



# Metal-phosphine chalcogenide interactions. Crystal structures of palladium(II)/mercury(II) complexes with 1,2-bis(diphenylthiophosphinyl)ethane containing seven-membered metallacyclic rings

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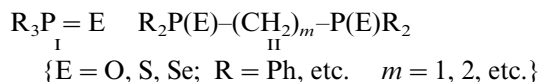
## Abstract

An organophosphorus ligand, namely, 1,2-bis(diphenylthiophosphinyl)ethane {Ph<sub>2</sub>P(S)–CH<sub>2</sub>–CH<sub>2</sub>–P(S)Ph<sub>2</sub>; dppeS<sub>2</sub>} reacted with palladium(II) chloride in acetonitrile forming [PdCl<sub>2</sub>(dppeS<sub>2</sub>)](CH<sub>3</sub>CN) (**1**). Similarly, it reacted with mercury(II) bromide in acetone to yield HgBr<sub>2</sub>(dppeS<sub>2</sub>) (**2**). In these compounds, Pd/Hg are bonded to two S atoms of chelating dppeS<sub>2</sub> ligand and to the respective halogen atoms. The geometry about Pd is distorted square planar with *trans*-bond angles S(1)–Pd–Cl(1) and S(2)–Pd–Cl(2) being 174.10(5)° and 172.85(5)°, respectively. The angles about Hg vary in the range 96.20(6)–124.56(4)°, suggesting highly distorted geometry about Hg. The bite angle S(1)–Hg–S(2) of the ligand is 118.85° in **2** versus 97.76° in **1**, and it demonstrates large flexibility of alkane moiety and stability of the seven-membered metallacyclic rings formed by dppeS<sub>2</sub>.  
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## 1. Introduction

Organophosphorus ligands such as tertiary phosphine oxides, sulphides, or selenides (I, II below) bearing O, S, or Se donor atoms have been the focus of several investigations related to their coordination chemistry, extractive metallurgy, catalytic properties, and structural chemistry [1,2].



In view of the importance of the study of metal–sulphur interactions, the structures and spectroscopic

properties of a number of metal complexes of heterocyclic thiones, thiosemicarbazones, and tertiary phosphine chalcogenides have been reported in the literature [1–11]. As a part of our interest in investigating the structural chemistry of metal–phosphine chalcogenide interactions, particularly with bis(tertiary phosphine chalcogenides), we have reported the structures of the complexes, viz. [HgCl<sub>2</sub>{Ph<sub>2</sub>P(S)–CH<sub>2</sub>–P(S)Ph<sub>2</sub>}] [11c] (compound **3**), [HgI<sub>2</sub>{Ph<sub>2</sub>P(S)–CH<sub>2</sub>–PPh<sub>2</sub>}] [11b] (compound **4**), [HgCl<sub>2</sub>{Ph<sub>2</sub>P(S)–CH<sub>2</sub>–CH<sub>2</sub>–P(S)Ph<sub>2</sub>}] [11b] (compound **5**), [HgPh<sub>2</sub>{Ph<sub>2</sub>P(S)–CH<sub>2</sub>–CH<sub>2</sub>–P(S)Ph<sub>2</sub>}] [11a] (compound **6**), [Cu<sub>2</sub>(μ-I)<sub>2</sub>(Ph<sub>3</sub>PSe)<sub>2</sub>(MeCN)<sub>2</sub>] [12] (compound **7**), [Cu<sub>2</sub>(μ-I)<sub>2</sub>(Ph<sub>3</sub>PS)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>] [13] (compound **8**), and [Cu<sub>2</sub>(μ-Cl)<sub>2</sub>(dppeS<sub>2</sub>)<sub>2</sub>] [13] (compound **9**; dppeS<sub>2</sub> is selenium analogue of dppeS<sub>2</sub>), [ZnI<sub>2</sub>(dppmSe<sub>2</sub>)] [14] (compound **10**, dppmSe<sub>2</sub> = Ph<sub>2</sub>P(Se)–CH<sub>2</sub>–P(Se)Ph<sub>2</sub>). As regards palladium, there are only two complexes, PdCl<sub>2</sub>L<sub>2</sub> {L = PhEt<sub>2</sub>PS, *i*-Bu<sub>3</sub>PS}, whose crystal structures are known and none

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among bis(tertiary phosphine sulphides or selenides) [1,15,16].

