Research Article

ZWITTERIONIC Hg(II) COMPLEXES OF BIDENTATE PHOSPHINE–PHOSPHONIUM SALTS: SYNTHESIS AND SPECTRAL CHARACTERIZATION

SYYED JAVAD SABOUNCHEI¹*, MOHAMMAD PANAHIMER², MAHBUBEH POURSHAHBAZ¹ and NEDA BERIMAVANDI³

¹Faculty of Chemistry, Bu-Ali Sina University, Hamedan, 65174, Iran
²Young Researchers and Elite Club, Gachsaran Branch, Islamic Azad University, Gachsaran, 65174, Iran
³Department of Chemistry, Payame Noor University (PNU), Hamedan, 65174, Iran
*Corresponding Author: jsabounchei@yahoo.co.uk

Abstract

The reaction of phosphonium salts of the type [Ph₂PCH₂PPh₂CH₂C(O)C₆H₄R]Br (R = Cl, Br, NO₂, OCH₃) with Hg(II) halides in 1:1 (HgCl₂ and HgBr₂) and 1:2 (HgI₂) mole ratio yielded the zwitterionic P-coordinated complexes [HgCl₂Br(L)], [HgBr₃(L)] and [HgBr₂I(L)] (L= Ligand). Characterization of these products was carried out by elemental analysis, IR, ¹H, ³¹P, and ¹³C NMR.

Graphical abstract: Pictogram. The reaction of phosphonium salts of the type [Ph₂PCH₂PPh₂CH₂C(O)C₆H₄R]Br (R = Cl, Br, NO₂, OCH₃) with Hg(II) halides in 1:1 (HgCl₂ and HgBr₂) and 1:2 (HgI₂) mole ratio yielded the zwitterionic P-coordinated complexes [HgCl₂Br(L)], [HgBr₃(L)] and [HgBr₂I(L)] (L= Ligand). Characterization of these products was carried out by elemental analysis, IR, ¹H, ³¹P, and ¹³C NMR.

Keywords: zwitterionic complexe, phosphonium salt, mercury (II) halide, spectroscopy.

1. Introduction

Phosphonium salts are useful intermediates in organic synthesis (Kosolapoff and Maier, 1972) and an important class of ligands that find widespread use in transition metal chemistry (Ebrahim et al., 2009). Different types of homo and heteropolynuclear ylide complexes of Hg(II), Pd(II) and Au(I) were prepared using the corresponding phosphonium salts, by deprotonation (Navarro and Urriolabeitia, 1999).
The alpha-keto stabilized phosphorus ylides can therefore engage in different kinds of bonding with metal ions (Oosawa et al., 1976; Takahashi et al., 1976; Takahashi et al., 1977; Uson et al., 1987; Lin et al., 1990; Falvello et al., 2000; Spannengberg et al., 2000; Falvello et al., 2003; Saravanabharathi et al., 2003; Ebrahima, 2007; Sbvata et al., 2008; Ebrahima et al., 2009). Mono keto ylides with a methylenic spacer, \( \text{PhH}_2\text{PCH}_2\text{PPH}_2\text{C}(\text{H})(\text{C})(\text{O})\text{PhR} \) \( R = \text{Cl} \) (1), \( \text{Br} \) (2), \( \text{NO}_2 \) (3), \( \text{OCH}_3 \) (4)] affords P,C-coordinated complexes with mercury(II) halides (Ebrahima et al., 2009; Sabounchei et al., 2010; Sabounchei et al., 2010). It is therefore of interest to investigate the reactivity of the hybrid phosphate—phosphinonium salt, \( \text{[PPh}_2\text{CH}_2\text{PPh}_2\text{CH}_2\text{COPh}]\text{Br} \) with mercury(II) halides which can in principle form (a) mercury-ylide complexes by deprotonation, (b) phosphonium metalates where the metal remains uncoordinated to the ligand or (c) zwitterionic complexes containing Hg—P bond. In this work, we report the formation of zwitterionic P-coordinated complexes of mercury(II) halides with phosphate—phosphinonium salts.

