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Mercury(II) complexes of unsymmetric phosphorus ylides: Synthesis, spectroscopic and antibacterial activity studies

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HIGHLIGHTS

- Synthesis and characterization of some monouclear Hg(II) complexes of the phosphorus ligands.
- IR, ^{1}H and ^{13}C NMR spectroscopy demonstrate P, C-coordination of the ligands to the metal.
- All of the compounds displayed antibacterial activity against most of the bacteria tested especially on Gram positive ones.

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ABSTRACT

The reaction of $Ph_2PCH_2PPh_2$ (dppm) with 2-bromo-3-nitroacetophenone and 2,2′,4′-trichloroacetophenone in chloroform produce the new phosphonium salts $[Ph_2PCH_2PPh_2CH_2C(O)C_6H_4NO_2]Br$ (**1**) and $[Ph_2PCH_2PPh_2CH_2C(O)C_6H_3Cl_2]Cl$ (**2**). Further, by reaction of the monophosphonium salts of dppm with the strong base triethylaminethe corresponding bidentate phosphorus ylides, $Ph_2PCH_2PPh_2{=}C(H)C(O)C_6H_4NO_2$ (**3**) and $Ph_2PCH_2PPh_2{=}C(H)C(O)C_6H_3Cl_2$ (**4**) were obtained. The reaction of these ligands with mercury(II) halides in dry methanol led to the formation of the mononuclear complexes $\{HgX_2[(Ph_2PCH_2PPh_2C(H)C(O)C_6H_4NO_2)]\}$ [X = Cl (**5**), Br (**6**), I (**7**)] and $\{HgX_2[(Ph_2PCH_2PPh_2C(H)C(O)C_6H_3Cl_2)]\}$ [X = Cl (**8**), Br (**9**), I (**10**)]. Characterization of the obtained compounds was performed by elemental analysis, IR, ^{1}H, ^{31}P and ^{13}C NMR. The structure of compound **1** being unequivocally determined by single crystal X-ray diffraction techniques. The mass spectrum of compound 6 (as an instance) also demonstrates the synthesize of these compounds. In all complexes the title ylides are coordinated through the ylidic carbon and the phosphine atom. These compounds form five membered ring under complexation. The antibacterial effects of DMSO solutions of the ligands and their metal complexes were evaluated by the disc diffusion method against six Gram positive and negative bacteria. All compounds represent antibacterial activity against these bacteria with high levels of inhibitory potency exhibited against the Gram positive species.

1. Introduction

Phosphorus ylides are important reagents in organic chemistry, especially in the synthesis of naturally occurring products with biological and pharmacological activities [1–5]. These ligands are reactive compounds, which take part in many reactions of value in the synthesis of organic products [6–9]. The coordination and organometallic chemistry of α-ketostabilized phosphorus ylides has been investigated and their ambidenticity explained in terms of a delicate balance between electronic and steric factors [10]. Transition metal complexes of these ligands have attracted much attention due to their versatile coordination chemistry and their application in catalysis [11–15]. The α-ketostabilized ylides derived from bisphosphines, $Ph_2PCH_2PPh_2{=}C(H)C(O)R$, $Ph_2PCH_2CH_2PPh_2{=}C(H)C(O)R$ (R = Me, Ph or OMe) [16] and $PhC(O)C(H){=}PPh_2CH_2CH_2PPh_2{=}C(H)C(O)Ph$ [15] 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. The P—C, coordinated mode had been previously observed for Pd(II), Pt(II), Rh(I), Hg(II) [5,7,11,14,15,17–22].

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 [23]. Much of the interest in the coordination properties of resonance stabilized phosphorus ylides stemming from their bond versatility due to

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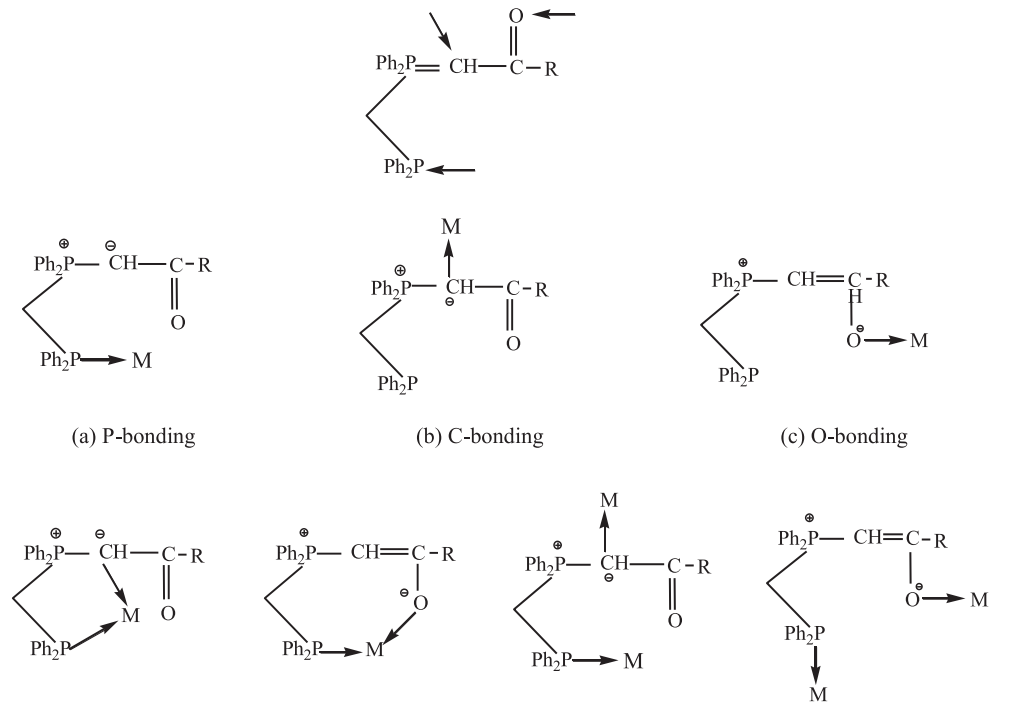


