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Reactivity of mercury(II) halides with the unsymmetrical phosphorus ylide $Ph_2PCH_2CH_2PPh_2$=C(H)C(O)Ph: Crystal structure of $\{HgI_2[PPh_2CH_2CH_2PPh_2$=C(H)C(O)Ph$]\}_n$

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Abstract

The unsymmetrical phosphorus ylide, $Ph_2PCH_2CH_2PPh_2$=C(H)C(O)Ph is shown to react with Hg(II) halides to form polymeric products with the composition $\{HgX_2[PPh_2CH_2CH_2PPh_2C(H)C(O)Ph]\}_n$, where X = Cl (**1**), Br (**2**), I (**3**). The complexes have been characterized by elemental analysis, IR, ^1H, ^{31}P NMR spectra as well as by ESI mass spectra. In product **1** the ylide exhibits a P, C-bridging mode of coordination, while in **2** and **3** it shows a monodentate P-coordination with the dangling ylide. The structure of complex **3** has been characterized crystallographically. The monomeric –Hg–I–Hg– bridging in **3** leads to a zig-zag polymeric chain in which mercury assumes a distorted tetrahedral geometry.

Keywords: Phosphorus ylides; Resonance stabilization; Coordination polymer; Mercury(II) complexes

1. Introduction

Resonance stabilized phosphorus ylides are versatile ligands for heavy metal ions [1–5]. The α-keto stabilized ylides derived from bisphosphines, viz., $Ph_2PCH_2PPh_2$=C(H)C(O)R, $Ph_2PCH_2CH_2PPh_2$=C(H)C(O)R (R=Me, Ph or OMe) [6] and PhC(O)C(H)=$PPh_2CH_2CH_2PPh_2$=C(H)C(O)Ph [7] form an important class of such ligands which can exist in ylidic and enolate forms. These ligands can therefore engage in different types of bonding as illustrated in Chart 1 for $Ph_2PCH_2CH_2PPh_2$=C(H)C(O)Ph.

The bonding mode (f) had been previously observed for Pd(II), Pt(II) and Rh(I) [6–13]. In addition, Rh(I) was shown to exhibit the P-bonding mode (a) [13]. We have been interested in investigating the different bonding modes adopted by ylides when ligated to Hg(II) and U(VI) [14]. Hg(II) forms C-coordinated complexes with Ph_3P=C(H)C(O)Ph [15,16] and Ph_3P=C(H)CO(OEt) [17]. On the other hand, regiospecific O-coordination of the acetyl oxygen has been observed for the reaction of Hg(II) halides with Ph_3P=C(COPh)(COMe). The remarkable change in reactivity arises from a subtle variation in the molecular-electronic structure of the ylide due to the presence of additional keto stabilization. Further, although $HgBr_2$ and HgI_2 form 1:1 dimeric halobridged complexes with the above ylide, $HgCl_2$ forms a 1:2 monomeric square planar complex [18]. Motivated by the above chemistry, we decided to study the interaction of Hg(II) halides with mixed ylide-phosphine ligands. In this paper, we report the reactivity of the ligand $Ph_2PCH_2CH_2PPh_2$=C(H)C(O)Ph, Benzoylmethylenediphenyl-2-diphenylphosphinoethylphosphorane (BDEP), towards mercury(II) halides.

