



REGULAR ARTICLE

# Palladium(II) and copper(I) complexes of wide angle bisphosphine, 1,4-bis((diphenylphosphino)methyl)benzene<sup>†</sup>

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**Abstract.** Oxidation reactions and synthesis of copper(I) and palladium(II) complexes of 1,4-bis((diphenylphosphino)methyl)benzene (**1**) have been described. Due to the larger separation of phosphorus atoms, bisphosphine exhibits only bridging mode of coordination. The ligand is also ideally suited to form binuclear complexes and 1-D coordination polymers. Reaction of **1** with  $[\text{Pd}(\eta^3\text{-allyl})\text{Cl}]_2$  results in dipalladium(II) complex  $[\{\text{Pd}(\eta^3\text{-allyl})\text{Cl}\}_2\{\mu\text{-Ph}_2\text{PCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{PPh}_2\}]$  (**4**), whereas with copper halides, dimeric complexes of the type  $[\{\text{CuX}\}\{\mu\text{-Ph}_2\text{PCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{PPh}_2\}]_2$  (**5** X = Cl, **6** X = Br and **7** X = I) were isolated. All the compounds have been fully characterized by spectroscopic and analytical methods. The molecular structures of bisulfide (**3**), Pd(II) and Cu(I) complexes were confirmed by single crystal X-ray analyses.

**Keywords.** Bisphosphine; coordination; palladium; copper; crystal structure.

## 1. Introduction

The deeper interest in the chemistry of sterically demanding wide angle bisphosphines is essentially due to their ability to act as bridging ligands and hence their utility in supramolecular assembly and metal-organic frameworks.<sup>1–4</sup> Tertiary phosphines and short-bite bisphosphines are appropriate ligands for stabilizing the transition metals in their low coordination numbers and/or unusual oxidation states as they can be employed in homogeneous catalysis.<sup>5</sup> In contrast, large bite or wide angle bisphosphines can form 1D, 2D or 3D-coordination polymers<sup>6</sup> with appropriate metal precursors and find applications in heterogeneous catalysis.<sup>7</sup> As a part of our interest in developing different types of phosphorus based ligands for catalytic<sup>8–11</sup> and material applications,<sup>12,13</sup> herein we describe the synthesis and palladium and copper complexes of a wide angle bisphosphine, 1,4-bis((diphenylphosphino)methyl)benzene.

## 2. Experimental

All experimental manipulations were performed under an inert atmosphere of dry nitrogen or argon, using standard Schlenk techniques. All the solvents were purified by conventional procedures and distilled prior to use.  $\text{CuX}$  [X = Cl and Br],<sup>14</sup> and  $[\text{Pd}(\eta^3\text{-allyl})\text{Cl}]_2$ ,<sup>15</sup> were prepared according to the published procedures.  $\text{CuI}$  was purchased from Aldrich chemicals and used without further purification. Other reagents were obtained from commercial sources and used after purification. The  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\delta$  in ppm) spectra were obtained from either Bruker Avance-400 MHz or Bruker Avance- 500 MHz spectrometer. The spectra were recorded in  $\text{CDCl}_3$  (or  $\text{DMSO-}d_6$ ) solutions with  $\text{CDCl}_3$  (or  $\text{DMSO-}d_6$ ) as an internal lock; TMS and 85%  $\text{H}_3\text{PO}_4$  were used as internal and external standards for  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR, respectively. Mass spectra were recorded on Bruker mass spectrometer using Electro-spray ionization mass spectrometry (ESI-MS) method. Microanalysis were carried out on a Carlo Erba (model 1112) elemental analyzer. Melting points of all compounds were determined on a Veego melting point apparatus and are uncorrected.

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<sup>†</sup> Dedicated to Professor K. C. Kumara Swamy on the occasion of his 60th birth anniversary.

