxygen atom.²⁶

The ^{13}C NMR spectra of the complexes 1-3 is the up field shift of the signals due to the ylidic carbon atoms. Such an up field shift was observed in other complexes is due to the change in hybridization of the ylidic carbon atom on coordination.³² Similar up field shifts of 2-3 ppm with reference to the parent ylide were also observed in the case of complexes of Hg (II) with BPPY complex.³³ The ^{13}C shifts of the CO group in the complexes are between 186-189 ppm, which is higher field than the 183.1 ppm noted for the same carbon in the parent ylide, indicating much lower shielding of the carbon atom of the CO group in the complexes. No coupling to Hg was observed at room temperature in the 1H , ^{13}C and ^{31}P NMR spectra. Failure to observe satellites in the above spectra was previously noted in the ylide complexes of Hg (II)³³

and Ag (I),³⁴ which had been explained by fast exchange of the ylide with the metal. In other hand it is possible that a fast equilibrium between complexes and free ylides is responsible for the failure observed either the NMR couplings or presence of two diastereoisomers.

X-ray crystallography

Table 2 provides the crystallographic results and refinement information for complexes 1 and 4 (Scheme 2). The molecular structures are shown in Figs. 1 and 2. Selected

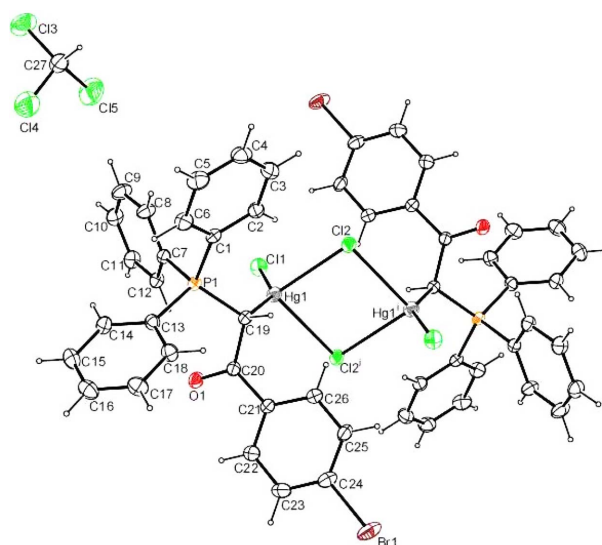


Fig. 1. ORTEP view of the X-ray crystal structure of complex 1.

Table 2. Crystal data and refinement details for complex 1 and 4

Empirical formula	C ₅₂ H ₄₀ Br ₂ Cl ₄ Hg ₂ O ₂ P ₂ · 2(CHCl ₃)	C ₆₄ H ₅₀ Cl ₄ Hg ₂ O ₂ P ₂
Formula weight	1700.3	
Crystal system	monoclinic	1416.37
Space group	P21/c	Triclinic
a (Å)	13.3444(7)	P 1
b (Å)	10.8412(4)	10.3826 (14)
c (Å)	22.3623(11)	12.7884 (18)
α	90	13.8852 (17)
β (°)	113.7	110.363 (10)
γ	90	101.145 (10)
V (Å ³)	2961.8(3)	95.724 (11)
Z	2	1667.6 (4)
D(calc)[g/cm ³]	1.907	1
Absorption coefficient (mm ⁻¹)	6.226	1.410
Collected reflections	49879	0.76
Independent reflections	9565	16240
R(int)	0.0917	6909
Observed reflections		0.109
[I > 2 σ (I)]	7035	
R1 (observed data)	0.0500	3480
		0.0640

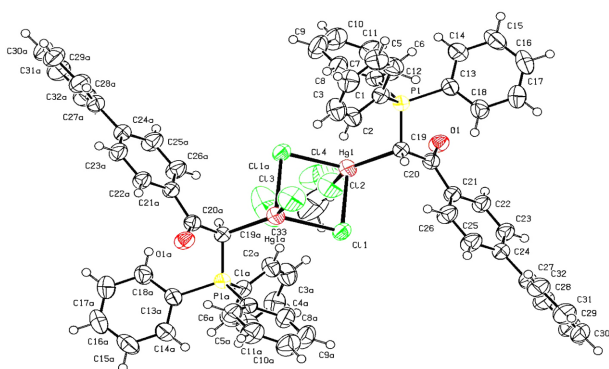


Fig. 2. ORTEP view of the X-ray crystal structure of complex 4.