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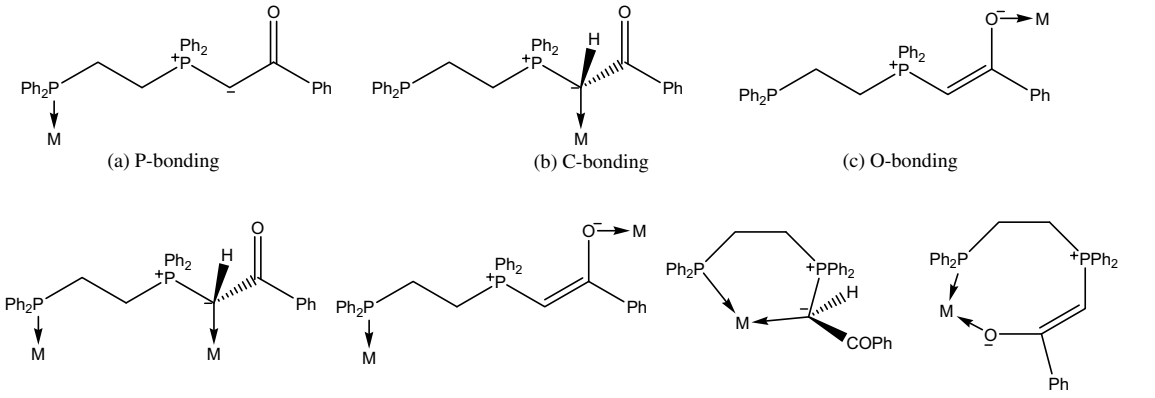

Chart 1. The possible bonding modes of $Ph_2PCH_2CH_2PPh_2$=C(H)C(O)Ph to metal M.

2. Experimental

All reactions were carried out under an atmosphere of dry nitrogen. Reactants and reagents were obtained from Aldrich Chemical Company and used without further purification. The solvents were dried and distilled using standard methods [19].

2.1. Instrumentation

The ^1H and ^{31}P–$\{^1H\}$ NMR spectra were recorded on a Bruker DPX400 or Varian Gemini 200 spectrometer, referenced relative to residual solvent and external 85% H_3PO_4, respectively. The IR spectra in the interval of 4000–400 cm^{-1} were recorded on a Perkin–Elmer 1720X FT-IR spectrophotometer using KBr pellets. ESI-mass spectra were measured on a Bruker FTMS 4.7T BioAPEX II instrument using the solution of the complexes in acetonitrile. Elemental analyses were performed at the Ecole d'ingénieurs de Fribourg, Switzerland.

2.2. Synthesis of compounds

2.2.1. $Ph_2PCH_2CH_2PPh_2$=C(H)C(O)Ph

The ligand was prepared by the treatment of triethylamine on the monophosphonium bromide derived from 1,2-bis(diphenylphosphino)ethane (dppe) as reported previously [6]. IR (cm^{-1}): 3054, 2912, 1585, 1521, 1482, 1434, 1396, 1308, 1175, 1108, 1061, 1025, 998, 898, 882, 794, 746, 739, 722, 701, 653, 507, 490. ^1H NMR (200 MHz, $CDCl_3$): 2.20–2.33 (m, 2H), 2.79–2.94 (m, 2H), 4.26 (d, 1H, $^2J_{P-H} = 23.0$), 7.33–8.01 (m, 25H). ^{31}P NMR (162 MHz, $CDCl_3$): −12.20 (d, $^3J_{P-P} = 47.5$), 17.54 (d, $^3J_{P-P} = 47.5$).

2.2.2. Synthesis of $\{HgX_2[PPh_2CH_2CH_2PPh_2C(H)C(O)Ph]\}_n$ {X = Cl (1), Br (2), I (3)}

The following general procedure was used for preparing the complexes. To a solution of HgX_2 (0.38 mmol) in methanol (10 ml), a solution of $PPh_2CH_2CH_2PPh_2CHCOPh$ (0.2 g, 0.38 mmol) also in methanol (10 ml) was added dropwise at 0 °C and stirred for 2 h. The resulting solid, admixed with grey material was treated with dichloromethane (25 ml) and filtered through celite. Addition of excess methanol to the concentrated filtrate caused the precipitation of the products as white solids. The complexes were purified by repeating the precipitation three times and the solid dried under vacuum.

