SYNTHESIS OF ORGANOPHOSPHORUS COMPLEXES AND STRUCTURAL CHARATERIZATION OF TWO DIMERIC TRIPHENYLPHOSPHINNE COMPLEXES OF MERCURY(II) IONS FROM DIMERIC COMPLEXES OF [4-METHYLBENZOYLMETHYLENETRI-*P*-TOLYLPHOSPHINE MERCURY(II) HALIDES

ALIREZA DADRASS*, HOJJATOLLAH RAHCHAMANI

Department of Chemistry, Faculty of Science, Urmia University, Urmia 57159, Iran

ABSTRACT

The organophousphorus complexes of $[(PPh_3)_2Hg_2Cl_4]$ (**4**), $[(PPh_3)_2Hg_2Br_4]$ (**5**) and $[(PPh_3)_2Hg_2I_4]$ (**6**) were resulted from nucleophilic substitution of triphenylphosphine ligand with tri-*p*-tolylphophine complexes (**1-3**). The crystal structures of two organophousphorus complexes of mercury(II) ions **4** and **6** have been determined by means of the X-ray diffraction. Both complexes were crystallized in the monoclinic space groups *P2(1)/c*, and have very similar bond lengths, angles pattern and same substituted triphenylphosphine ligand. Single crystal X-ray analysis of title structures reveal the presence of a centrosymmeteric dimeric structure containing the ligand and mercury halides.

Keywords: Organophousphorus complexes; Phosphorus complexes; Theoretical studies of dimeric compounds; crystal structure triphenyl complexes

INTRODUCTION

The validity of metalated phosphorus ligands in organometallic chemistry has been well documented.[1,2] Phosphorus ylides are reactive compounds, which take part in many reactions of value in the synthesis of organic products.[3-6] They are synthetic targets of interest, because of their importance for a variety of industrial, biological and chemical synthetic uses.[7-9] The electronic and steric effects of bulky phosphines in metal complexes such as those of Hg(II), Au(I), and Mo(0)[10-13], have attracted attention for several years. Our interest stems primarily from the effects that the phosphines exert on the stereochemistry of the metal atoms to which they are bonded. Mercury phosphine complexes embody a wide range of structural types, with those of 1:1 complexes being especially diverse.[6] We are reporting both crystal structures of **4** and **6** by the nucleophilic substitution of strong triphenylphosphine ligand with α-keto stabilized tri-*p*-tolyl phosphine ligand. By a comparison of the data collected and single crystal X-ray diffraction of **4** and **6**, they demonstrate nucleophilic substitution of PPh_3 with [4-methylbenzoylmethylene tri-*p*-tolylphosphine in mercury(II) halides complexes through P-coordination as *trans*-like structure.

EXPERIMENTAL

Instruments and reagents

Diethyl ether (Et_2O) was distilled over a mixture of sodium and benzophenone just before use. All other solvents were reagent grade and used without further purification. Mercury halides, triphenylphosphine mercury halides, tri- *p*-tolylphophine were purchased from Merck. Melting points were measured on a SMPI apparatus. Elemental analysis for C and H were performed using a PE 2400 series analyzer. Fourier transform IR spectra were recorded on a Shimadzu 435-U-04 spectrophotometer and samples were prepared as KBr pellets. X-ray analysis was performed on a Bruker Smart Apex diffractometer using SMART software diffractometer. The ^1H, ^{13}C and ^{31}P-NMR spectra were recorded at 300.13, 75.46 and 121.49 MHz, respectively on BRUKER DRX-300 AVANCE spectrometer in DMSO-d_6, as solvent.

General Procedure *for the synthesis of compounds* **1-3:** The binuclear complexes were prepared by the following general procedure and their structure suggested according to published article.[13] To tri-*p*-tolylphophine (152 mg, 0.5 mmol) in MeOH (20 mL) was added to $HgCl_2$ (135 mg, 0.5 mmol). The mixture was stirred for 24 h at room temperature. The solution was filtered off, and white product was washed with Et_2O. The corresponding bromo and iodo complexes were prepared with $HgBr_2$ (180 mg, 0.5 mmol) and HgI_2 (229 mg, 0.5 mmol), respectively by the same method.

General Procedure *for the synthesis of componds* **4-6:** A solution of triphenylphosphine (131 mg, 0.5 mmol) in methanol (15 mL) was added to a solution of complex **1** (708 mg, 0.5 mmol) in dry methanol (5 mL) and stirred for 24 h. The colorless solution was concentrated to 5 mL, and diethyl ether (15 mL) added to precipitate the complex **4**, which was recrystallized from chloroform/diethyl ether.