Chart 1. The possible bonding modes of $Ph_2PCH_2PPh_2C(H)C(O)R$ to metal M.

the presence of different functional groups in their molecular structure [24,25]. Nowadays, microorganisms resistant to antimicrobial agents are serious problems worldwide in the fight against infectious diseases and the development of materials with the ability to inhibit bacterial growth have been of great interest in recent years due to their potential use in everyday products like paints, kitchenware, school and hospital utensils [26]. Ligands and their metal complexes display a wide range of biological activity including antitubercular, antithroid, antihelmintic, rodenticidal, insecticidal, herbicidal, and plant-growth regulator properties [27–31]. Recently the antibacterial potency of many new synthesized compounds and metal complexes was investigated [32–41]. Although some metal complexes are among the most widely used antibacterial, but assessment of antibacterial activity of new metal complexes with ligands system is very necessary. In the present work, we have prepared a series of Hg(II) complexes with ligands system and investigated their antibacterial activity.

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 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 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

Data collection from suitable crystals of **1**was performed on an Oxford Diffraction single-crystal X-ray diffractometer using mirror monochromated Mo Kα radiation (0.71073 Å) at 130 K. Gaussian absorption corrections were carried out using a multifaceted crystal model, using CrysAlisPro [42]. The structure was solved by direct methods and refined by the full-matrix least-squares method on F^2 using the SHELXTL-97 crystallographic package [43]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted at calculated positions using a riding model, with isotropic displacement parameters.

2.3. Antibacterial activity

The potential antibacterial effects of the ligands and Hg(II) complexes were investigated by disc diffusion method against 3 Gram positive bacteria, namely *Bacillus cereus* (PTCC 1247), *Staphylococcus aureus* (Wild) and *Bacillus megaterium* (PTCC 1017), and 3 Gram negative bacteria, namely *Escherichia coli* (Wild), *Proteus vulgaris*(PTCC 1079), and *Serratia marcescens* (PTCC 1111) [44]. The complexes were dissolved in DMSO to a final concentration of 1 mg mL^{-1} and then sterilized by filtration using 0.45 μm Millipore. All tests were carried using 10 mL of suspension containing 1.5×10^8 bacteria/mL and spread on nutrient agar medium. Negative controls were prepared by using DMSO. Gentamicin, Penicillin, Neomycinand, Nitrofurantoin were used as positive reference standards. The diameters of inhibition zones generated by the complexes were measured.

2.3.1. Statistical analysis

All data, for both antibacterial tests, are the average of triplicate analyses. Analysis of variance was performed by Excel and SPSS procedures. Statistical analysis was performed using student's *t*-test, and p value < 0.05 was regarded as significant.

2.4. Sample preparation

2.4.1. Synthesis of monophosphonium salts

*2.4.1.1. Synthesis of $[Ph_2PCH_2PPh_2CH_2C(O)C_6H_3Cl_2]Cl$(**1**).* Bis(diphenylphosphino)methane (dppm) (0.50 g, 1.30 mmol) was dissolved in 8 ml of chloroform and then a solution of 2,2′,4′-trichloroacetophenone (0.29 g, 1.30 mmol) in the same solvent (5 ml) was added dropwise to the above solution. The resulting solution was stirred for 10 h at room temperature and then was concentrated under reduced pressure to about 2 ml. Diethyl ether (20 ml) was added and the white solid formed was filtered off, and dried under reduced pressure. Yield: 0.60 g (77%); m.p. 185–187 °C. Anal. Calc. for $C_{33}H_{27}Cl_3OP_2$ (%): C, 65.34; H, 4.48. Found: C, 65.55; H, 4.54. Selected IR absorption in KBr (cm^{-1}): 1683 ($\nu_{C=O}$). ^1H NMR ($CDCl_3$). δ_H: 4.29 (d, 2H, PCH_2P, $^2J_{PH}$ = 14.4); 6.07 (d, 2H, PCH_2CO, $^2J_{PH}$ = 12.6); 7.20–8.45 (m, 23H, Ph). ^{31}P NMR ($CDCl_3$) δ_P: −29.03 (d, PPh_2, $^2J_{PP}$ = 64.76); 20.34 (d, PCH_2CO, $^2J_{PP}$ = 63.56). ^{13}C NMR ($CDCl_3$) δ_C: 21.18 (br, PCH_2P); 33.96 (d, PCH_2, $^1J_{PC}$ = 58.01); 126.63–139.79 (Ph); 184.90 (s, CO).