Table 3. Selected bond lengths (Å) and angles (°) for the structure $[Y_1 \text{HgCl}_2]_2 \cdot 2\text{CHCl}_3$ (1)

Hg1-Cl1	2.3953	Cl1-Hg1-Cl2	106.71
Hg1-Cl2	2.7345	Cl1-Hg1-C19	147.14
Hg1-C19	2.1979	Cl1-Hg1-Cl2a	97.34
Hg1-Cl2	2.7090	Cl2-Hg1-C19	98.01
P1-C7	1.7916	Cl2-Hg1-Cl2a	85.13
P1-C1	1.7969	Cl2a-Hg1-C19	106.16
P1-C13	1.8018	Hg1-Cl2Hg1_	94.87
P1-C19	1.7890	Hg1-C19-P1	113.90
O1-C20	1.2195	Hg1-C19-C20	105.17
C19-C20	1.4964	P1-C19-C20	112.07
O1-C20-C21	120.20	O1-C20-C19	120.74

Table 4. Selected bond lengths (Å) and angles (°) for the structure $[Y_2 \text{HgCl}_2]_2 \cdot \text{CH}_2\text{Cl}_2$

C19-C20	1.489 (4)	Cl1-Hg1 ⁱ	2.5630 (8)
C19-P1	1.786 (3)	Cl1-Hg1	2.7857 (8)
C19-Hg1	2.200 (3)	Cl2-Hg1	2.3898 (10)
C20-O1	1.221 (4)	Hg1-Cl1 ⁱ	2.5630 (8)
C20-C21	1.490 (4)	C13-P1	1.809 (3)
C21-C26	1.391 (4)	Cl1 ⁱ -Hg1-Cl	87.20 (2)
C21-C22	1.394 (4)	Cl2-Hg1-Cl1	101.93 (4)
C1-C2	1.383 (5)	C19-Hg1-Cl1	97.51 (8)
C1-C6	1.395 (5)	Cl2-Hg1-Cl1 ⁱ	102.10 (4)
C1-P1	1.799 (3)	C19-Hg1-Cl1 ⁱ	120.74 (8)
C2-C3	1.385 (5)	C19-Hg1-Cl2	133.55 (8)
C7-P1	1.793 (3)	Hg1 ⁱ -Cl1-Hg1	92.80 (2)

bond distances and angles for 1 and 4 are given in *Tables 3* and 4, respectively. The Hg (II) centre in complex 1 forms four close contacts with sp^3 hybridization and has a 4-coordinate environment with one short Hg–Cl (2.393 Å) bond, one Hg–C bond and two asymmetric bridging Hg–Cl (bonds at distances of 2.7345 and 2.7090 Å (*Fig. 1*)). The crystal structure of 1 shows the strongly distorted tetrahedral geometry at the Hg(II) Cl1-Hg1-C19, 147.14.²⁴

The significant shortening of the Hg–C bond length, 2.1979 Å compared to analogous distances in $[\text{C}_6\text{H}_5]_3\text{PCHCOC}_6\text{H}_5\text{HgI}_2$ ³¹ and in $[(\text{C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_3\text{HgI}_2)_2]$ ³³ (2.312(13) and 2.292(8) Å, respectively) must be attributed to the use of mercury orbital with high s character for bonding to the ylidic carbon. The use of non-equivalent hybrid orbital with high s character to bond to low electronegative atoms was proposed by Bent in the concept of isovalent hybridization to account for the variation in bond lengths and bond angles around a central atom.³⁵ The terminal Hg–Cl bond length, 2.3953 Å is comparable to 2.352 (3) Å³⁰ observed in the case of $[(\text{EPPY})(\text{HgCl}_2)]_2$, which has a tetrahedral coordination environment around.