### 2.1 Synthesis of 1,4-bis((diphenylphosphino)methyl)benzene (**1**)

A solution of n-BuLi in hexanes (6 mL, 0.009 mol, 1.6 M) was added at  $-78^{\circ}\text{C}$  to a stirred solution of HPPH<sub>2</sub> (1.5 mL, 0.008 mol) in THF (15 mL). After the completion of addition, the reaction mixture was allowed to warm to room temperature and stirred for 3 h. Subsequently, 1,4-(dibromomethyl)benzene (1 g, 0.004 mol) with THF (25 mL) was introduced dropwise to the lithiated solution at  $-78^{\circ}\text{C}$  and stirring was continued overnight at room temperature followed by reflux for 1 h. Solvent was removed under vacuum and the residue obtained was dissolved in 50 mL of dichloromethane and filtered through celite to remove lithium salt. The solvent was removed, and the residue was washed with diethyl ether ( $2 \times 25$  mL) and dried under vacuum to give analytically pure product of **1** as white solid. Yield: 85% (1.5 g). M.p.:  $173\text{--}175^{\circ}\text{C}$ . MS (ESI): m/z: calcd. for  $[\text{C}_{32}\text{H}_{20}\text{P}_2]^+$  475.1739; found, 475.1734.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.36–6.84 (m, Ph, 24H), 3.34 (s,  $2\text{CH}_2\text{P}$ , 4H) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ ):  $\delta$  -10.0 (s). Anal. Calcd for  $\text{C}_{32}\text{H}_{28}\text{P}_2$ : C, 67.12; H, 4.93%. Found: C, 67.43; H, 4.75%.

### 2.2 Synthesis of $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{P}(\text{O})\text{Ph}_2$ (**2**)

A 30% aqueous solution  $\text{H}_2\text{O}_2$  (0.005 g, 0.004 mL, 0.126 mmol) in 5 mL of THF was introduced dropwise to a well-stirred THF solution (5 mL) of **1** (0.030 g, 0.063 mmol). The reaction mixture was stirred for 6 h at room temperature and solvent was removed under reduced pressure to give **2** as a white solid. Yield: 90% (0.029 g). MS (ESI): m/z: calcd. for  $[\text{C}_{32}\text{H}_{28}\text{P}_2\text{O}_2\text{Na}]^+$  529.1456; found, 529.1452. M.p.:  $175^{\circ}\text{C}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.65–6.92 (m, ArH, 24H), 3.5 (d,  $^2J_{\text{PH}} = 13.2$  Hz,  $2\text{CH}_2\text{P}$ , 4H) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ ):  $\delta$  30.0 (s). Anal. Calcd. for  $\text{C}_{32}\text{H}_{28}\text{P}_2\text{O}_2$ : C, 75.88; H, 5.57%. Found: C, 76.04; H, 5.34%.

### 2.3 Synthesis of $\text{Ph}_2\text{P}(\text{S})\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{P}(\text{S})\text{Ph}_2$ (**3**)

A mixture of **1** (0.040 g, 0.084 mmol) and elemental sulphur (0.006 g, 0.210 mmol) in toluene (20 mL) was refluxed for 24 h. After cooling the solution to room temperature and filtering through celite, the solvent was removed under reduced pressure and the residue obtained was dissolved in 5 mL of dichloromethane and diluted with 3 mL of petroleum ether and stored at room temperature for 24 h to give analytically pure product of **3** as white crystalline solid. Yield: 87% (0.039 g). M.p.:  $> 250^{\circ}\text{C}$ . MS (ESI): m/z: calcd. for  $[\text{C}_{32}\text{H}_{28}\text{P}_2\text{S}_2\text{Na}]^+$  561.1000; found, 561.0997.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.76–6.76 (m, ArH, 24H), 3.7 (d,  $^2J_{\text{PH}} = 12.0$  Hz,  $2\text{CH}_2\text{P}$ , 4H) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ ):  $\delta$  42.0 (s). Anal. Calcd. for  $\text{C}_{32}\text{H}_{28}\text{P}_2\text{S}_2$ : C, 71.36; H, 5.24%. Found: C, 71.62; H, 5.06%.