*2.4.1.2. Synthesis of $[Ph_2PCH_2PPh_2CH_2C(O)C_6H_4NO_2]Br$ (**2**).* A solution of dppm (0.50 g, 1.30 mmol) and 2-bromo-3-nitroacetophenone (0.31 g, 1.30 mmol) in chloroform was stirred at room temperature for 10 h. The orange solid formed was filtered off, and dried under reduced pressure. Yield: 0.70 g (87%); m.p. 172–174 °C. Anal. Calc. for $C_{33}H_{28}BrNO_3P_2$ (%): C, 63.15; H, 4.50; N, 2.23. Found: C, 62.94; H, 4.48; N, 2.29. Selected IR absorption in KBr (cm^{-1}): 1682 ($\nu_{C=O}$). ^1H NMR ($CDCl_3$) δ_H: 4.31 (d, 2H, PCH_2P, $^2J_{PH}$ = 14.35); 5.83 (d, 2H, PCH_2CO, $^2J_{PH}$ = 12.8); 7.25–7.82 (m, 24H, Ph). ^{31}P NMR ($CDCl_3$) δ_P: −29.64 (d, PPh_2, $^2J_{PP}$ = 64.51); 20.68 (d, PCH_2CO, $^2J_{PP}$ = 64.70). ^{13}C NMR ($CDCl_3$) δ_C: 20.89 (br, PCH_2P); 36.05 (d, PCH_2, $^2J_{PC}$ = 60.53); 115.41–147.53 (Ph); 190.31 (s, CO).

2.4.2. Synthesis of bidentate phosphorus ylides

*2.4.2.1. Synthesis of $Ph_2PCH_2PPh_2{=}C(H)C(O)C_6H_3Cl_2$ (**3**).* The monophosphonium salt (**1**) (0.30 g, 0.50 mmol) was treated with triethyl amine (0.50 mL) in toluene (15 mL). The triethylamine hydrobromide thus obtained was filtered off. Concentration of the toluene layer to about 2 mL and subsequent addition of diethyl ether (20 mL) resulted in the precipitation of the desired ligand as white solid. Yield: 0.17 g (61%); m.p. 163–165 °C. Anal. Calc. for $C_{33}H_{26}Cl_2OP_2$(%): C, 69.46; H, 4.59. Found: C, 69.81; H, 4.57. Selected IR absorption in KBr (cm^{-1}): 1583 ($\nu_{C=O}$). ^1H NMR ($CDCl_3$) δ_H: 3.68 (d, 2H, CH_2, $^2J_{PH}$ = 14.25); 4.27 (br, 1H, CH); 7.24–7.82 (m, 23H, Ph). ^{31}P NMR ($CDCl_3$) δ_P: −29.74 (d, PPh_2, $^2J_{PP}$ = 65.99); 10.31 (d, PCH, $^2J_{PP}$ = 67.28). ^{13}C NMR ($CDCl_3$) δ_C: 23.20 (br, PCH_2P); 49.54 (d, CH, $^1J_{PC}$ = 114.15); 115.9–141.84 (Ph); 180.25 (s, CO).

*2.4.2.2. Synthesis of $Ph_2PCH_2PPh_2{=}C(H)C(O)C_6H_4NO_2$ (**4**).* This *phosphorus ylide* was obtained using the same procedure as adopted for the preparation of **3** using monophosphonium salt (**2**) (0.31 g, 0.50 mmol). Yield: 0.20 g (76%); m.p. 155–157 °C. Anal. Calc. for $C_{33}H_{27}NO_3P_2$ (%): C, 72.37; H, 4.97; N, 2.56. Found: C, 72.34; H, 4.99; N, 2.63. Selected IR absorption in KBr (cm^{-1}): 1584 ($\nu_{C=O}$). ^1H NMR ($CDCl_3$) δ_H: 3.66 (d, 2H, CH_2, $^2J_{PH}$ = 14.15); 4.23 (bd, 1H, CH, $^2J_{PH}$ = 7.70); 7.22–8.58 (m, 24H, Ph). ^{31}P NMR ($CDCl_3$) δ_P: −30.19 (d, PPh_2, $^2J_{PP}$ = 63.13); 11.79 (d, PCH, $^2J_{PP}$ = 64.94). ^{13}C NMR ($CDCl_3$) δ_C: 21.87 (br, CH_2); 51.12 (d, CH, $^1J_{PC}$ = 105.28); 121.12–149.62 (Ph); 184.11 (s, CO).