The Hg(II) centre in complex 4 is coordinated by one carbon and three chloro atoms in a distorted tetrahedral geometry. The two different Hg–Cl distances in 4 (2.3898(10) and 2.5630(8) Å) are less than those of found in mononuclear complex of $[\text{HgCl}_2(\text{PPh}_3)_2]$ ³⁶ (2.559(2) and 2.545(3) Å), indicating relatively strong Hg–Cl bonds in 4. Difference between two distances in these complexes might be arising from steric effects of the large ylidic groups. The angles around mercury in complex 4 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 orbital involved in the above bonds and the steric effects of phosphine group needing the C–Hg–Cl angle to be larger mercury with a bridging structure.³⁷ The two bridged Hg–Cl bonds fall within the range 2.620–3.080 Å reported for other structures³⁸ containing chloro bridged mercury. The angles around mercury in complex 1 and 4 vary from 85.13 to 147.14 and 87.20(2) to 133.55(8) for the chloride very distorted tetrahedral environment. This distortion must be due to the higher s character of the sp^3 hybrid mercury orbital involved in the above bonds and the formation of a strong chloro bridge between the Hg atoms which requires the internal ClHgCl angle to be considerably smaller. The stabilized resonance structure for the title ylide have been destroyed by the complexes formation. Thus, the C(19)–C(20) bond lengths (1.4964, 1.489(4) Å) is significantly longer than the corresponding bond found in a similar free ylide (1.407(8) Å) (*Table 5*).³⁹ On the other hand, the bond length of P(1)–C(19) in the similar elide is 1.706 Å^{24,27,40} which show that the above bond is considerably elongated to 1.7890 and 1.786(3) Å in these complexes (*Table 5*). The elongation of the P–C (methine) bond in 1 and 4 relative to the free ylide supports the localization of the positive charge at the phosphorus (*Table 5*). The adaptation of dimeric structures in Hg(II) ylide complexes may

Table 5. Comparison of selected bond lengths in 1 and 4 with Ph₃PCHC (O) Ph, [Ph₃PCHC (Me)O] TiCl₄ (THF)

Compounds	P=CH or (P(1)-C(19))	PCH-C or C19-C20	C=O	Ref
Ph ₃ PCHC(O)Ph	1.711	1.390	1.255	[34]
[Ph ₃ PCHC(O)Ph]TiBr ₂ (NMe ₂) ₂	1.746(5)	1.355(7)	1.303(5)	[18]
[Br-BPPY HgCl ₂] ₂ ·2CHCl ₃ (1)	1.7890	1.4964	1.2195	This work
[Ph-BPPY HgCl ₂] ₂ ·(4)	1.786 (3)	1.489 (4)	1.221 (4)	This work

be explained by both the preference of Hg(II) to four coordination and the stability of the 18 electron configuration around Hg(II). The lengthening of the C–O bond is in the range of a C–O double bond and comparable with that in free ylide (Table 5).

The C-coordination of the title ylides (Scheme 2 and 3) is in contrast to the O-coordination of the phosphorus ylide Ph₃PC (COMe) (COPh) (ABPPY) in a different Hg (II) complex.⁴¹ The difference in the coordination mode between ABPPY and the Y₁ and Y₂ 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. Belluco *et al.* have studied steric influences on the coordination modes of ylide molecules to Pt (II) systems.⁴² 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, Y₁ and Y₂ are slightly less sterically demanding than ABPPY and are C-coordinated to Hg (II).

EXPERIMENTAL

Materials

All the reactions were performed in air. The starting materials were purchased from commercial sources and used without further purification.

Physical measurements

All solvents were reagent grade and used without further purifications. Solution-state ¹H and ³¹P NMR spectra at 300 K were obtained in CDCl₃ using a 500 MHz Bruker spectrometer operating at 500.13 MHz for ¹H and 161.97 MHz for ³¹P and referenced to H₃PO₄ (85%) for ³¹P{¹H}NMR spectra. IR spectra were recorded on a FT-IR JASCO 680 spectrophotometer, and the measurements were made by the KBr disk method. Melting points were measured on a Gallenamp 9B 3707 F apparatus. Elemental analysis for C, H and N were performed using a PE 2400 series analyzer. The data collection was performed at room temperature using the X-scan technique and using the STOE X-Area software package.⁴³ The crystal structures were

solved by direct methods and refined by full-matrix least-squares on F² by SHELXL97⁴⁴ and using the ORTEP-3 crystallographic software package.⁴⁵ The independent reflections was measured on an automatic STOE IPDS 2 diffractometer (graphite monochromated Mo–K α radiation). All non-hydrogen atoms were refined anisotropically using reflections I > 2 σ (I). Hydrogen atoms were inserted at calculated positions using a riding model with fixed thermal parameters.