In this paper, the structures of complexes of palladium(II)/mercury(II) with 1,2-bis(diphenylthiophosphinyl)ethane are described which represent rare examples of seven-membered chelate ring formation among metal-phosphine sulphides or selenides [11b]. In a copper(I) complex,  $[\text{Cu}_2\text{Cl}_2\{\text{dppeS}_2\}_2]$ , dppeS<sub>2</sub> bridges two Cu atoms [13]. Furthermore, for palladium(II) it is the first structurally characterised complex with a bis(tertiary phosphine chalcogenide) [1,2,18].

## 2. Experimental

### 2.1. General materials

Palladium(II) chloride and mercury(II) bromide were of standard grade and used as such. The compound 1,2-bis(diphenylphosphino)ethane,  $\{\text{Ph}_2\text{P}-\text{CH}_2-\text{CH}_2-\text{PPh}_2, \text{dppe}\}$ , was prepared by lithiation of  $\text{PPh}_3$  in dry tetrahydrofuran followed by the reaction with dichloroethane [17]. Treatment of dppe with elemental sulphur (1:2 mole ratio) in benzene formed  $\text{Ph}_2\text{P}(\text{S})-\text{CH}_2-\text{CH}_2-\text{P}(\text{S})\text{Ph}_2$  {dppeS<sub>2</sub>} [18].

### 2.2. Preparation of $[\text{PdCl}_2(\text{dppeS}_2)](\text{CH}_3\text{CN})$ (**1**)

To a solution of palladium(II) chloride (0.100 g, 0.56 mmol) in hot acetonitrile (25 cm<sup>3</sup>) was added to the solution of the ligand, dppeS<sub>2</sub> (0.260 g, 0.56 mmol), and the contents refluxed for 3 h. The solution was filtered and allowed to crystallise, whereupon light red-coloured crystals were formed. The crystals were separated and dried at room temperature (r.t.). Yield 70%; melting point (m.p.) 245–47 °C. *Anal.* Found: C, 49.4; H, 4.3; N, 1.97. Calc. for  $\text{C}_{28}\text{H}_{27}\text{Cl}_2\text{NPdS}_2$ : C, 49.4; H, 4.0; N, 2.05%. Main IR bands: 1098 cm<sup>-1</sup> {νP–C}; 575 cm<sup>-1</sup> {νP–S}; ligand band(dppeS<sub>2</sub>): 1097 cm<sup>-1</sup> {νP–C}; 600 cm<sup>-1</sup> {νP–S}.

### 2.3. Preparation of $[\text{HgBr}_2(\text{dppeS}_2)]$ (**2**)

To a solution of mercury(II) bromide (0.050 g, 0.14 mmol) in acetone (20 cm<sup>3</sup>) was added the solution of the ligand, dppeS<sub>2</sub> (0.065 g, 0.14 mmol), in acetone (20 cm<sup>3</sup>) and the contents were stirred for 1 h, followed by refluxing for half an hour. The solution was filtered and allowed to crystallise at r.t. whereupon colourless crystals were formed. The crystals were separated and dried at r.t. Yield 60%; m.p. 206–08 °C. *Anal.* Found: C, 39.2; H, 3.2. Calc., for  $\text{C}_{26}\text{H}_{24}\text{Br}_2\text{HgS}_2$ : C, 38.0; H, 2.9%. Main IR bands: 1110 cm<sup>-1</sup> {νP–C}; 585 cm<sup>-1</sup> {νP–S}; ligand band: 1097 cm<sup>-1</sup> {νP–C}; 600 cm<sup>-1</sup> {νP–S}.

### 2.4. Elemental analyses and spectroscopic techniques

The C, H, and N elemental analyses were obtained with a Carlo–Erba 1108 microanalyser. The melting points were determined with a Gallenkamp electrically heated apparatus. IR spectra were recorded using KBr pellets on a Pye–Umicam SP3-300 Infrared Spectrophotometer in the 4000–400 cm<sup>-1</sup> range.