2.4.3. Preparation of the complexes

General procedure: To a solution of HgX_2 (0.40 mmol) in methanol (8 mL), a solution of **3** or **4** (0.40 mmol) in the same solvent (8 mL) was added dropwise at 0 °C and the reaction allowed to proceed under stirring for 2 h. The resulting solid, admixed with gray material was treated with dichloromethane (25 mL) and filtered through a short plug of Celite. Addition of excess methanol to the concentrated filtrate caused the precipitation of the products as solids.

*2.4.3.1. Data for $\{HgCl_2[(Ph_2PCH_2PPh_2C(H)C(O)C_6H_3Cl_2)]\}$(**5**).* Yield 0.18 g, 54%. M.p. 215–217 °C. Anal. Calc. for $C_{33}H_{26}Cl_4HgOP_2$: C, 47.03; H, 3.11. Found: C, 46.84; H, 3.13%. IR (KBr, cm^{-1}): 1583 (C=O), 1436, 1324, 1183, 1109, 774, 736, 688. ^1H NMR (DMSO-d_6): δ_H = 3.42 (br, 2H, CH_2); 4.74 (br, 1H, CH); 7.43–7.96 (m, 23H, Ph). ^{31}P NMR (DMSO-d_6): δ_p = 9.67 (br, PPh_2); 22.86 (d, PCH, $^2s_{P\text{-}P}$ = 48.59). ^{13}C NMR (DMSO-d_6): δ_c = 22.56 (br, CH_2); 32.43 (br, CH); 117.62–136.61 (Ph); 190.41 (s, CO).

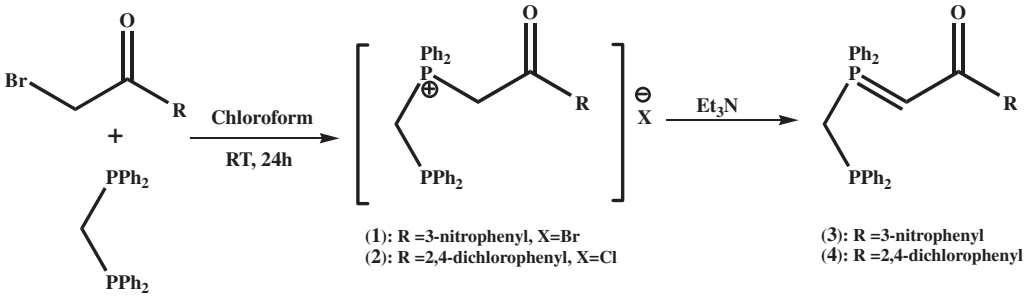
*2.4.3.2. Data for $\{HgBr_2[(Ph_2PCH_2PPh_2C(H)C(O)C_6H_3Cl_2)]\}$ (**6**).* Yield: 0.22 g, 59%. M.p. 220–222 °C. Anal. Calc. for $C_{33}H_{26}Br_2Cl_2HgOP_2$: C, 42.53; H, 2.81. Found: C, 42.25; H, 2.85%. IR (KBr, cm^{-1}): 1587 (C=O), 1438, 1178, 1121, 784, 742, 692. ^1H NMR (DMSO-d_6): δ_H = 3.37 (br, 2H, CH_2); 4.7 (br, 1H, CH); 7.48–8.01 (m, 23H, Ph). ^{31}P NMR (DMSO-d_6): δ_p = 1.348 (br, PPh_2); 20.43 (d, PCH, $^2J_{P\text{-}P}$ = 16.28). ^{13}C NMR (DMSO-d_6): δ_c = 22.71 (br, CH_2); 32.06 (br, CH); 118.30–136.75 (Ph); 190.59 (s, CO). MS m/z(%): 932(M), 757, 571, 547, 417, 384, 360, 261, 201, 187, 77, 51.

*2.4.3.3. Data for $\{HgI_2[(Ph_2PCH_2PPh_2C(H)C(O)C_6H_3Cl_2)]\}$(**7**).* Yield 0.22 g, 55%. M.p. 228–230 °C. Anal. Calc. for $C_{33}H_{26}Cl_2HgI_2OP_2$: C, 38.60; H, 2.55. Found: C, 38.78; H, 2.53%. IR (KBr, cm^{-1}): 1584 (C=O), 1437, 1321, 1186, 1103, 792, 740, 688. ^1H NMR (DMSO-d_6): δ_H = 3.31 (br, 2H, CH_2); 4.61 (br, 1H, CH); 7.44–8.13 (m, 23H, Ph). ^{31}P NMR (DMSO-d_6): δ_p = −7.12 (br, PPh_2); 21.07 (d, PCH, $^2J_{P\text{-}P}$ = 35.79). ^{13}C NMR (DMSO-d_6): δ_c = 22.75 (br, CH_2); 30.12 (br, CH); 118.16–135.62 (Ph); 191.42 (s, CO).