Data for ligands

Synthesis of PhC₆H₄COCH=PPh₃: To dichloromethane solution (15 ml) of 2-Bromo 4-Phenyl acetophenone (1.38 g, 5 mmol) was added of PPh₃ (1.31g, 5 mmol) and the resulting mixture was stirred for 5h, the suspension was filtered off, the precipitate washed with diethyl ether (25 ml) and air-dried. Further treatment with aqueous NaOH solution (0.5 M) led to elimination of HBr (PH = 7), giving the free ligand. M.p. 230-231 C; Yield (1.87 g, 81.9%); IR (KBr, cm⁻¹): ν 1507; ¹H NMR (500 MHz, CDCl₃, ppm): δ = 4.52 (d, 1H, CHP, ²J_{PH} = 24 Hz), 7.38 (t 1H, H_p, C₆H₅) 7.48 (t, 2H, H_m, C₆H₅), 7.47 (t 2H, H_m, C₆H₄) 7.53 (m, 6H, H_m, PPh₃), 7.6 (m, 2H, H_o, C₆H₅, ³J_{HH} = 6 Hz), 7.65 (t, 3H, H_p, PPh₃, ³J_{HH} = 6 Hz), 7.84 (m, 6H, H_o, PPh₃), 8.08 (d, 2H, H_o, C₆H₄), ³¹P{¹H}NMR (CDCl₃): δ = 17.2 (s, 1P, CHP). 2.4.2.

Data for BrC₆H₄COC=HPPH₃ [25]: M.p: 142 °C, Anal. Calc for C₂₆H₂₀OPBr: C, 68.03; H, 4.39 Anal Found: C, 68.22; H, 4.28. ¹³C NMR (CDCl₃) δ C: 51.3 (d, ¹J_{PC} = 111.2 Hz, CH); 126.2 (d, ¹J_{PC} = 93.24 Hz, PPh₃ (i)); 127.81 (COPh (m)); 128.88 (PPh₃ (p)); 129.34 (d, ³J_{PC} = 12.41 Hz, PPh₃ (m)); 131.80 (d, ⁴J_{PC} = 2.81 Hz, COPh (o)); 133.40 (d, ²J_{PC} = 10.25 Hz, PPh₃ (o)); 135.86 (COPh (p)); 140.63 (d, ²J_{PC} = 14.69 Hz, COPh (i)); 183.1 (d, ²J_{PC} = 3.3 Hz, CO).

Synthesis of the complexes of complexes HgX₂Y₂ {Ye = Y₁; X = Cl (1), Br(2), I(3), Ye = Y₂; X = Cl(4), Br(5), I(6)}. General procedure for complexes

The following general procedure was used for preparing the complexes 1-6. To a solution (5 ml) of HgX₂ (0.5 mmol) in ethanol (5 ml), a solution of Y₁ (0.223 g, 0.5

mmol) in ethanol (10 ml) was added drop wise at room temperature and stirred for 4h. The resulting solid was treated with dichloromethane (25 ml) and filtered through celite. Addition of excess diethylether (15 ml) to the concentrated filtrate caused the precipitation of products as white or pale yellow solids. These solid products have been separated by filtration and washed with ethanol. The complexes were purified by repeating the precipitation two times and the solid dried under vacuum.