### 2.4 Synthesis of $[\{\text{Pd}(\eta^3\text{-allyl})\text{Cl}\}_2\{\mu\text{-Ph}_2\text{PCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{PPh}_2\}]$ (**4**)

A dichloromethane (10 mL) solution of  $[\text{Pd}(\eta^3\text{-allyl})\text{Cl}]_2$  (0.027 g, 0.073 mmol) was added dropwise to well stirred solution of **1** (0.035 g, 0.073 mmol) also in dichloromethane (10 mL). Stirring was continued for 6 h at room temperature with minimum exposure to light. Solvent was removed under reduced pressure to give analytically pure product of **4** as yellow solid. Yield: 85% (0.052 g). M.p.:  $168^{\circ}\text{C}$ . MS (ESI): m/z: calcd. for  $[\text{C}_{32}\text{H}_{28}\text{P}_2\text{Pd}_2\text{Cl}_2\text{K}]^+$  794.8750; found, 794.0289.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.39–6.80 (m, Ph, 24H), 2.53–5.42 (m,  $2\text{C}_3\text{H}_5$ ,  $2\text{CH}_2\text{P}$  14H) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CDCl}_3$ ):  $\delta$  24.7 (s). Anal. Calcd. for  $\text{C}_{32}\text{H}_{38}\text{P}_2\text{Pd}_2\text{Cl}_2$ : C, 50.13; H, 4.99%. Found: C, 51.03; H, 4.67%.

### 2.5 Synthesis of $[\{\text{CuCl}\}\{\mu\text{-Ph}_2\text{PCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{PPh}_2\}]_2$ (**5**)

An acetonitrile solution (5 mL) of cuprous chloride (0.008 g, 0.084 mmol) was introduced dropwise to a solution of **1** (0.040 g, 0.084 mmol) in dichloromethane (5 mL). The reaction was allowed to stir at room temperature for 6 h. After that, solvent was evaporated under vacuum to give microcrystalline product of **5** as a white solid. Yield: 84% (0.040 g). M.p.:  $> 250^{\circ}\text{C}$ . MS (ESI): m/z: calcd. for  $[\text{C}_{64}\text{H}_{56}\text{P}_4\text{Cu}_2\text{Cl}]^+$  1109.1607; found, 1111.1551.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  7.39–7.10 (m, ArH, 48H), 3.6 (s,  $4\text{CH}_2\text{P}$ , 8H) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  -4.2 (s). Anal. Calcd. for  $\text{C}_{32}\text{H}_{28}\text{P}_2\text{CuCl} \cdot \text{CH}_2\text{Cl}_2$ : C, 67.12; H, 4.93%. Found: C, 67.47; H, 4.75%.

### 2.6 Synthesis of $[\{\text{CuBr}\}\{\mu\text{-Ph}_2\text{PCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{PPh}_2\}]_2$ (**6**)

Compound **6** was synthesized by a procedure similar to that of **5** using cuprous bromide (0.012 g, 0.084 mmol) and **1** (0.040 g, 0.084 mmol). Yield: 80% (0.042 g). M.p.:  $> 250^{\circ}\text{C}$ . MS (ESI): m/z: calcd. for  $[\text{C}_{64}\text{H}_{56}\text{P}_4\text{Cu}_2\text{Br}]^+$  1153.1102; found, 1155.1099.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  7.39–7.12 (m, ArH, 48H), 3.6 (s,  $4\text{CH}_2\text{P}$ , 8H) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  -3.9 (s). Anal. Calcd. for  $\text{C}_{64}\text{H}_{56}\text{P}_2\text{Cu}_2\text{Br}_2$ : C, 62.33; H, 4.58%. Found: C, 62.32; H, 4.46%.