2. Materials and Methods

2.1. Chemicals and Instrumentation

All reactions were carried out under an atmosphere of dry nitrogen. The starting materials were purchased from commercial sources and used without further purification. Melting points were measured on a SMPI apparatus. Elemental analyses for C, H and N atoms were performed using a Perkin–Elmer 2400 series analyzer. IR spectra were recorded on a Shimadzu 435-U-04 FT spectrophotometer from KBr pellets. \(^1\)H, \(^{13}\)C and \(^{31}\)P NMR spectra were recorded on 300 MHz Bruker and 90 MHz Jeol spectrometer in DMSO-d_6 as solvent at 25 °C. Chemical shifts (ppm) are reported according to internal TMS and external 85% phosphoric acid.

2.2. Synthesis and Characterization

The phosphonium salts \( \text{[PhH}_2\text{PCH}_2\text{PPh}_2\text{CH}_2\text{C}(\text{O})\text{CH}_3]\text{Br} \) (\( R = \text{Cl} \) (1), \( \text{Br} \) (2), \( \text{NO}_2 \) (3), \( \text{OCH}_3 \) (4)) were prepared based on the published methods (Alyea et al., 1978; Sabounchei et al., 2010; Sabounchei et al., 2010).

2.2.1. Synthesis of \([1\text{HgCl}_2\text{Br}]\) (5) (general procedure for Hg(II) halide complexes)

General procedure: To a solution of HgX₂, \( X = \text{Cl} \) and \( \text{Br} \) (0.30 mmol) or Hgl₂ (0.15 mmol) in methanol (10 mL), a solution of phosphonium salt (1-4) (0.30 mmol) in the same solvent (5 mL) was added dropwise at 25 °C and the reaction allowed to proceed under stirring for 5 h. The resulting solid was isolated, washed twice with 10 mL methanol and 10 mL diethyl ether and dried under reduced pressure. Yield: 0.273 g (78%); m.p. 144–146 °C. Anal. Calcd. for \( \text{C}_{33}\text{H}_{32}\text{BrC}_{3}\text{HOP}_{2}\% \): C, 44.56; H, 3.17. Found: C, 45.37; H, 3.11. Selected IR absorption in KBr (cm⁻¹): 1683 (\( \nu_{\text{C} = \text{O}} \)). \(^1\)H NMR (DMSO-d_6) \( \delta_i \): 4.25 (d, 2H, PCH₂P, \( \frac{J_{\text{PP}}}{2} = 15.59 \)); 5.63 (d, 2H, PCH₂CO, \( \frac{J_{\text{PP}}}{2} = 13.79 \)); 7.27–8.31 (m, 24H, Ph). \(^{31}\)P NMR (DMSO-d_6) \( \delta_i \): 28.66 (d, PPh₂, \( \frac{J_{\text{PP}}}{2} = 67.59 \)); 23.44 (d, PCH, \( \frac{J_{\text{PP}}}{2} = 67.54 \)). \(^{13}\)C NMR (DMSO-d_6) \( \delta_i \): 124.30–151.16 (Ph); 191.72 (s, CO). (CH₂ and CH were not been see).
2.2.6. Data for [(2)HgBr₂] (10)

Yield: 0.314 g (81%); m.p. 102–103 °C. Anal. Calcd. for C₃₃H₂₈Br₂HgOP₃ (%): C, 37.05; H, 2.64. Found: C, 38.13; H, 2.75. Selected IR absorption in KBr (cm⁻¹): 1676 (νC=O). ¹H NMR (DMSO-d₆) δH: 4.34 (d, 2H, PCH₂P₂); 2JHP = 14.06; 5.60 (b, 2H, PCH₂CO, 2JHP = 12.27); 7.29–7.95 (m, 24H, Ph). ³¹P NMR (DMSO-d₆) δp: -24.09 (d, PPh₂, 2Jpp = 63.20); 23.30 (d, PCH, 2Jpp = 62.87). ¹³C NMR (DMSO-d₆) δC: 19.63 (br, CH₂); 33.51 (db, CH); 119.08–134.89 (Ph); 191.74 (s, CO).