### 2.5. Crystal structure determinations

A red prismatic crystal of compound **1** (colourless for compound **2**) was mounted on a glass fibre and used for data collection. Cell constants and orientation matrices for data collection were obtained by least-squares refinement of the diffraction data from 25 reflections in the range of  $21.513 < \theta < 45.145^\circ$  for **1** and  $4.682 < \theta < 20.743^\circ$  for **2**, on an Enraf–Nonius CAD 4 automatic diffractometer [19]. Data were collected at 293 K using Cu K $\alpha$  radiation ( $\lambda = 1.54184 \text{ \AA}$ ) for **1** or Mo K $\alpha$  radiation (0.71073 Å) for **2** and the  $\omega$  scan technique and corrected for Lorentz and polarisation effects [20]. A semi-empirical absorption correction ( $\psi$ -scan) was made [21].

The structures were solved by direct methods [22] and subsequent difference Fourier maps and refined on  $F^2$  by a full-matrix least squares procedure using anisotropic displacement parameters [23]. All hydrogen atoms were located from difference Fourier maps in their calculated positions (C–H, 0.93–0.97 Å) and were refined isotropically. Atomic scattering factors were used from International Tables for X-ray crystallography [24] and molecular graphics from PLATON 98 [25]. A summary of the crystal data, experimental details, and refinement results is given in Table 1.

## 3. Results and discussion

### 3.1. General comments

Reactions of  $\text{Ph}_2\text{P}(\text{S})-\text{CH}_2-\text{CH}_2-\text{P}(\text{S})\text{Ph}_2$  {dppeS<sub>2</sub>} with  $\text{PdCl}_2(\text{CH}_3\text{CN})_2$  in hot  $\text{CH}_3\text{CN}$  or with  $\text{HgBr}_2$  in acetone (room temperature) formed 1:1 complexes, viz.  $\text{MX}_2(\text{dppeS}_2)$ , as revealed by the physical properties and analytical data. The IR spectra for the ligand and the complexes were different, and the diagnostic peak νP–S of free dppeS<sub>2</sub> at 600 cm<sup>-1</sup> shifted to 575 cm<sup>-1</sup> in compound **1** and to 585 cm<sup>-1</sup> in compound **2**, and it clearly shows that dppeS<sub>2</sub> is coordinating to Pd(II)/Hg(II) metal centres via S donor atoms. The shift is more pronounced for Pd(II) vis-à-vis Hg(II) even though the latter is believed to be softer than the former in the terminology of the HSAB principle. The crystal structures of both the compounds are described below.