Data for [Y₁. HgCl₂]₂ (1): Yield: 92.0%, M.p: 214 °C, IR (cm⁻¹), ν(C=O):1635 Anal. Calc for C₅₂H₄₀Br₂Cl₄Hg₂P₂O₂: C, 42.75; H, 2.76 Anal Found: C, 42.45; H, 2.83. ¹H NMR (500 MHz, CDCl₃, and ppm); 5.51(d, 1H, CH, ²J_{PH} = 10.25 Hz), 7.1-8.2 (m, 19H, Ph) ppm and ³¹P NMR (CDCl₃): 21.79 ppm. ¹³C NMR (CDCl₃) δ: 47.2 (d, ¹J_{PC} = 73.2 Hz, CH); 123.33 (d, ¹J_{PC} = 86.7 Hz, PPh₃ (i)); 127.81 (COPh (m)); 129.8 (d, ³J_{PC} = 12.35 Hz, PPh₃ (m)); 130.5 (COPh (p)); 129.74 (PPh₃ (p)); 132.8 (d, ²J_{PC} = 9.46 Hz, PPh₃ (o)); 136.8 (COPh (o)); 137.3(COPh (i)); 189.82 (s, CO).

Data for [Y₁. HgBr₂]₂ (2): Yield: 81%, M.p: 214 °C, IR (cm⁻¹), ν(C=O):1621 Anal. Calc for C₅₂H₄₀Br₆Hg₂P₂O₂: C, 38.10; H, 2.46 Anal Found: C, 38.08; H, 2.33. ¹H NMR (500 MHz, CDCl₃, and ppm); 4.62 (d, 1H, CH, ²J_{PH} = 5.5 Hz), 7.1-8 (m, 19H, Ph) ppm and ³¹P NMR (CDCl₃): 20.34 ppm. ¹³C NMR (CDCl₃) δ: 48.45 (d, ¹J_{PC} = 81.3 Hz, CH); 126.13 (d, ¹J_{PC} = 89.97 Hz, PPh₃ (i)); 129.12 (COPh (m)); 121.13(d, ³J_{PC} = 11.52 Hz, PPh₃ (m)); 130.54 (PPh₃ (p)); 133.25 (d, ²J_{PC} = 9.61 Hz, PPh₃ (o)); 134.43 (COPh (p)); 137.3(COPh (o)); 137.92 (COPh (i)); 188.31 (s, CO).

Data for [Y₁. HgI₂]₂: Yield: 76%, M.p: 204 °C (dec), IR (cm⁻¹), ν(C=O): 1618 Anal. Calc for C₅₂H₄₀Br₄Hg₂I₂P₂O₂: C, 34.19; H, 2.21 Anal Found: C, 34.05; H, 2.13. ¹H NMR (500 MHz, CDCl₃, ppm): 5.48 (s br, 1H, CH), 7. -8.1 (m, 19H, Ph) ppm and ³¹P NMR (CDCl₃): 21.86 ppm. ¹³CNMR (CDCl₃) δ: 49.52 (d, ¹J_{PC} = 83.77 Hz, CH); 123.62 (d, ¹J_{PC} = 90.23 Hz, PPh₃ (i)); 126.15 (COPh (m)); 128.89 (d, ³J_{PC} = 12.15 Hz, PPh₃ (m)); 131.62 (PPh₃ (p)); 133.25 (d, ²J_{PC} = 10.12 Hz, PPh₃ (o)); 134.21 (COPh (p)); 136.94 (COPh (o)); 138.65 (d, ³J_{PC} = 10.64 Hz, COPh (i)); 186.83 (s, CO).

Data for [Y₂. HgCl₂]₂ (4): M.p. 218-220 °C. Yield: 0.1098 gr (75.4%), IR (cm⁻¹), ν (C=O): 1644.98, Anal. Calc for C₆₄H₅₀Cl₄Hg₂P₂O₂: C, 52.78; H, 3.46; Found: C; 51.7 H; 3.19 ¹H NMR (500 MHz, CDCl₃, ppm); δ = 5.5 (s, 1H, CHP), δ = 7.36 (t, 1H, Hp C₆H₅, ³J_{HH} = 7.3HZ), δ = 7.425

(t, 2H, Hm C₆H₅, ³J_{HH} = 7.74Hz), δ = 7.56 (m, 6H, Hm, PPh₃), δ = 7.625 (m, 5H, Hp PPh₃+ Ho C₆H₅), δ = 7.678 (d, 2H, Hm C₆H₄, ³J_{HH} = 13.86HZ), δ = 7.775 (d of d, 6H, Ho, PPh₃), δ = 8.21 (d, 2H, Ho C₆H₄, ³J_{HH} = 8.235 HZ). ³¹P{¹H} NMR (CDCl₃): δ = 27.45 (s, 1P CHP).