1. Yield: 0.16 g (56%). M.p. 142–144 °C. *Anal.* Calc. for $C_{34}H_{30}Cl_2HgOP_2$: C, 51.82; H, 3.84. Found: C, 51.26; H, 3.78%. IR (cm^{-1}): 3055, 2910, 1637, 1594, 1577, 1483, 1436, 1403, 1322, 1289, 1189, 1105, 998, 841, 778, 733, 688, 509, 481. ^1H NMR (200 MHz, DMSO-d_6): 3.18–3.47 (br, 4H merged with residual H_2O), 5.15 (d, 1H, $^2J_{P-H} = 9.4$), 7.47–8.07 (m, 25H). ^{31}P NMR (81 MHz, DMSO-d_6): 23.78 (br, d), 35.88 (br, d). Mass spectrum: ESI [*m*/*z*, ion, %]: 753 $[M-Cl]^+$(100), 1269 $[M^*-Cl]$ (83), where $M^* = [HgCl_2(PPh_2CH_2CH_2PPh_2C(H)C(O)Ph)_2]$.
2. Yield: 0.18 g (54%). M.p. >120 °C (decomposes). *Anal.* Calc. for $C_{34}H_{30}Br_2HgOP_2$: C, 46.57; H, 3.45. Found: C, 46.62; H, 3.40%. IR (cm^{-1}): 3053, 2920, 1584, 1511, 1484, 1436, 1391, 1182, 1107, 998, 1025, 894, 734, 723, 704, 691, 509, 491. ^1H NMR (200 MHz, DMSO-d_6): 3.06–3.36 (br, 4H merged with residual H_2O), 4.68 (d, 1H, $^2J_{P-H} = 19.4$), 7.18–7.79 (m, 25H). ^{31}P NMR (81 MHz, DMSO-d_6): 20.27 (br, d), 30.12 (br). Mass spectrum: ESI [*m*/*z*, ion, %]: 797 $[M-Br]^+$ (23).
3. Yield: 0.25 g (68%). M.p. >152 °C (decomposes). *Anal.* Calc. for $C_{34}H_{30}HgI_2OP_2$: C, 42.06; H, 3.11. Found: C, 41.85; H, 3.08%. IR (cm^{-1}): 3053, 1629, 1585, 1504, 1482, 1435, 1398, 1181, 1110, 1026, 998, 891, 727, 706, 690, 506, 493. ^1H NMR (400 MHz, $CDCl_3$): 3.16 (br, 2 H), 3.37 (br, 2H), 4.34 (d, 1H, $^2J_{P-H} = 21.7$), 7.39–8.01 (m, 25H). ^{31}P NMR (162 MHz, $CDCl_3$): 6.46 (br), 19.33 (d, $^3J_{P-P} = 57.1$). Mass spectrum: ESI [*m*/*z*, ion, %]: 845 $[M-I]^+$ (16).

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

	ν (C=O)	δ PC*H* ($^2J_{P-H}$)	δ *P*Ph$_2$ ($^3J_{P-P}$)	δ *P*CHCOPh ($^3J_{P-P}$)
BDEP	1521	4.26 (23.0)	−12.20 (47.5)	17.54 (47.5)
1	1637	5.15 (9.4)	35.88	23.78
2	1511	4.68 (19.4)	30.12	20.27 (55.6)
3	1504	4.34 (21.7)	6.46	19.33 (57.1)

Table 2
Crystal data and refinement details for complex **3**

Empirical formula	$C_{34}H_{30}HgI_2$ OP_2,0.5($C_4H_{10}O$)
Formula weight	1007.97
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	22.9215(13)
b (Å)	8.3325(3)
c (Å)	19.8801(11)
β (°)	111.565(4)
V (Å^3)	3531.2(3)
Z	4
Absorption coefficient (mm^{-1})	6.226
Collected reflections	49879
Independent reflections	9565
R(int)	0.0917
Observed reflections [$I > 2\sigma(I)$]	7035
R_1 (observed data)	0.0500
wR_2 (all data)	0.1185