Table 1  
Crystal data and structure refinement for compounds **1** and **2**

|   | <b>1</b>   | <b>2</b>  |
|---|--|---|
| Empirical formula                                     | C <sub>28</sub> H <sub>27</sub> Cl <sub>2</sub> NP <sub>2</sub> PdS <sub>2</sub> | C <sub>26</sub> H <sub>24</sub> Br <sub>2</sub> HgP <sub>2</sub> S <sub>2</sub> |
| Formula weight ( <i>M</i> )                           | 680.87   | 822.92  |
| Crystal system  | monoclinic   | monoclinic  |
| Space group   | <i>P</i> 2 <sub>1</sub> / <i>n</i> (no. 14)                                      | <i>P</i> 2 <sub>1</sub> / <i>c</i> (no. 14)                                     |
| Unit cell dimensions                                  |  |   |
| <i>a</i> (Å)  | 10.1009(3)   | 21.911(5)   |
| <i>b</i> (Å)  | 20.905(2)  | 8.2046(7)   |
| <i>c</i> (Å)  | 14.1048(6)   | 16.576(4)   |
| $\beta$ (°)   | 102.636(3)   | 107.066(17)   |
| <i>V</i> (Å <sup>3</sup> )                            | 2906.2(4)  | 2848.6(10)  |
| <i>Z</i>  | 4  | 4   |
| <i>D</i> <sub>calc</sub> (Mg m <sup>-3</sup> )        | 1.556  | 1.919   |
| <i>F</i> (000)  | 1376   | 1568  |
| Crystal size (mm)                                     | 0.35 × 0.15 × 0.10   | 0.35 × 0.25 × 0.15  |
| $\theta$ Range for data collection (°)                | 3.85–75.95   | 2.47–27.97  |
| Index ranges  | 0 ≤ <i>h</i> ≤ 12,<br>−26 ≤ <i>k</i> ≤ 0,<br>−17 ≤ <i>l</i> ≤ 17                 | −28 ≤ <i>h</i> ≤ 27,<br>0 ≤ <i>k</i> ≤ 10,<br>0 ≤ <i>l</i> ≤ 21                 |
| Reflections collected                                 | 6403   | 7097  |
| Independent reflections                               | 6057<br>[ <i>R</i> <sub>int</sub> = 0.0216]                                      | 6856<br>[ <i>R</i> <sub>int</sub> = 0.0433]                                     |
| Max/min transmission                                  | 0.983 and 0.885  | 0.983 and 0.547   |
| Data/restraints/parameters                            | 6057/0/433   | 6856/0/298  |
| Goodness-of-fit on <i>F</i> <sup>2</sup>              | 1.033  | 0.924   |
| Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]   | <i>R</i> <sub>1</sub> = 0.0474,<br><i>wR</i> <sub>2</sub> = 0.1209               | <i>R</i> <sub>1</sub> = 0.0445,<br><i>wR</i> <sub>2</sub> = 0.0806              |
| <i>R</i> indices (all data)                           | <i>R</i> <sub>1</sub> = 0.0833,<br><i>wR</i> <sub>2</sub> = 0.1370               | <i>R</i> <sub>1</sub> = 0.2303,<br><i>wR</i> <sub>2</sub> = 0.1137              |
| Largest difference peak and hole (e Å <sup>-3</sup> ) | 1.951 and −1.247   | 0.746 and −2.217  |

Table 2  
Bond lengths (Å) and bond angles (°) for compounds **1** and **2**

| Compound <b>1</b>     | Compound <b>2</b> |                   |            |
|-----------------------|-------------------|-------------------|------------|
| <i>Bond distances</i> |                   |                   |            |
| Pd(1)–S(1)            | 2.3005(14)        | Hg(1)–S(1)        | 2.678(2)   |
| Pd(1)–S(2)            | 2.3018(13)        | Hg(1)–S(2)        | 2.552(2)   |
| Pd(1)–Cl(1)           | 2.3161(15)        | Hg(1)–Br(1)       | 2.5592(11) |
| Pd(1)–Cl(2)           | 2.3347(14)        | Hg(1)–Br(2)       | 2.5509(11) |
| P(1)–S(1)             | 2.0181(18)        | P(1)–S(1)         | 1.990(3)   |
| P(2)–S(2)             | 2.0089(18)        | P(2)–S(2)         | 1.999(3)   |
| P(1)–C(11)            | 1.803(5)          | P(1)–C(11)        | 1.815(8)   |
| P(1)–C(21)            | 1.804(5)          | P(1)–C(21)        | 1.777(8)   |
| P(1)–C(1)             | 1.832(5)          | P(1)–C(1)         | 1.794(7)   |
| P(2)–C(31)            | 1.799(6)          | P(2)–C(31)        | 1.811(8)   |
| P(2)–C(41)            | 1.802(5)          | P(2)–C(41)        | 1.810(8)   |
| P(2)–C(2)             | 1.808(5)          | P(2)–C(2)         | 1.809(7)   |
| C(1)–C(2)             | 1.531(7)          | C(1)–C(2)         | 1.544(9)   |
| <i>Bond angles</i>    |                   |                   |            |
| Pd(1)–S(1)–P(1)       | 113.54(7)         | Hg(1)–S(1)–P(1)   | 108.96(11) |
| Pd(1)–S(2)–P(2)       | 105.11(7)         | Hg(1)–S(2)–P(2)   | 104.79(11) |
| S(1)–Pd(1)–S(2)       | 97.76(5)          | S(1)–Hg(1)–S(2)   | 118.85(8)  |
| S(1)–Pd(1)–Cl(1)      | 174.10(5)         | S(1)–Hg(1)–Br(1)  | 96.20(6)   |
| S(2)–Pd(1)–Cl(1)      | 88.06(5)          | S(2)–Hg(1)–Br(1)  | 110.40(6)  |
| S(1)–Pd(1)–Cl(2)      | 83.19(5)          | S(1)–Hg(1)–Br(2)  | 101.47(6)  |
| S(2)–Pd(1)–Cl(2)      | 172.85(5)         | S(2)–Hg(1)–Br(2)  | 105.81(6)  |
| Cl(1)–Pd(1)–Cl(2)     | 91.17(5)          | Br(1)–Hg(1)–Br(2) | 124.56(4)  |
| P(1)–C(1)–C(2)        | 117.2(4)          | P(1)–C(1)–C(2)    | 112.8(5)   |
| P(2)–C(2)–C(1)        | 115.0(4)          | P(2)–C(2)–C(1)    | 112.9(5)   |
| S(1)–P(1)–C(1)        | 114.35(19)        | S(1)–P(1)–C(1)    | 111.5(3)   |
| S(2)–P(2)–C(2)        | 112.00(19)        | S(2)–P(2)–C(2)    | 111.7(3)   |