Data for [Y₂. HgBr₂]₂ (5): M.p. 236 °C. Yield: .126gr (77.1%), IR (cm⁻¹), ν (C=O):1627.63, Anal. Calc for C₆₄H₅₀Br₄Hg₂P₂O₂: C, 47.05; H, 3.08. Found: C; 46.88, H; 3.12. ¹H NMR (500 MHz, CDCl₃, ppm): δ = 5.1 (s, 1H, CHP), 7.38 (m, 2H, Hm, C₆H₅), δ = 7.33(t, 2H, Hm, C₆H₄CO) δ = 7.46 (sbr, 6H, Hm) δ = 7.51(2H, Ho C₆H₅), δ = 7.56 (sbr, 5H, Hp PPh₃+Ho C₆H₄) δ = 7.65 (m, 6H, Ho PPh₃) δ = 8.025 (d, 2H, Ho, C₆H₄CO, ³J_{HH} = 7.6Hz), ³¹P{-¹H}NMR (CDCl₃): δ = 25.6 (s, 1P, PPh₃)

Data for [Y₂. HgI₂]₂ (6): M.p. 130-132 °C. Yield: 1.27 gr (69.5%), IR (cm⁻¹), ν (C=O):1622.8, Anal. Calc for C₆₄H₅₀Hg₂I₄P₂O₂: C, 42.19; H, 2.77. Found: C;41.7 H; 2.83, ¹H NMR (500 MHz, CDCl₃, ppm); δ = 5.06 (s, 1H CHP), δ = 7.36 (t, 1H Hp C₆H₅, ³J_{HH} = 6.9HZ), δ = 7.45 (t, 2H, Hm C₆H₅, ³J_{HH} = 7.14Hz), δ = 7.58 (s br, 6H, Hm, PPh₃), δ = 7.70 (m, 13H, 3Hp PPh₃+ 6Ho C₆H₅+ 2Ho C₆H₅+ 2Hm C₆H₄), δ = 8.01 (d, 2H, Ho C₆H₄, ³J_{HH} = 7.46HZ). ³¹P {¹H} NMR (CDCl₃): δ = 20.54 (s, 1P, PPh₃).

Syntheses of [Ag (Y₂)₂] X (X = BF₄ (7), OTf (8)) General procedure for complexes

The ylide PhBPPY (0.457 g, 1 mmol) was added to a solution of AgX (0.5 mmol) in acetone (10 mL). The solution was stirred for 1 h during which it was protected from light and then filtered. The volume of solvent was reduced under vacuum to 2 mL. Diethyl ether (25 mL) was added to precipitate white solid.

Data for [Ag (Y₂)₂] BF₄ (7): M.p.150 °C (dec). Yield: 0.068 (61.4%), IR (cm⁻¹), ν (C=O): 1600.63, Anal. Calc for C₆₄H₅₀AgBF₄P₂O₂: C, 69.39; H, 4.55, Found: H; 69.12, H; 4.51. ¹H NMR (500 MHz, CDCl₃, ppm): δ = 5.35 (s, 1H, CHP), 7.42(s br, 8H, Hm C₆H₅+Hm PPh₃), δ = 7.65 (m br, 13H, Hp PPh₃+Ho C₆H₅+Hm C₆H₄), δ = 8.11 (d, 2H, Ho C₆H₄, ³J_{HH} = 7.65Hz), ³¹P {¹H}NMR (CDCl₃): δ = 24.8 (s, 1P, PPh₃).

Data for [Ag (Y₂)₂] TfO (8): M.p. 210 °C, Yield: 0.0744gr (63.6%), IR (cm⁻¹), ν (C=O): 1600.68, Anal. Calc C₆₅H₅₀AgF₃P₂O₅S, : C, 66.75; H, 4.31. Found: H; 65.15, H; 4.21. ¹H NMR (500 MHz, CDCl₃, ppm): δ = 5.4 (s, 1H, CHP), 7.26 (m br, 6H, Hm PPh₃), δ = 7.35(d, 1H, Hp C₆H₅, ³J_{HH} =

7.86 Hz), $\delta = 7.58$ (d, 2H Hm, C₆H₄, $^3J_{\text{HH}} = 7.6$ Hz), $\delta = 8.14$ (d, 2H, Ho C₆H₄, $^3J_{\text{HH}} = 7.89$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl₃): $\delta = 24.48$ (s, 1P, PPh₃).