2.2.7. Data for [(3)HgCl₂Br] (11)

Yield: 0.294 g (84%); m.p. 177–175 °C. Anal. Calcd. for C₃₃H₂₈BrCl₂HgNO₃P₂ (%): C, 44.04; H, 3.14. Found: C, 45.35; H, 3.27. Selected IR absorption in KBr (cm⁻¹): 1686 (νC=O). ¹H NMR (DMSO-d₆) δH: 4.48 (d, 2H, PCH₂P₂); 2JHP = 16.75; 5.79 (d, 2H, PCH₂CO, 2JHP = 11.91); 7.32–8.33 (m, 24H, Ph). ³¹P NMR (DMSO-d₆) δp: -19.90 (d, PPh₂, 2Jpp = 57.18); 22.92 (d, PCH, 2Jpp = 58.56). ¹³C NMR (DMSO-d₆) δC: 19.27 (br, CH₂); 34.71 (br, CH); 118.71–151.15 (Ph); 191.64 (s, CO).

2.2.8. Data for [(3)HgBr₃] (12)

Yield: 0.312 g (77%); m.p. 163–164 °C. Anal. Calcd. for C₃₃H₂₈Br₃HgNO₃P₂ (%): C, 40.08; H, 2.85. Found: C, 41.14; H, 2.93. Selected IR absorption in KBr (cm⁻¹): 1685 (νC=O). ¹H NMR (DMSO-d₆) δH: 4.37 (d, 2H, PCH₂P₂); 2JHP = 15.68; 5.73 (d, 2H, PCH₂CO, 2JHP = 11.91); 7.30–8.30 (m, 24H, Ph). ³¹P NMR (DMSO-d₆) δp: -24.68 (d, PPh₂, 2Jpp = 62.33); 23.32 (d, PCH, 2Jpp = 61.97). ¹³C NMR (DMSO-d₆) δC: 32.81 (db, CH); 113.87–134.40 (Ph); 190.07 (s, CO). (CH₂ was not been seen)

2.2.9. Data for [(3)HgBr₂] (13)

Yield: 0.342 g (91%); m.p. 152–154 °C. Anal. Calcd. for C₃₃H₂₈Br₂HgNO₃P₂ (%): C, 38.26; H, 2.72. Found: C, 39.27; H, 2.83. Selected IR absorption in KBr (cm⁻¹): 1674 (νC=O). ¹H NMR (DMSO-d₆) δH: 4.21 (d, 2H, PCH₂P₂); 2JHP = 15.33; 5.75 (d, 2H, PCH₂CO, 2JHP = 11.82); 7.24–8.23 (m, 24H, Ph). ³¹P NMR (DMSO-d₆) δp: -27.67 (d, PPh₂, 2Jpp = 68.53); 23.60 (d, PCH, 2Jpp = 68.46). ¹³C NMR (DMSO-d₆) δC: 19.35 (br, CH₂); 33.41 (br, CH); 112.22–136.05 (Ph); 191.64 (s, CO).

2.2.10. Data for [(4)HgCl₂Br] (14)

Yield: 0.241 g (69%); m.p. 214–216 °C. Anal. Calcd. for C₃₄H₃₅BrCl₂HgO₂P₂ (%): C, 46.14; H, 3.53. Found: C, 47.06; H, 3.62. Selected IR absorption in KBr (cm⁻¹): 1665 (νC=O). ¹H NMR (DMSO-d₆) δH: 3.85 (s, 3H, CH₃); 4.46 (d, 2H, PCH₂P₂); 2JHP = 16.13); 5.66 (d, 2H, PCH₂CO, 2JHP = 10.93); 7.08–7.94 (m, 24H, Ph). ³¹P NMR (DMSO-d₆) δp: -19.09 (d, PPh₂, 2Jpp = 47.39); 23.44 (d, PCH, 2Jpp = 55.45). ¹³C NMR (DMSO-d₆) δC: 20.10 (db, CH₂); 34.19 (db, CH); 56.30 (s, CH₃); 114.47–165.14 (Ph); 190.46 (s, CO).

2.2.11. Data for [(4)HgBr₃] (15)

Yield: 0.367 g (92%); m.p. 203–201 °C. Anal. Calcd. for C₃₄H₃₅Br₃HgO₂P₂ (%): C, 41.93; H, 3.21. Found: C, 42.84; H, 3.34. Selected IR absorption in KBr (cm⁻¹): 1666 (νC=O). ¹H NMR (DMSO-d₆) δH: 3.87 (s, 3H, CH₃); 4.33 (d, 2H, PCH₂P₂); 2JHP = 15.59); 5.82 (br, 2H, PCH₂CO); 7.00–8.00 (m, 24H, Ph). ³¹P NMR (DMSO-d₆) δp: -24.43 (d, PPh₂, 2Jpp = 63.45); 23.70 (d, PCH, 2Jpp = 61.79). ¹³C NMR (DMSO-d₆) δC: 20.31 (br, CH₂); 33.38 (db, CH); 56.35 (s, CH₂); 114.43–164.91 (Ph); 190.55 (s, CO).