The corresponding bromo and iodo complexes **5**, **6** were prepared with $HgBr_2$ (180 mg, 0.5 mmol) and HgI_2 (229 mg, 0.5 mmol), respectively by the same method.

Selected data for the compound 4: White crystals; 312-314 ºC; Yield: 91%. FT-IR (KBr) (v_{max}, cm^{-1}): 3053 (w), 1570 (m). ^1H NMR (DMSO-d_6, 300.13 MHz) δ_H (ppm): 7.57-8.73 (15H, m, arom). ^{13}P NMR (CDCl$_3$, 121.49 MHz) δ_P (ppm): 32.05 (s). ^{13}C NMR (CDCl$_3$, 75.46 MHz) δ_C (ppm): 126.25, 129.83, 133.59, 133.72 (4C). Anal. Calcd. for $C_{36}H_{30}Hg_2Cl_4P_2$ (1068): C, 40.50; H, 2.83. Found: C, 40.79; H, 2.70 %.

Selected data for the compound 5: White crystals; 300-303 ºC; Yield: 85%. FT-IR (KBr) (v_{max}, cm^{-1}): 3054 (w), 1581 (m). ^1H NMR (DMSO-d_6, 300.13 MHz) δ_H (ppm): 7.96-8.75 (15H, m, arom). ^{13}P NMR (CDCl$_3$, 121.49 MHz) δ_P (ppm): 32.08 (s). ^{13}C NMR (CDCl$_3$, 75.46 MHz) δ_C (ppm): 127.17, 130.33, 133.89, 134.52 (3C). Anal. Calcd. for $C_{36}H_{30}Hg_2Br_4P_2$ (1244): C, 34.72 ; H, 2.43 . Found: C, 34.95; H, 2.32 %.

Selected data for the compound 6: White crystals; 247-249 ºC; Yield: 85%. FT-IR (KBr) (v_{max}, cm^{-1}): 3051 (w), 1583 (m). ^1H NMR (DMSO-d_6, 300.13 MHz) δ_H (ppm): 7.51-8.67 (15H, m, arom). ^{13}P NMR (CDCl$_3$, 121.49 MHz) δ_P (ppm): 32.04 (s). ^{13}C NMR (CDCl$_3$, 75.46 MHz) δ_C (ppm): 126.04 129.61, 133.38, 133.49 (4C). Anal. Calcd. for $C_{36}H_{30}Hg_2I_4P_2$ (1435): C 30.17, H 2.11 . Found: C 30.47, H 2.03%.

RESULTS AND DISCUSSION

Reactions of PPh_3 ligand with complexes **1-3** in a 2:1 stoichiometry afforded halide-bridged structures **4-6** containing P-coordinated PPh_3 ligand to metal halides (Scheme 1).
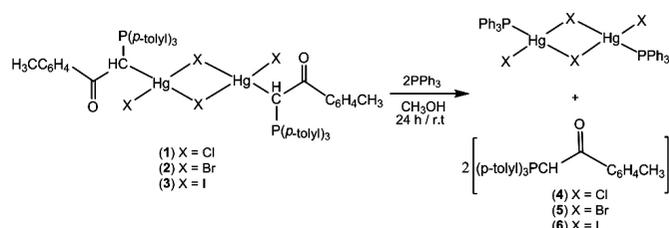
Scheme 1. Synthetic route for the compounds 4-6.

X-ray crystallography: Single crystals were carefully selected under a polarizing microscope in order to perform their structural analysis by X-ray diffraction. Single-crystals of two complexes **4** and **6** were used for data collections on a Bruker Smart Apex diffractometer using SMART software.[14] A block colorless crystals of **4** and **6** having approximate dimensions of 0.46×0.38×0.30 mm and 0.62×0.13×0.07 mm were mounted on a glass fiber

e-mail: dadrassi@yahoo.com

using epoxy-based glue. The data sets were collected at 293(2) K for both samples employing a scan of 0.3° in ω with an exposure time of 20 s/frame. The cell refinement and data reduction were carried out with SAINT.[15] The program SADABS was used for the absorption correction.[15] The structures were solved by direct methods using SHELXS-97[16] and difference Fourier syntheses. Full-matrix least-squares refinement against |F2| were carried out using the SHELXTL-PLUS[16], suit of programs. All non-hydrogen atoms were refined anisotropically.

Computational methods: The geometry of the free ligand PPh₃ and their metal complexes $[(PPh_3)_2Hg_2X_4]$ (X = Cl, Br and I) were performed using density functional theory (DFT) calculations. The three-parameter hybrid functional B3LYP[17] was used with the CEP-31G and CEP-121G[18] basis sets, implemented in the program package Gaussian 03.[19] Furthermore, the natural bonding orbital (NBO) calculations[20] were performed using the NBO 3.1 program as implemented in the Gaussian 03 package at the CEP-121G level of theory.