### 3.2. Description of crystal structures of compounds **1** and **2**

The atomic numbering schemes for [PdCl<sub>2</sub>(dppeS<sub>2</sub>)]-(CH<sub>3</sub>CN) (**1**) and HgBr<sub>2</sub>(dppeS<sub>2</sub>) (**2**) are shown in Figs. 1 and 2, respectively. While Table 1 contains crystal data, experimental details, and refinement results, Table 2 contains important bond lengths and bond angles. Both compounds adopt a monoclinic crystal system similar to that of [HgCl<sub>2</sub>{Ph<sub>2</sub>P(S)–CH<sub>2</sub>–CH<sub>2</sub>–P(S)Ph<sub>2</sub>}] [11b]. The basic unit is [MX<sub>2</sub>(dppeS<sub>2</sub>)] (X, M = Cl, Pd; Br, Hg) with no evidence for intermolecular interaction, and in compound **1**, CH<sub>3</sub>CN lies in the lattice as a non-bonded molecule.

In compound **1**, palladium(II) is bonded to two S atoms of the chelating dppeS<sub>2</sub> ligand and two chlorine atoms. The *trans*-bond angles S(1)–Pd–Cl(1) and S(2)–Pd–Cl(2) are 174.10(5)° and 172.85(5)°, respectively, with the bite angle S(1)–Pd–S(2) of the ligand being 97.76°. Whereas Cl(1)–Pd–Cl(2) and S(2)–Pd–Cl(1) bond angles are close to 90°, the angle S(1)–Pd–Cl(2) of 83.19(5)° is unusually short. Thus the square planar geometry about Pd is severely distorted and is the consequence of the effect of the large bulk of the ligand and the tendency of the Pd metal to form square planar geometries. The angles at the S atom differ significantly [cf. Pd–S(1)–P(1), 113.54(7)°,

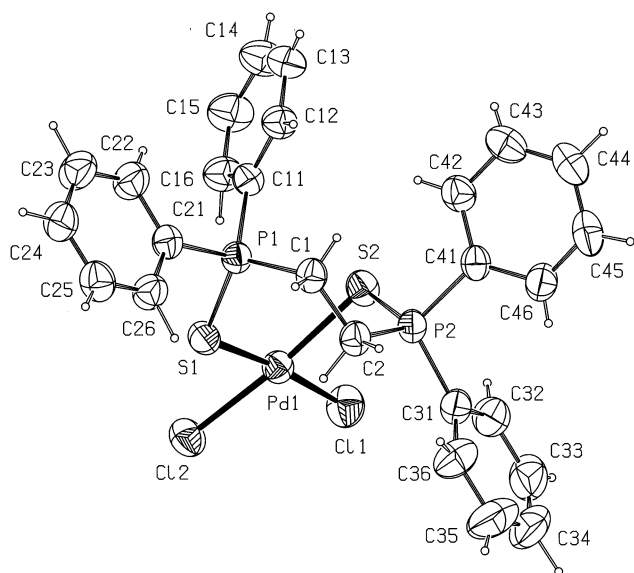


Fig. 1. Perspective view of the structure of compound [PdCl<sub>2</sub>(dppeS<sub>2</sub>)](CH<sub>3</sub>CN) (**1**) with numbering scheme (CH<sub>3</sub>CN lies in the lattice as a non-bonded molecule – not shown).