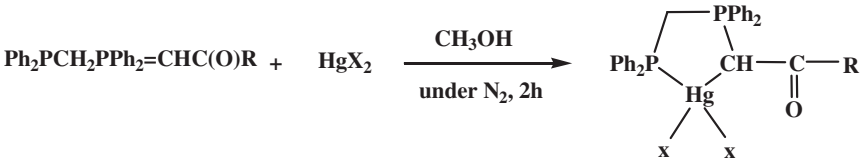
*2.4.3.4. Data for $\{HgCl_2[(Ph_2PCH_2PPh_2C(H)C(O)C_6H_4NO_2)]\}$(**8**).* Yield 0.22 g, 68%. M.p. 180–182 °C. Anal. Calc. for $C_{33}H_{27}Cl_2HgNO_3P_2$: C, 48.34; H, 3.32; N, 1.7. Found: C, 48.41; H, 3.36; N, 1.78%. IR (KBr, cm^{-1}): 1581 (C=O), 1437, 1345, 1153, 1109, 772, 741, 690. ^1H NMR (DMSO-d_6): δ_H = 4.69 (t, 2H, CH_2, $^2J_{PH}$ = 12.9); 5.32 (d, 1H, CH, $^2J_{PH}$ = 13.08); 7.46–8.68 (m, 24H, Ph). ^{31}P NMR (DMSO-d_6): δ_p = 3.07 (br, PPh_2); 23.39 (d, PCH, $^2J_{PP}$ = 40.10). ^{13}C NMR (DMSO-d_6): δ_c = 21.35 (br, CH_2); 33.14 (br, CH); 123.16–146.12 (Ph); 193.41 (s, CO).

*2.4.3.5. Data for $\{HgBr_2[(Ph_2PCH_2PPh_2C(H)C(O)C_6H_4NO_2)]\}$(**9**).* Yield 0.25 g, 70%. M.p. 189–191 °C. Anal. Calc. for $C_{33}H_{27}Br_2HgNO_3P_2$: C, 43.66; H, 3.00; N, 1.54. Found: C, 43.51; H, 3.03; N, 1.68%. IR (KBr, cm^{-1}): 1580 (C=O), 1486, 1342, 1151, 1110, 791, 739, 688. ^1H NMR (DMSO-d_6): δ_H = 4.68 (t, 2H, CH_2, $^2J_{PH}$ = 12.24); 5.40 (d, 1H, CH, $^1J_{PH}$ = 14.04); 7.44–8.64 (m, 24H, Ph). ^{31}P NMR (DMSO-d_6): δ_p = −5.82 (br, PPh_2); 24.95 (d, PCH, $^2J_{PP}$ = 38.62). ^{13}C NMR (DMSO-d_6): δ_c = 21.87 (br, CH_2); 34.38 (br, CH); 123.9–147.33 (Ph); 193.07 (s, CO).

*2.4.3.6. Data for $\{HgI_2[(Ph_2PCH_2PPh_2C(H)C(O)C_6H_4NO_2)]\}$(**10**).* Yield 0.24 g, 61%. M.p. 203–205 °C. Anal. Calc. for $C_{33}H_{27}I_2HgNO_3P_2$: C, 39.48; H, 2.71; N, 1.39. Found: C, 39.47; H, 2.74; N, 1.36%. IR (KBr, cm^{-1}): 1587 (C=O), 1436, 1346, 1173, 1103, 776, 739, 687. ^1H NMR (DMSO-d_6): δ_H = 4.72 (t, 2H, CH_2, $^2J_{PH}$ = 12.99); 5.40 (d, 1H, CH, $^1J_{PH}$ = 8.78); 7.44–8.64 (m, 24H, Ph). ^{31}P NMR (DMSO-d_6): δ_p = −9.37 (br, PPh_2); 24.44 (d, PCH, $^2J_{PP}$ = 43.62). ^{13}C NMR (DMSO-d_6): δ_c = 22.28 (br, CH_2); 33.47 (br, CH); 122.58–141.64 (Ph); 192.53 (s, CO).



Scheme 1. Synthetic route for the preparation of ligands **3–4**.



(**5**): R = 3-nitrophenyl, X = Cl
(**6**): R = 3-nitrophenyl, X = Br
(**7**): R = 3-nitrophenyl, X = I
(**8**): R = 2,4-dichlorophenyl, X = Cl
(**9**): R = 2,4-dichlorophenyl, X = Br
(**10**): R = 2,4-dichlorophenyl, X = I

Scheme 2. Synthetic route for the preparation of complexes **5–10**.

3. Results and discussion

3.1. Synthesis

The ligands were synthesized by treating bis(diphenylphosphino)methane with 2-bromo-3-nitroacetophenone and 2,2′,4′-trichloroacetophenone and removal of the proton from the phosphonium salts by triethylamine (Scheme 1) [11]. Reaction of HgX_2 with the ylides **3** and **4** in a 1:1 stoichiometry afforded the P, C-coordinated complexes with a chelating structure (Scheme 2). All complexes soluble in dichloromethane and all were obtained in good yields.

3.2. IR spectra

The IR data confirm the complete formation of the carbonylic ylides with the disappearance of the CO band at 1683 and 1682 cm^{-1} in phosphonium salts **1** and **2** and the presence of a new strong CO band at 1583 and 1587 cm^{-1} in resulting carbonyl stabilized ylides **3** and **4**, respectively [18,45]. The coordination of the ylide through carbon causes a significant increase in the ν(C═O) frequency [46]. Thus infrared absorption bands observed around 1590 cm^{-1} for all complexes indicate coordination of the ylides through ylidic carbon atom [47].