Crystal structures analysis: Table 1. provides the crystallographic results and refinement in formations for complexes **4** and **6**. The molecular structures of **4** and **6** are shown in (Figure 1). Table 2. lists key bond lengths and angles for both complexes. The dimeric structure adopted by complexes **4** and **6** as

P-coordinated dinuclear mercury(II) complexes of the triphenylphosphine ligand,[21] are similar to the structure of the C-coordinated dinuclear mercury(II) halide complexes of Ph₃PCHCOOEt[22a] and Ph₃PCHCOPh.[22b] The difference in coordination mode between P-coordinated and C-coordinated to Hg(II) can be rationalized in terms of the electronic properties and steric requirements of the ligands. The Hg(II) in **4** and **6** are sp³ hybridized and have a tetrahedral coordination environments with one short Hg–Cl bond at distance 2.3875(14), one Hg–p bond at distance 2.4040(12), two asymmetric bridging Hg–Cl bonds at distances of 2.6242(14), 2.6372(14) Å for **4** and one short Hg–I bond at distance 2.4745(13), one Hg-p bond at distance of 2.6854(13), two asymmetric bridging Hg–I bonds at distances of 2.9583(11), 2.9583(11) Å for **6**. The internuclear distances between mercury atoms were found to be 3.85844, and 4.00411A˚ in structures **4** and **6** respectively. These distances are much longer than the sum of Van der Waals radius (1.5 A˚) of the two mercury atoms[23] indicating the absence of significant bonding interactions between the mercury atoms in the molecular structures. The adaptation of dimeric structures in Hg(II) ylide complexes may be explained by both the preference of Hg(II) for four coordination and the stability of the 18 electron configuration around Hg(II).

Figure 1. Molecular structures of the complexes **4** and **6**.

Theoretical studies

The geometry of the corresponding complexes $[(PPh_3)_2Hg_2X_4]$ (X = Cl, Br and I) have been optimized and also the calculated structures have C₁ symmetry. The final optimized geometries for complexes are shown in (Figure 2) and the optimized structure parameters are listed in (Table 2).

As can be shown in (Table 2), two different standard basis sets CEP-121G and CEP-31G were used for complexes **4** and **6** in calculations to study the possible effect of the basis set. The result of two latter calculations for these complexes agrees well with the structures determined by X-ray crystallography.

The HOMO–LUMO gap (H–L gap) is an important parameter to characterize the chemical reactivity and kinetic stability.[24] It is well known that the energy gap retains close connection to some molecular properties.[25] A soft molecule has a small HOMO–LUMO gap energy, more polarizable, high chemical reactivity and low kinetic stability. The distribution of the HOMO and LUMO orbitals for the studied compounds are presented in (Figure 3) and the energy gap for all compounds are collected in (Table 3). A comparison between the HOMO-LUMO gap for PPh₃ and their complexes indicates that the energy gap for free ligand is higher than that in the entitled complexes. The calculated energy gap between the latter orbitals for the complex **6** containing iodine is smaller than that for other complexes and the trend is as Cl > Br > I. The most important terms in this kind of interaction are contributed from the partial charge transfer between the highest occupied molecular orbital (HOMO) of one component and the lowest unoccupied molecular orbital (LUMO) of another. As shown in (Table 3), the $\left| \text{HOMO}_{(Y)} - \text{LUMO}_{(M)} \right|$ energy deference

is considerably smaller than $\left| \text{HOMO}_{(Y)} - \text{LUMO}_{(M)} \right|$. Furthermore, based on the theory of frontier molecular orbital, in the ligand/metal systems a significant overlap and electron density transfer can be performed between the HOMO of ligands and the LUMO of metals so that the electron transfer was occurred from HOMO of ligands (Y) to the LUMO of metals. In continuous, we interpret the electronic structure such as partial charge of atoms and bond order via NBO analysis for the studied compounds. Table 3 gives the Wiberg bond indices (WBI)[26] and the results of the natural bond orbital analysis. As it can be seen, the P atom of phosphine group and metal center carry a positive charge and halogens carry a negative charge. Note that the total charge of the molecules is zero. Positive charge on the phosphorus atom increase for complexes compared to the PPh₃ ligand (0.768 esu) that nicely explained by electron transfer from the ligand to the metal and halogen atoms. This is in accord with the above conclusion deduced from $\left| \text{HOMO}_{(Y)} - \text{LUMO}_{(M)} \right|$ energy deference. Comparing different metal complexes, the negative charge on the halogens and the positive charge on the mercury atom increase with the order Cl > Br > I, which is consistent with the electronegativity decrease. The Wiberg Bond Index (WBI) value,[26] arises from the manipulation of the density matrix in the orthogonal natural atomic orbital basis derived through the natural population analysis. The WBI expresses the sum of squares of density matrix elements (p_{jk}) and equals two times the charge density in the atomic orbital (p_{jj}) minus the square of the charge density, and so is mathematically defined as bellow Equation:

$$WBI = \sum_k p_{jk}^2 = 2p_{jj} - p_{jj}^2$$

Table 1. Crystal and experimental data for complexes **4** and **6.**

Complexes	4	6
Empirical formula	$C_{36}H_{30}Hg_2I_4P_2$	$C_{36}H_{30}Cl_4Hg_2P_2$
Formula weight	1433.32	1067.52
Crystal system	Monoclinic	Monoclinic
space group	*P2(1)/c*	*P2(1)/c*
a	11.682(5)	12.183(5)
b	12.501(5)	11.380(5)
c	17.283(7)	17.685(7)
α (º)	90	90
β (º)	126.214(5)	130.589(5)
γ (º)	90	90
Volume (A³)	2036.6(14)	1861.8(13)
Z, Calculated density (Mg/m³)	2, 2.337	2, 1.904
Absorption coefficient (mm⁻¹)	10.662	8.633
Theta range for data collection (º)	2.16 to 28.33	2.20 to 28.26
Limiting indices	$-15 \leq h \leq 15, -16 \leq k \leq 16,$	$-16 \leq h \leq 16, -15 \leq k \leq 15,$
	$-23 \leq l \leq 22$	$23 \leq l \leq 23$
Reflections collected/unique	24061/5045 [R(int) = 0.0602]	22197/4586 [R(int) = 0.0625]
Completeness to θ = 28.26º (%)	99.3	99.4
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.2644 and 0.0374	0.1816 and 0.1105
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5045/0/199	4586/0/199
Goodness-of-fit on F^2	1.069	1.030
Final R indices [I>2sigma(I)]	R1 = 0.0433, wR2 = 0.1038	R1 = 0.0345, wR2 = 0.0867
R indices (all data)	R1 = 0.0529, wR2 = 0.1089	R1 = 0.0405, wR2 = 0.0900
Largest diff. peak and hole (e.A⁰⁻³)	0.813 and -3.466	0.958 and -2.097

Table 2. The selected DFT-optimized bond lengths (Å) and angles (°) for the studied complexes and compared with experimental data for compounds $[(PPh_3)_2Hg_2X_4]$ (X = Cl (**4**), Br (**5**) and I (**6**)).

X	4				5	6		
	CEP-31G	CEP-121G	X-ray			CEP-31G	CEP-121G	X-ray
Bond lengths								
Hg(1)–P(1)	2.622	2.634	2.4040(12)		2.657	2.69733	2.717	2.6854 (13)
Hg(1)–X(1)	2.489	2.488	2.3875(14)		2.610	2.77990	2.7786	2.4745 (13)
Hg(1)–X(2)	2.750	2.724	2.6372(14)		2.843	3.03614	3.037	2.9583 (11)
Hg(1)–X(2)i	2.723	2.744	2.6242(14)		2.844	2.97469	2.970	2.8721 (13)
Bond angles								
P(1)–Hg(1)–X(1)	122.52	121.57	129.81 (5)		118.86	116.51	115.40	119.93 (4)
P(1)–Hg(1)–X(2)	101.57	102.01	110.94 (5)		103.66	103.64	103.61	113.09 (4)
X(1)–Hg(1)–X(2)	115.66	116.51	102.87 (6)		116.56	103.64	115.72	112.624(16)
P(1)–Hg(1)–X(2)i	107.87	107.75	114.48 (4)		106.69	105.95	106.08	104.37 (4)
X(1)–Hg(1)–X(2)i	115.51	115.67	103.80 (6)		116.31	118.32	119.27	109.713(19)
X(2)–Hg(1)–X(2)i	87.53	87.541	85.67 (4)		90.569	93.94	93.720	93.260 (11)