CONCLUSION

The present study describes the synthesis and characterization of a series of dimeric mercury (II) and bisylide silver (I) complexes derived from mercuric halides or silver (I) with phosphorus ylides. On the basis of the physico-chemical and spectroscopic data, we propose that the ligands herein exhibit monodentate C-coordination to the metal centre, which is further confirmed by the X-ray crystal structure of the complexes.

Acknowledgements. The authors acknowledge the department of Chemistry Isfahan University of Technology and the Faculty of Arts and Sciences, Ondokuz Mayıs University, Turkey, for the use of the Stoe IPDSII diffractometer (purchased under grant F. 279 of the University Research Fund). The author thanks the Isfahan University of Technology (IUT) Research Council and Center of Excellence in Sensor and Green Chemistry for supporting this study.

Appendix A. Supplementary material

CCDC 690436 and 760103 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk/deposit> or deposit@ccdc.cam.ac.uk.

REFERENCES

1. Falvello, L. R.; Gines, J. C.; Carbo, J. J.; Lledos, A.; Navarro, R.; Soler, T.; Urriolabeitia, E. P. *Inorg. Chem.*, **2006**, *45*, 6803.
2. Belluco, U.; Michelin, R. A.; Mozzon, M.; Bertani, R.; Facchin, G.; Zanutto, L.; Pandolfo, L. *J. Organomet. Chem.*, **1998**, *557*, 37.
3. Kolodiaznyy, O. I. *Tetrahedron* **1996**, *52*, 1855.
4. Navarro, R.; Urriolabeitia, E. P. *J. Chem. Soc. Dalton Trans.*, α -Stabilized Phosphoylides as Versatile Multifunctional Ligands, **1999**, 4111.
5. Taillefer, M.; Cristau, H.J. *Top. Curr. Chem.*, **2003**, *229*, 41.
6. Shen, Y. *Acc. Chem. Res.* **1998**, *31*, 584.
7. Puke, C.; Erker, G.; Aust, N.C.; Wurthweine, E. U.; Frohlich, R. *J. Am. Chem. Soc.*, **1998**, *120*, 4863.
8. Kolodiaznyy, O. I. *Russ. Chem. Rev.*, **1997**, *66*, 225.
9. Cobridge, D. E. *Phosphorus an Outline of Chemistry, Biochemistry and Uses*, 5th ed.; Elsevier; Amsterdam, 1995.
10. Vicente, J.; Chicote, M. T.; Lagunas, M. C.; Jones, P.G. *J. Chem. Soc. Dalton Trans.*, **1991**, 2579.
11. Buckle, J.; Harrison, P. G. *J. Organomet. Chem.* **1973**, *49*, C17.
12. Oosawa, Y.; Urabe, H.; Saito, T.; Sasaki, Y. *J. Organomet. Chem.*, **1976**, *122*, 113.
13. Nishiyama, H.; Itoh, K.; Ishii, Y. *J. Organomet. Chem.*, **1975**, *87*, 129.
14. Vicente, J.; Chicote, M. T.; Fernandez-Baeza, J. *J. Organomet. Chem.* **1989**, *364*, 407.
15. Onishi, M.; Ohama, Y.; Hiraki, K.; Shintani, H. *Polyhedron* **1982**, *1*, 539.
16. Vicente, J.; Chicote, M. T.; Lagunas, M. C.; Jones, P. G. *J. Chem. Soc. Dalton Trans.*, **1991**, 2579.
17. Buckle, J.; Harrison, P. G.; King, T. J.; Richards, J. A. *J. Chem. Soc., Chem. Commun.* **1972**, 1104.
18. Albanese, J. A.; Staley, D. A.; Rheingold, A. L.; Burmeister, J. L. *Inorg. Chem.* **1990**, *29*, 2209.
19. Kawafune, I.; Matsubayashi, G. *Inorg. Chim. Acta* **1983**, *1*, 70.
20. Grey, R. A.; Anderson, L. R. *Inorg. Chem.* **1977**, *16*, 3187.
21. Holy, N. L.; Baenziger, N. C.; Flynn, R. M. *Angew. Chem.* **1978**, *90*, 732.
22. Starzewski, K. A.; Witte, O. J. *Angew. Chem.* **1988**, *100*, 861.
23. Keim, W.; Bauer, R. S.; Chung, C.; Glockner, H. U.S. Patent, 3,635,937, 1969. Keim, W.; Mason, R. F.; Glockner, P. U.S. Patent, 1,364,791, 1972.
24. Akkurt, M.; Karam, K.; Pinar Yalcina is; Buyukgungor, O. *Acta Crystallogr. E* **2007**, *64*, 612.
25. Karami, K. *J. Chem. Res.* **2007**, 725.
26. Karami, K.; Buyukgungor, O. *Inorganica Chimica Acta* **2009**, *362*, 2093.
27. Karami, K.; Buyukgungor, O. *Journal of Coordination Chemistry* **2009**, *62*(18), 2949.
28. Kalyanasundari, M.; Panchanatheswaran, K.; Robinson, W. T.; Wen, H. *J. Organomet. Chem.* **1995**, *491*, 103.
29. Kalyanasundar, B.; Panchanatheswaran, K.; Parthasarathi, V.; Robinson, W. T. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 33.
30. Spencer, E. C.; Mariyatra, M. B.; Howard, J. A. K.; Kenwright, A. M.; Panchanatheswaran, K. *J. Organomet. Chem.* **2007**, *692*, 1081.
31. Kalyanasundari, B.; Panchanatheswaran, K.; Robinson, W. T. *J. Organomet. Chem.* **1995**, *491*, 103.
32. Facchin, G.; Bertani, R.; Calligaris, M.; Nardin, G.; Mari, M. *J. Chem. Soc., Dalton Trans.* **1987**, 1381.
33. Holy, N. L.; Baenziger, N. C.; Flynn, R. M.; Swenson, D. C. *J. Am. Chem. Soc.* **1976**, *98*, 7823.
34. Vicente, J.; Chicote, M. T.; Fernandez-Baeza, J.; Martin, J.; Saura-Llamas, I. *J. Organomet. Chem.* **1987**, *331*, 409.
35. Bent, H. A. *Chem. Rev.* **1961**, *61*, 275.
36. Bell, N. A.; Dee, T. D.; Goldstein, M.; McKenna, P. J.; Novel, I. W. *Inorg. Chim. Acta*, **1983**, *71*, 135.