2.3. X-ray crystallography

Single crystals of **3** were obtained as colourless needles, when a hot 1-butanol solution containing the complex was allowed to stand at room temperature for a week. The intensity data were collected at 173 K (−100 °C) on a Stoe Mark II-Image Plate Diffraction System [20] equipped with a two-circle goniometer using Mo Kα graphite monochromated radiation. Image plate distance 100 mm, ω rotation scans 0–180° at ϕ 0°, and 0–20° at ϕ 90°, step $\Delta\omega = 1.0°$, 2θ range 2.29–59.53°, d_{min}–d_{max} = 17.779–0.716 Å. The structure was solved by direct methods using the program SHELXS-97 [21]. The refinement and all further calculations were carried out using SHELXL-97 [22]. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. An empirical absorption correction was applied using the MULscanABS routine in PLATON [23]; transmission factors: $T_{min}/T_{max} = 0.2744/0.6083$. A region of disordered electron density was squeezed out using the SQUEEZE routine in PLATON; 68 electrons for a volume of 346.9 Å^3, which was equated to 0.5 molecule of 1-butanol per asymmetric unit. Further crystallographic data are given in Table 2.

3. Results and discussion

The reactions of mercury(II) halides with unsymmetrical phosphorus ylide, $Ph_2PCH_2CH_2PPh_2$=C(H)C(O)Ph in 1:1 molar ratio yield two different polymeric products. While mercury(II) chloride forms a P, C-coordinated bridging complex [type (d), Chart 1], the mercury(II) bromide, and iodide, produce monodentate P-coordinated complexes with dangling ylide [type (a), Chart 1].

Complexes **1** and **2** are moderately soluble in acetonitrile and DMSO whereas the solubility of the complex **3** is higher in chloroform than in DMSO or acetonitrile. The yields of **1** and **2** are low due to some decomposition during the reaction. The IR spectrum of **1** shows the ν(CO) absorption at 1637 cm^{-1}, in the region typical for the C-bonded phosphonium ylides [24]. Similarly, in the ^{1}H NMR spectrum, both the downfield shift of the signal due to the PCH group and the decrease in the coupling constant are ascribed to C-coordination of the ylide (Table 1). The ^{31}P NMR spectrum of **1** exhibits two broad doublets at 23.78 and 35.88 ppm, which are assigned to the coordinated P=CHCOPh and PPh_2 groups, respectively. The spectral data thus indicate the bidentate coordination of the ligand through both P and C atoms. Although, complex **1** gives satisfactory elemental analysis for the 1:1 metal to ligand stoichiometry, the ESI-mass spectrum in acetonitrile solvent shows, in addition to the parent pseudomolecular ion, $[HgCl_2L–Cl]^+$ observed at m/z 753 as the base peak, another peak at m/z 1269 (83%) which is attributed to an $[HgCl_2(L)_2–Cl]^+$ ion. Such an observation is best explained by the polymeric structure with bridging mode of coordination of the ylide where both 1:1 and 1.2 (metal: ligand) fragmentation is possible.

In the IR spectra of **2** and **3**, the ν(CO) absorptions are shifted only slightly from that of the free ligand (Table 1). As noted previously [15], the coordination of the ylide through carbon or oxygen causes a significant increase or decrease, respectively, in the ν(CO) frequency. In the ^{1}H NMR spectra of **2** and **3**, the doublets due to the methine proton at 4.68 and 4.34 ppm, respectively, appear in the same region as observed for the free ligand (4.26 ppm). The ^{31}P NMR signals due to P=CHCOPh group are not much shifted from the corresponding value for the free ylide (Table 1). However, the signals due to PPh_2 group exhibit the expected downfield shifts for coordination. Thus, IR and NMR data indicate that interaction of ligand to $HgBr_2$ and HgI_2 is only through the phosphine part, as proved for the crystal structure of **3**. This is corroborated by the absence of any species containing two ligands in the ESI Mass spectra in acetonitrile for both **2** and **3**. The absence of ^{199}Hg satellites in the ^{31}P NMR spectra of all the complexes can be attributed to the fast exchange of ligand with metal, as noted previously for Hg(II)–phosphine complexes [25,26].