(a)   (b)   (c)
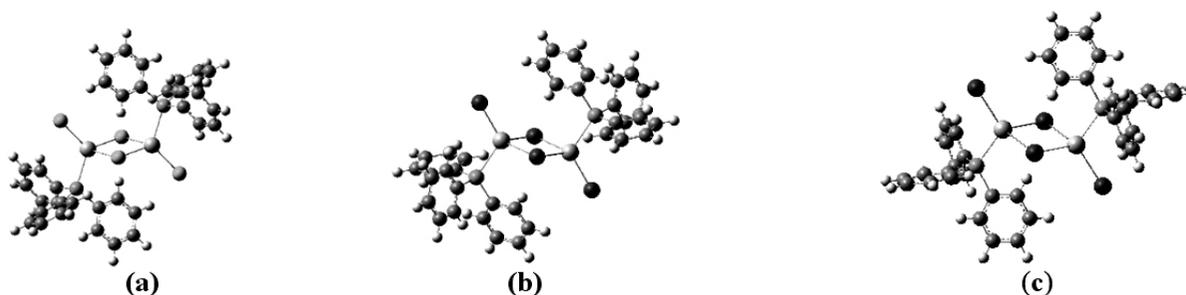
Figure 2. Optimized structure for the complex $(PPh_3)_2Hg_2X_4$ investigated here at the B3LYP/CEP-121G level of theory.

The WBI closely relates to the bond character, that is, larger WBI means stronger covalent character. For all metal complex, the most value of the WBI is related to Hg–X(1) bond (terminal halogen), which means that the Hg–X(1) bond have the stronger covalent character than the other bond around mercury(II) (Table 3).

Table 3. Energies of the relevant frontier orbitals and gap energies (H–L) (eV) of the investigated compounds at B3LYP/ CEP-121G level, Wiberg bond indices results of the NBO analysis, dipole moment (De) of the PPh_3, and $[(PPh_3)_2Hg_2X_4]$ (X = Cl (**4**), Br (**5**) and I (**6**)).

Species	PPh_3	4	5	6
HOMO (eV)	-0.223	-0.246	-0.240	-0.230
LUMO (eV)	-0.026	-0.082	-0.084	-0.085
H-L (eV)	5.34	4.27	4.22	3.94
		Wiberg bond		
Hg(1)–P(1)	-	0.450	0.433	0.412
Hg(1)–X(1)	-	0.628	0.689	0.805
Hg(1)–X(2)	-	0.305	0.367	0.433
Hg(1)–X(2)i	-	0.319	0.364	0.495
		Dipole moment (De)		
X		Y		Z
0.00		0.00		0.00
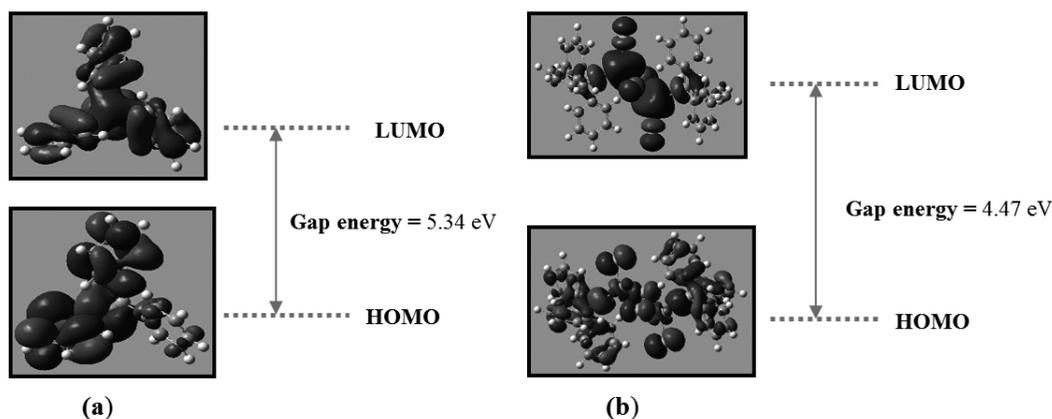
Figure 3. The frontier molecular orbital pictures of the studied sample compounds **a)** PPh$_3$ **b)** (PPh$_3$)$_2$Hg$_2$Cl$_4$

CONCLUSONS

The present study describes the synthesis and characterization of tri-phenylphosphorus complexes of mercury(II) halides from nucleophilic substitution of dimeric complexes of 4-methybenzoylmethyllene tri-*p*-tolylphosphine mercury(II) halides. On the basis of the physicochemical and spectroscopic data we propose that all complexes are P-coordinated to the mercury(II) ions. In addition theoretical studies on the gas phase structures of **4, 5** and **6** confirms the trans-like dimeric structures for these compounds. The structures of both complexes **4** and **6** were determined by single crystal X-ray analysis.

SUPPLEMENTARY MATERIAL

CCDC 940104 and 940105 contain the supplementary crystallographic data for **4** and **6**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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