37. Albinati, A.; Meille, S. V.; Cariati, F.; Marcotrigiano, G.; Menabue, L.; Pellacani, G. C. *Inorg. Chim. Acta.* **1980**, *38*, 221.
38. Bell, N. A.; Coles, S. J.; Hursthouse, M. B.; Light, M. E.; Malik, K. A.; Mansor, R. *Polyhedron* **2000**, *19*, 1719.
39. Kalyanasundari, M.; Panchanatheswaran, K.; Parthasarathi, V.; Robinson, W. T. *Acta Crystallogr.* **1994**, *50*, 1738.
40. Uson, R.; Fornies, J.; Navarro, R.; Espinet, P.; Mendivil, C. *J. Organomet. Chem.* **1985**, *290*, 125.
41. Laavanya, P.; Venkatasubramanian, U.; Panchanatheswaran, K.; Bauer, J. A. K. *Chem. Commun.* **2001**, 1660.
42. Belluco, U.; Michelin, R. A.; Bertani Facchin, R. G.; Pace, G.; Zanotto, L.; Mozzon, M.; Furlan, M.; Zangrando, E. *Inorg. Chim. Acta* **1996**, *252*, 355.
43. Stoe, C. X-Area; Version 1.18: Program for the Acquisition and Analysis of Data; Stoe and Cie, Darmstadt, Germany, 2002.
44. Sheldrick, G. M. SHELX97 Program for Crystal Structure Solution and Refinement; University of Göttingen, Germany, 1997.
45. Stoe, C. X-RED32 (Version 1.04); Crystallographic Package, Stoe & Cie.
-