3.3. NMR spectra

The ^{31}P NMR spectrum of **1** exhibits two doublets at 20.34 and −29.03 ppm that indicate the PCH_2CO and PPh_2 groups, respectively. The ^{1}H NMR spectrum exhibits a doublet at 6.07 ppm, with a coupling constant $^{2}J_{PH}$ of 12.6 Hz, due to a CH_2 group bonded to a phosphonium moiety [48]. The ^{31}P NMR spectrum of **3** exhibits two doublets at 10.31 ppm and −29.74 ppm that indicate the phosphonium phosphorous and free phosphine atoms, respectively. 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 [45]. The ^{1}H NMR spectrum of **3** shows, in addition to the aromatic resonances, three signals centered at 3.68 (d) and 4.27 (br) of relative intensity 2:1 attributed to the PCH_2P and P═CH, respectively [20]. The ^{31}P NMR spectrum for complexes exhibit the presence of the PCH group as a doublet around 21 and 24 ppm for complexes **5–7** and **8–10**, respectively. These chemical shifts are lower field to that observed for the corresponding free ylides, indicating that coordination of the ylides have occurred. The ^{31}P NMR spectrum of **5** exhibits a doublet at 22.86 with a coupling constant $^{2}J_{PP}$ of 48.59 Hz and a broad signal at 9.67 ppm, attributable to PCH_2 and PPh_2 groups, respectively. The ^{1}H NMR spectrum exhibits a

Table 1
Crystal data and refinement details for **1**.

Compound	**1**
Empirical formula	$C_{34}H_{28}Cl_6OP_2$
Formula weight	723.97
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	C2/c
a (Å)	30.1043(11)
b (Å)	16.1198(4)
c (Å)	16.1617(6)
α (°)	90
β (°)	117.564(5)
γ (°)	90
Z	8
Absorption coefficient (mm^{-1})	0.180
θ Range for data collection (°)	2.14–29.18
Index ranges	$-18 \leqslant h \leqslant 17$ $-21 \leqslant k \leqslant 25$ $-15 \leqslant l \leqslant 15$
Reflections collected	19449
Independent reflections	7552 [R(int) = 0.1159]
Absorption correction	Numerical
Max. and min. transmission	0.945 and 0.940
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.136
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.1011$, $wR_2 = 0.2111$
R indices (all data)	$R_1 = 0.1864$, $wR_2 = 0.2471$
Largest diff. peak and hole (e $Å^{-3}$)	0.386 and −0.279

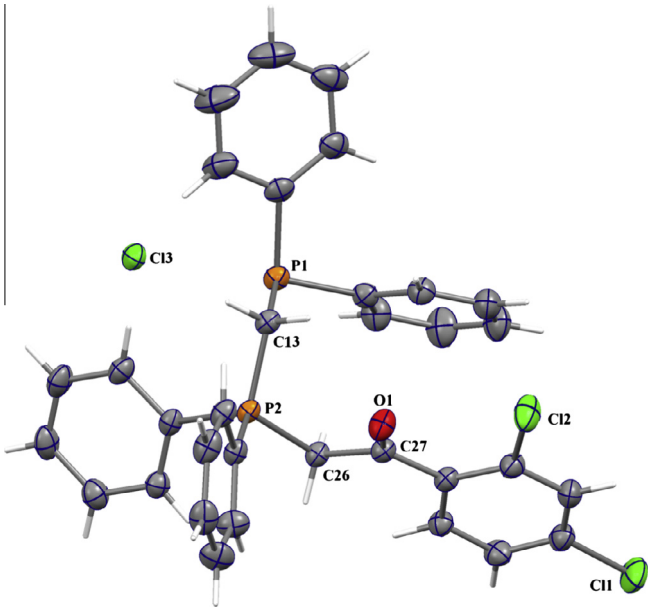


Fig. 1. Crystal structure of **1**.

Table 2
Selected bond lengths (Å) and bond angles (°) for **1**.

C(13)—P(2)	1.796(2)
C(26)—C(27)	1.522(3)
C(27)—O(1)	1.218(3)
C(26)—P(2)	1.806(2)
C(13)—P(2)—C(14)	109.9(1)
C(13)—P(2)—C(20)	112.0(1)
C(13)—P(2)—C(26)	109.95(9)
C(14)—P(2)-C(20)	106.9(1)
C(14)—P(2)—C(26)	108.83(9)
C(20)—P(2)—C(26)	109.17(9)

broad signal at 4.74 ppm, related to a CH group bonded to mercury atom that be shifted downfield with respect to the parent ylide **3** [18]. The ^{31}P NMR spectrum of **8** shows a doublet at 23.39 ppm with a coupling constant $^{2}J_{PP}$ of 40.10 Hz and a broad signal at 3.07 ppm, which are assigned to the PC(H) and PPh_2 groups, respectively. The ^{1}H NMR spectrum shows a doublet at 5.32 ppm attributable to the ylidic proton with a coupling constant $^{2}J_{PH}$ of 13.08 Hz [49]. The ^{13}C NMR shifts of the CO group in the complexes are about 190–193 ppm, relative to 180.25 and 184.11 ppm noted for the same carbon in the parent ylides, indicating much lower shielding of the carbon of the CO group in these complexes.