2.2.12. Data for [(4)HgBr₂] (16)

Yield: 0.322 g (85%); m.p. 196–198 °C. Anal. Calcd. for C₃₄H₃₅Br₂HgO₂P₂ (%): C, 40.00; H, 3.06. Found: C, 41.07; H, 3.12. Selected IR absorption in KBr (cm⁻¹): 1662 (νC=O). ¹H NMR (DMSO-d₆) δH: 3.87 (s, 3H, CH₃); 4.46 (d, 2H, PCH₂P₂); 2JHP = 15.50); 5.51 (d, 2H, PCH₂CO, 2JHP = 12.54); 7.01–8.14 (m, 24H, Ph). ³¹P NMR (DMSO-d₆) δp: -27.48 (d, PPh₂, 2Jpp = 65.59); 23.75 (d, PCH, 2Jpp = 65.88). ¹³C NMR (DMSO-d₆) δC: 19.54 (br, CH₂); 33.08 (br, CH); 56.37 (s, CH₂); 114.47–164.89 (Ph); 190.64 (s, CO).

3. Results and Discussion

3.1. Synthesis

Reaction of the phosphine–phosphonium salts [PPh₂PCH₂PPh₂CH₂C(Ο)OHP]Br (R = Cl (1), Br (2), NO₂ (3), OCH₃ (4)), in 1:1 (HgCl₂ and HgBr₂) and 1:2 (HgI₂) mole ratio with mercury(II) halides in methanol as a solvent yield two different types of zwitterionic mercury(II) complexes as shown in Scheme 1. The mercury(II) chloride and bromide produce simple complexation products while the formation of iodide complexes involve a halogen exchange (Ebrahim et al., 2009).
3.2. Spectroscopy

The $^{31}$P NMR spectra of all complexes exhibit two mutually coupled doublets corresponding to PCH$_2$CO and PPh$_2$ groups. The former peak remains sharp and unaltered, while the latter peak is relatively broad. In contrast to the $^{31}$P NMR spectrum of Hg(II)-phosphine complexes (Sabounchei et al., 2010), the coordination of phosphorous atom to mercury in these complexes did not cause significant downfield shifts. All complexes show downfield shifts compared to that of phosphine of the related phosphonium salts. These data indicate that the presence of a formal negative charge on the metal may effectively reduce the deshielding experienced by the phosphorus due to complexion (Ebrahim et al., 2009).

In the $^1$H NMR spectra, the doublet in the region of 4.25-4.72 ppm attributed to PCH$_3$P, and the doublet in the region of 5.63-5.91 ppm attributed to PCH$_2$COPh that remains unaffected due to complexation. Rest of the chemical shifts are more or less the same in the ligands and their complexes. These observations support the assigned structure to the complexes. In the $^{13}$C NMR spectra, signals observed in the complexes due to the various carbons have either remained unaffected or shifted slightly with reference to those of the parent ligands. The IR spectra of complexes 5–16 show a strong absorption around 1662-1686 cm$^{-1}$, due to the carbonyl stretch which is close to the same frequency in free phosphonium salts (1659–1684 cm$^{-1}$) and indicate the non-involvement of the PCH$_2$C(O)R group in the reactions (Ebrahim et al., 2009). The selected IR and NMR data for all compounds and free ligands are given in Table 1.
Table 1. Selected $^1$H, $^{31}$P and $^{13}$C NMR [$\delta$ (ppm), $J$ (Hz)] and IR ($cm^{-1}$) data for free phosphorus ligands 1-4 and compounds 5-16. $^a$bd, broad doublet; $^b$t, triplet; $^c$br, broad