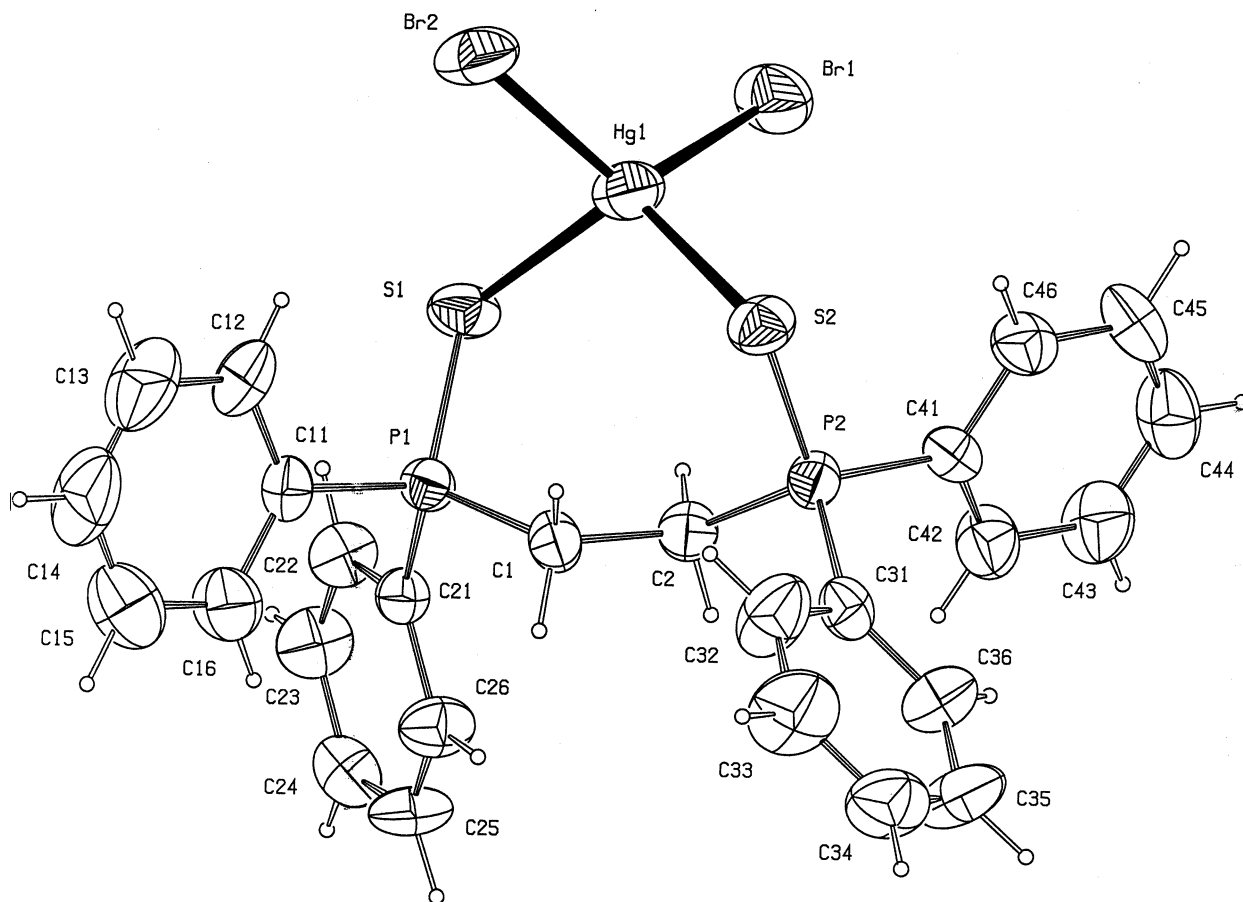
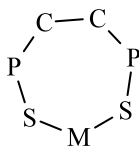


Fig. 2. Perspective view of the structure of compound  $\text{HgBr}_2(\text{dppeS}_2)$  (**2**) with numbering scheme.