3.4. X-ray crystallography study

Colorless crystals of **1** were obtained from a chloroform solution by slow evaporation of the solvent. Table 1 provides the crystallographic results and refinement information for compound **1.** Thermal ellipsoid plot shows that in this molecule the geometry around the P atom is nearly tetrahedral, and the O atom is oriented *cis* to the P(2) atom. The C(26)—P(2) (1.806(2)) and C(27)—O(1) (1.218(3)) bond lengths are comparable with the (P^{+}—C (sp^3) (1.800) and (C—O) (1.210) normal values, respectively. C(26)—P(2) bond length is shorter and C(27)—O(1) bond length is longer than P—C and CO bond lengths in phosphorus ylides [50,51]. This bond distances suggest no electron delocalization in this molecule. For complex **1**, about the slightly high *R*-factors, it is to be noted that some atoms have a high thermal parameter due to data collection in room temperature. We tried refining these atoms in two positions with reduced occupancy but while this model converged satisfactorily, there was no decrease in *R* value and therefore we consider that our original refinement is the best that can be achieved and should be reported. On the other hand, this compound slowly decomposed even under perfluoro-polyether oil and the crystal used for data collection had some damage. Therefore, the raw data for this compound is slightly poor (R_1 = 0.1011). The molecular structure of complex **1** is shown in Fig. 1 and relevant bond lengths and angles are given in Table 2.

3.5. Antibacterial activity

Results from the antibacterial assessment of the ligands and metal complexes are presented in Tables 3 and 4, respectively. Positive and negative controls are shown in Table 5. All of the compounds displayed antibacterial activity against most of the bacteria tested especially on Gram positive ones. However, *Staphylococcus saprophyticus* (+) was the most resistant bacterium. Also free ligands and Hg ions, separately displayed antibacterial activity against these bacteria. According to our results from comparison of the effect of ligands, Hg ions and also Hg complexes on growth inhibition of bacteria, the complexes exhibit higher antibacterial activity than the free ligands. However, Hg ions exhibit a higher antibacterial activity than its complexes (Tables 3 and 4). Generally, antibacterial activities of the compounds are attributed mainly to their major components. However, today it is well known that the synergistic or antagonistic effect of one compound present in a minor percentage of a mixture has to be considered [52,53]. It is known that certain metal ions or their complex penetrate into bacteria and inactivate their enzymes, or some metal ions can generate hydrogen peroxide, thus killing bacteria. We can consider that different coordination of the ligands to metal complex may facilitate the ability of a metal complex to cross the lipid layer of the bacterial cell membrane and in this way may be affected the mechanisms of growth and development of

Table 3
Antibacterial activity of ligands.

Ligands	Inhibition zone (mm)						
	Concentration (mg ml^{-1})	*S. marcescens* (−)	*C. amalonaticus* (−)	*E. aerogenes* (−)	*B. megaterium* (+)	*S. aureus* (+)	*S. saprophyticus* (+)
	1	11.5 ± 0.26^{a}	na	na	9 ± 0.33^{a}	12.5 ± 0.28^{a}	na
3	0.1	10.5 ± 0.34^{b}	na	na	9 ± 0.17^{a}	10 ± 0.28^{b}	na
	0.01	9 ± 0.21^{c}	na	na	8 ± 0.00^{b}	na	na
	1	9 ± 0.28^{a}	na	11 ± 0.28^{a}	8 ± 0.46^{a}	9 ± 0.25^{a}	na
4	0.1	8.5 ± 0.28^{a}	na	10.5 ± 0.41^{ab}	8 ± 0.54^{a}	8 ± 0.34^{b}	na
	0.01	8.5 ± 0.21^{a}	na	9.5 ± 0.28^{b}	na	8 ± 0.00^{b}	na

Experiment was performed in triplicate and expressed as mean ± SD. Values with different superscripts within each column (for any bacteria in different concentrations) are significantly different ($P < 0.05$).
na: No active.

Table 4
Antibacterial activity of metal complexes.