3.1. Crystal structure of complex 3

The molecular structure of **3** is shown in Fig. 1 and selected bond lengths and angles are given in Table 3. The X-ray analysis reveals the coordination of the ligand through the phosphorus atom only. The Hg(II) atom is

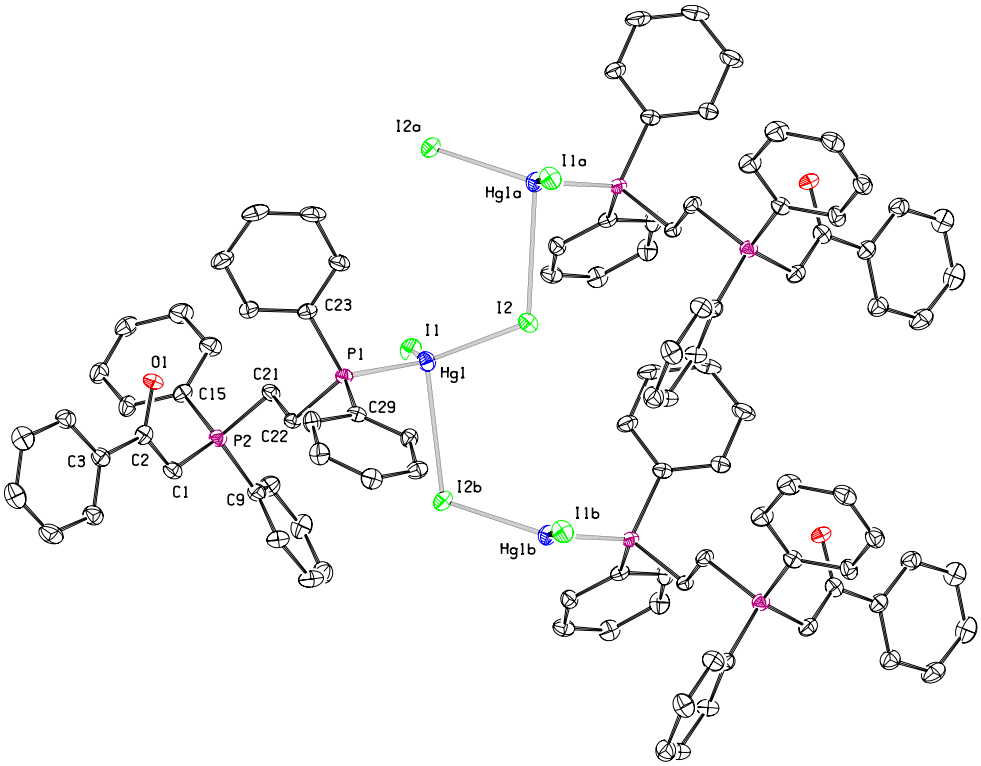

Fig. 1. Polymeric structure of **3** showing part of the chain running parallel to *b*-axis. The hydrogen atoms have been omitted for clarity. (*Symmetry codes*: $a = -x, -1/2 + y, 1/2-z$; $b = -x, 1/2 + y, 1/2-z$.)