$\text{Pd-S}(2)\text{-P}(2)$ ,  $105.11(7)^\circ$ ]. Similarly, in compound **2** Hg is bonded to two S atoms of the chelating  $\text{dppeS}_2$  ligand and two bromine atoms. The angles about Hg vary in the range  $96.20(6)^\circ\text{--}124.56(4)^\circ$ , suggesting highly distorted geometry about Hg. The bite angle  $\text{S}(1)\text{-Hg-S}(2)$  of the ligand expands to  $118.85(8)^\circ$  in **2**, and interestingly this angle is still higher at  $122.3(1)^\circ$  in the analogous complex,  $[\text{HgCl}_2(\text{dppeS}_2)]$  [11b] (compound **5**). This is clearly the effect of the bulky Br atoms, which has not only affected the bite angle  $\text{S}(1)\text{-Hg-S}(2)$  of the ligand, but also affected other bond angles. Note that the  $\text{Br}(1)\text{-Hg-Br}(2)$  bond angle of  $124.56(4)^\circ$  is much larger than the analogous  $\text{Cl}(1)\text{-Hg-Cl}(2)$  angle of  $111.4(1)^\circ$  in compound **5**. In the three examples of complexes of  $\text{dppeS}_2$  discussed above {compounds **1**, **2**, **5**}, the flexibility of the alkane moiety is very apparent, which is tuning to the steric requirements of the metal or the anion. Thus the seven-



III

membered metallacyclic rings (III) are interestingly stable and flexible.

The Pd-S bond distances, 2.3005(14) and 2.3018(13) Å, are shorter than those reported for  $\text{PdCl}_2\text{L}_2$  {2.334, 2.350 Å for  $\text{L} = i\text{-Bu}_3\text{PS}$ ,  $\text{PhEt}_2\text{PS}$ , respectively} [15,16]. The Pd-Cl bond distances are normal, though unequal. The P-S bond distances for **1** {2.0181(18), 2.0089(18) Å} are equal to those for the above Pd complexes [2.014, 2.013 Å, respectively [15,16]] and a bit longer than those found in **2** {1.990(3), 1.999(3) Å}. Other bond distances of the metallacyclic ring, namely  $\text{P}(1)\text{-C}(1)$  and  $\text{P}(2)\text{-C}(2)$ , are also unequal, but similar for both the compounds (Table 2). In compound **2** Hg-S distances are unequal {2.678(2), 2.552(2) Å} and quite different from those for compound **5** {2.559(3), 2.546(3) Å} [11b]. The longer Hg-S distance in **2** is comparable to that observed in  $\text{HgI}_2\text{L}$  { $\text{Hg-S} = 2.760$  Å,  $\text{L} = \text{Ph}_2\text{P-CH}_2\text{-P}(\text{S})\text{Ph}_3$ } [11b] for which a flattened tetrahedral structure was concluded. In **2** also, the sum of the bond angles of the trigonal plane formed by Hg, S(2), Br(1) and Br(2), is  $340.77^\circ$  [ $\text{S}(2)\text{-Hg-Br}(1)$ ,  $\text{S}(2)\text{-Hg-Br}(2)$ , and  $\text{Br}(1)\text{-Hg-Br}(2)$ ], similar to that in  $\text{HgI}_2\text{L}$  { $353.7^\circ$ } [11b]. The lengthening of the Hg-S(1) bond distance is reflected in the shorter  $\text{P}(1)\text{-S}(1)$  and  $\text{P}(1)\text{-C}(1)$  distances.

#### 4. Supplementary material

Supplementary data are available from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>) on request, quoting the deposition numbers 166375 for compound **1**, 166374 for compound **2**.

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