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu$ CO</th>
<th>$\delta$PCH ($^2J_{PH}$)</th>
<th>$\delta$ PPH$<em>2$ ($^2J</em>{PP}$)</th>
<th>$\delta$ PCH ($^2J_{PP}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1674</td>
<td>5.89 (12.37)</td>
<td>-29.53 (73.68)</td>
<td>20.94 (64.40)</td>
</tr>
<tr>
<td>5</td>
<td>1683</td>
<td>5.63 (13.79)</td>
<td>-28.66 (96.29)</td>
<td>23.44 (67.59)</td>
</tr>
<tr>
<td>6</td>
<td>1674</td>
<td>5.75 (5.73)</td>
<td>-19.65 (db)</td>
<td>23.18 (57.54)</td>
</tr>
<tr>
<td>7</td>
<td>1675</td>
<td>5.65 (t, 13.17, 13.88) $^b$</td>
<td>-26.26 (65.74)</td>
<td>23.51 (64.94)</td>
</tr>
<tr>
<td>2</td>
<td>1673</td>
<td>5.93 (12.90)</td>
<td>-29.38 (64.07)</td>
<td>20.92 (64.04)</td>
</tr>
<tr>
<td>8</td>
<td>1673</td>
<td>5.56 (13.35)</td>
<td>-28.03 (68.06)</td>
<td>23.62 (67.51)</td>
</tr>
<tr>
<td>9</td>
<td>1674</td>
<td>5.72 (db, 9.49)</td>
<td>-19.13 (50.25)</td>
<td>22.98 (54.71)</td>
</tr>
<tr>
<td>10</td>
<td>16.76</td>
<td>5.60 (12.27)</td>
<td>-24.09 (63.20)</td>
<td>23.30 (62.87)</td>
</tr>
<tr>
<td>3</td>
<td>1684</td>
<td>5.91 (12.81)</td>
<td>-29.52 (64.57)</td>
<td>20.70 (64.55)</td>
</tr>
<tr>
<td>11</td>
<td>1686</td>
<td>5.79 (11.91)</td>
<td>-19.90 (57.18)</td>
<td>22.92 (58.56)</td>
</tr>
<tr>
<td>12</td>
<td>1685</td>
<td>5.73 (11.91)</td>
<td>-24.68 (62.33)</td>
<td>23.32 (61.97)</td>
</tr>
<tr>
<td>13</td>
<td>1674</td>
<td>5.75 (11.82)</td>
<td>-27.67 (68.53)</td>
<td>23.60 (68.46)</td>
</tr>
<tr>
<td>4</td>
<td>1659</td>
<td>5.75 (12.72)</td>
<td>-29.29 (64.28)</td>
<td>21.19 (62.33)</td>
</tr>
<tr>
<td>14</td>
<td>1665</td>
<td>5.66 (10.93)</td>
<td>-19.09 (47.39)</td>
<td>23.44 (55.45)</td>
</tr>
<tr>
<td>15</td>
<td>1666</td>
<td>5.82 (br) $^c$</td>
<td>-24.43 (63.45)</td>
<td>23.70 (61.79)</td>
</tr>
<tr>
<td>16</td>
<td>16.62</td>
<td>5.51 (12.54)</td>
<td>-27.48 (65.59)</td>
<td>23.75 (65.88)</td>
</tr>
</tbody>
</table>

Figure 1
Conclusions

The reactions of the phosphine–phosphonium salt with mercury(II) halides offers an easy method for the preparation of zwitterionic mixed halogen mercurates. On the basis of the physicochemical and spectroscopic data we propose that ligands herein exhibit a P-coordination behavior to the metal center affording a zwitterionic complexes. In the $^{31}$P NMR spectra the absence of significant downfield shifts due to complexation could be ascribed to the presence of formal negative charge on the metal which effectively reduces the deshielding experienced by the phosphine phosphorus atom.

Acknowledgments

We are grateful to Bu-Ali-Sina University for financial support.

References


Ebrahim, M.M., 2007. Reactivity of mercury(II) halides with the unsymmetrical phosphorus ylide Ph$_2$PCH$_2$CH$_2$PPh$_2$=C(H)C(O)Ph: Crystal structure of {HgI$_2$[PPh$_2$CH$_2$CH$_2$PPh$_2$=(H)C(O)Ph]}$_n$. Polyhedron. 26: 3491-3495.


Lin, I.J.B., Shy, H.C., Liu, C.W., Liu, L.K., Yeh, S.K., 1990. Mixed sulphur and phosphorus ylide complexes of palladium formed by phase-transfer catalysis. X- Ray crystal structure of...
[Pd((CH2)2S(O)Me)[Ph2PCH2PPh2CHC(O)Ph]]I