located in a distorted tetrahedral environment with one 'P', one terminal 'I' and two bridging 'I' atoms, resulting in an one-dimensional polymeric chain. The Hg–P bond length of 2.472(2) Å is consistent with the values reported for monomeric mercury(II)–phosphine complexes [27]. However, this distance is shorter when compared to those in the polymeric complex, $[Hg(CN)_2dppe]_n$ [2.606(3) Å and 2.534(4) Å] containing the bridging phosphine ligand [28]. The Hg–I(terminal) bond distance [2.705(1) Å] is comparable to those of 2.727(2) and 2.693(2) Å found in $[Hg\{Ph_2P(S)CH_2PPh_2\}I_2]$ [29]. The asymmetric bridging nature of the other two iodo ligands is indicated by the two different Hg–I(bridging) distances of 2.728(1) and 3.321(1) Å. The latter distance being rather long, indicates a weak Hg–I(bridging) interaction. The bond angles around Hg atom (Table 3) indicate a severe distortion from ideal tetrahedral geometry. The deviation of atom Hg1 from the best least-squares plane defined by atoms I1, I2 and P1, is only 0.254 Å. This is comparable to the previous observations in the complexes $[HgX_2\{Ph_2PCH_2CH_2P(O)Ph_2\}]_n$ (X = Br, I) [30] and $[HgI_2\{Ph_2P(S)CH_2PPh_2\}]$ [29], where a weak coordination of the one of the ligands lead to a flattened tetrahedral geometry as shown by the small deviations (ranging from 0.244 to 0.406 Å) of the Hg atom from the plane defined by other three strongly bonded atoms. On the basis of the high solubility of complex **3** in most of the solvents and the long Hg–I(bridging) distance, it is possible that the polymer could dissociate to form a monomeric species in solution as indicated by the ESI mass spectral data. The ylidic moiety shows no interaction with mercury. The bond angles around C1 (~120°) and the P2–C1 distance [1.716(7) Å] indicate that the ylidic carbon remains unprotonated. Similarly, the short C1–C2 and long C=O distances show the resonance delocalization in the free ylide. As observed previously for α-stabilized phosphorus ylides [31], the phosphorus and oxygen atoms are *cis* oriented due to significant interaction between P^+ and O^- centres, as shown by the appropriate length and torsion angle (Table 3).

Table 3
Selected geometric parameters for **3**

Bond lengths (Å)			
Hg(1)–P(1)	2.472(2)	P(2)–C(15)	1.810(6)
Hg(1)–I(1)	2.706(1)	P(2)–C(9)	1.810(7)
Hg(1)–I(2)	2.728(1)	P(2)–C(21)	1.830(6)
Hg(1)–I(2^i)	3.321(1)	O(1)–C(2)	1.283(8)
P(2)–C(1)	1.716(7)	C(1)–C(2)	1.392(9)
P(1)–C(29)	1.805(6)	C(2)–C(3)	1.480(9)
P(1)–C(23)	1.819(6)	C(21)–C(22)	1.522(8)
P(1)–C(22)	1.827(6)	P2···O1	2.828(7)
Angles (°)			
P(1)–Hg(1)–I(1)	120.11(4)	C(2)–C(1)–P(2)	116.6(5)
P(1)–Hg(1)–I(2)	122.07(4)	C(2)–C(1)–H(1)	121.7
I(1)–Hg(1)–I(2)	115.04(2)	P(2)–C(1)–H(1)	121.7
P(1)–Hg(1)–I(2^i)	90.57(3)	P(2)–C(1)–C(2)–O(1)	−3.1(8)
I(1)–Hg(1)–I(2^i)	91.12(2)	P(2)–C(21)–C(22)–P(1)	−178.3(3)
I(2)–Hg(1)–I(2^i)	105.06(1)		

Symmetry transformation: (i) $-x, y + 1/2, -z + 1/2$.

4. Conclusions

In this study, we have shown that Hg(II) halides react with the unsymmetrical phosphorus ylide, Ph_2PCH_2-CH_2PPh_2=C(H)C(O)Ph, to form complexes in which the ylide exhibits different coordination modes. The difference can be accounted for by hardness associated with $HgCl_2$ compared to the softness of other two mercuric halides. Further, it is interesting to note that the monodentate P-coordination to mercury in the complexes **2** and **3**, with dangling ylide moiety, is in stark contrast to the product of the same ligand with $UO_2(NO)_2 \cdot 6H_2O$. The latter displays a monodentate O-coordination with the dangling phosphino group [32].

Acknowledgements

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Appendix A. Supplementary material

CCDC 630609 contains the supplementary crystallographic data for **3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2007.03.059.

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