Complex	Inhibition zone (mm)						
	Concentration (mg ml^{-1})	*S. marcescens* (−)	*C. amalonaticus* (−)	*E. aerogenes* (−)	*B. megaterium* (+)	*S. aureus* (+)	*S. saprophyticus* (+)
	1	9.5 ± 0.28^{a}	11 ± 11^{a}	9 ± 0.28^{a}	13 ± 0.33^{a}	15.5 ± 0.28^{a}	10 ± 0.28
5	0.1	9 ± 0.18^{a}	8 ± 33^{b}	8 ± 16^{b}	9 ± 0.14^{b}	11 ± 0.28^{b}	na
	0.01	9 ± 0.46^{a}	na	na	8 ± 0.21^{c}	9 ± 0.25^{c}	na
	1	10 ± 0.28^{a}	12 ± 0.14^{a}	11 ± 0.18^{a}	15 ± 0.22^{a}	17 ± 0.28^{a}	10 ± 0.25
6	0.1	9.5 ± 0.56^{a}	9.5 ± 0.18^{b}	8 ± 0.00^{b}	9 ± 0.21^{b}	11 ± 0.28^{b}	na
	0.01	8 ± 0.10^{b}	8 ± 0.00^{c}	8 ± 0.34^{b}	7.5 ± 0.28^{c}	8 ± 0.11^{c}	na
	1	10 ± 0.28^{a}	12 ± 0.28	12 ± 0.36^{a}	15.5 ± 0.28^{a}	17 ± 0.12^{a}	9.5 ± 0.28
7	0.1	9 ± 0.33^{b}	na	9 ± 0.00^{b}	9 ± 0.22^{b}	10 ± 0.21^{b}	na
	0.01	7.5 ± 0.17^{c}	na	na	8 ± 14^{c}	8.5 ± 0.24^{c}	na
	1	9 ± 12^{a}	11.5 ± 0.28	12 ± 0.45^{a}	14 ± 0.22^{a}	20 ± 0.24^{a}	10 ± 0.14
8	0.1	8 ± 0.28^{b}	na	8 ± 0.54^{b}	9 ± 0.28^{b}	13 ± 0.16^{b}	na
	0.01	8 ± 34^{b}	na	8 ± 13^{b}	na	na	na
	1	9 ± 0.18^{a}	9 ± 0.28^{a}	10.5 ± 0.28^{a}	12 ± 0.28^{a}	16 ± 0.23^{a}	na
9	0.1	8 ± 0.21^{b}	8 ± 16^{b}	8 ± 0.44^{b}	8 ± 0.43^{b}	8 ± 0.12^{b}	na
	0.01	8 ± 0.43^{b}	na	8 ± 0.17^{b}	na	na	na
	1	9 ± 0.28^{a}	9.5 ± 0.28	10 ± 0.11^{a}	12 ± 0.28^{a}	15 ± 0.11^{a}	na
10	0.1	8 ± 0.45^{b}	na	9 ± 0.13^{b}	9 ± 0.23^{b}	11 ± 0.28^{b}	na
	0.01	8 ± 0.34^{b}	na	8.5 ± 0.28^{b}	na	na	na

Experiment was performed in triplicate and expressed as mean ± SD. Values with different superscripts within each column (for any bacteria in different concentrations) are significantly different ($P < 0.05$).
na: No active.

Table 5
Antibacterial activity of antibiotics as positive controls and DMSO solve as negative control.

Microorganism	Inhibition zone				
	Positive controls				Negative controls
	Penicillin	Gentamicin	Neomycin	Nitrofurantoin	DMSO
B. megaterium (+)	na	20 ± 0.14	20 ± 0.28	15 ± 0.28	na
S. aureus (+)	10.5 ± 0.21	17 ± 0.18	14 ± 0.33	20 ± 0.33	na
S. saprophyticus (+)	16 ± 0.24	15 ± 0.16	13.5 ± 0.14	12 ± 0.25	na
S. marcescens (−)	na	16.5 ± 0.22	18 ± 0.55	9.5 ± 0.22	na
E. aerogenes (−)	na	16 ± 0.10	14 ± 0.34	12.5 ± 0.18	na
C. amalonaticus (−)	na	12 ± 0.33	11.5 ± 0.18	15 ± 0.54	na

Experiment was performed in triplicate and expressed as mean ± SD.
na: No active.

bacteria [54,55]. The antibacterial activity can also be influenced by the slow release of the ligands inside the bacterial cell. The antibacterial activity of the samples in comparison to some reference antibiotics indicates that the inhibitory potency of the tested ligands and chiefly metal complexes was found to be remarkable. Although most of the bacteria tested are resistant to Penicillin, the inhibitory effects of all complexes on resistant species were higher than the mentioned antibiotic. The above results indicate that the studied complexes may be used in the treatment of diseases caused by the bacteria tested. Further studies are needed to evaluate the *in vivo* potential of these new compounds in animal models.

4. Conclusions

The present study describes the synthesis and characterization of a series of chelate mercury(II) complexes derived from mercuric halides and new mixed phosphine–phosphonium ylides. On the basis of the physicochemical and spectroscopic data we propose that ligands herein exhibit bidentate P, C-coordination to the metal centre. Metal based drug represents a novel group of antimicrobial agents with potential application for the control of bacterial and fungal infections. Results from present study clearly demonstrated that the Hg(II) complexes exhibit acceptable antibacterial activity, which might be helpful in preventing the progress of various infections and can be used as alternative systems for medicines. However, possible side deleterious effects of these compounds on human health should be more investigated. Future research should envision studies on modification of these complexes to increase their antibacterial activity.

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Appendix A. Supplementary material

CCDC 881012 contains the supplementary crystallographic data for the compound **1**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Center, 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 http://dx.doi.org/10.1016/j.molstruc.2013.12.066.

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