### 2.7 Synthesis of $[\{\text{CuI}\}\{\mu\text{-Ph}_2\text{PCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{PPh}_2\}]_2$ (**7**)

This compound was synthesized by a procedure similar to that of **5** using cuprous iodide (0.016 g, 0.084 mmol) and **1** (0.040 g, 0.084 mmol). Yield: 81% (0.045 g). M.p.:  $> 250^{\circ}\text{C}$ . MS (ESI): m/z: calcd. for  $[\text{C}_{64}\text{H}_{56}\text{P}_4\text{Cu}_2\text{I}]^+$  1201.0969; found, 1201.0487.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  7.39–7.11 (m, ArH, 48H), 3.6 (s,  $4\text{CH}_2\text{P}$ , 8H) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  -3.3 (s). Anal. Calcd. for  $\text{C}_{64}\text{H}_{56}\text{P}_2\text{Cu}_2\text{I}_2$ : C, 57.85; H, 4.24%. Found: C, 57.61; H, 3.94%.

**Table 1.** Crystallographic data for compounds **1**, **2**, **4** and **7** Final *R* indexes [ $I \geq 2\sigma(I)$ ]

	<b>1</b>	<b>2</b>	<b>4</b>	<b>7</b>
Emp. formula	C <sub>32</sub> H <sub>28</sub> P <sub>2</sub>	C <sub>32</sub> H <sub>28</sub> O <sub>2</sub> P <sub>2</sub>	C <sub>38</sub> H <sub>38</sub> Cl <sub>2</sub> P <sub>2</sub> Pd <sub>2</sub>	C <sub>32</sub> H <sub>28</sub> CuIP <sub>2</sub>
Fw	474.48	506.48	840.32	664.92
Cryst. Sys.	triclinic	triclinic	monoclinic	monoclinic
space group	P-1	P-1	P2 <sub>1</sub> /n	I2/a
<i>a</i> , Å	7.3247(3)	5.8667(3)	11.3520(9)	31.282(5)
<i>b</i> , Å	8.7562(4)	9.3881(5)	8.4118(6)	9.8600(14)
<i>c</i> , Å	9.6805(4)	12.3450(9)	19.4062(16)	38.046(5)
$\alpha$ , deg	89.150(4)	101.155(5)	90	90
$\beta$ , deg	84.874(4)	98.308(5)	105.158(8)	104.871(11)
$\gamma$ , deg	81.254(4)	104.435(4)	90	90
<i>V</i> , Å <sup>3</sup>	611.20(5)	632.59(7)	1788.6(2)	11347(3)
<i>Z</i>	1	1	2	8
<i>D</i> <sub>calc</sub> , g cm <sup>-3</sup>	1.289	1.330	1.560	1.557
$\mu$ (MoK $\alpha$ ), mm <sup>-1</sup>	0.197	0.201	1.270	1.990
<i>F</i> (000), <i>T</i> (K)	250, 150	266, 150	844, 100	5312, 293
2 $\theta$ range, deg	4.2–49.9	6.3–49.9	3.7–49.9	6.0–49.9
Total no. reflns	4408	3668	14981	50324
No. of indep reflns	2136 [R <sub>int</sub> = 0.0273]	3668 [R <sub>int</sub> = 0.0236]	3141 [R <sub>int</sub> = 0.0871]	9912 [R <sub>int</sub> = 0.0501]
<i>S</i>	1.101	1.139	1.086	1.059
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub>	0.0552, 0.1303	0.0581, 0.1814	0.0699, 0.1859	0.0447, 0.1081

## 2.8 X-ray crystallography

A crystal of each of the compounds in the present work suitable for single-crystal X-ray diffraction studies was mounted in a cryoloop with a drop of paratone oil and placed in the cold nitrogen stream of the kryoflex attachment of the Rigaku Saturn 724 diffractometer. Data were collected at temperature as mentioned in Table 1 using graphite-monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å) with the  $\omega$ -scan technique. The data were reduced by using Crystal Clear- SMeExpert 2.1 b24 software. Summary of data for compounds **1**, **2**, **4** and **7** is given in Table 1. The structures were solved by direct methods and refined by least-squares against *F*<sup>2</sup> utilizing the software packages SHELXL-97/2013,<sup>16</sup> and SIR-92.<sup>17</sup> All non-hydrogen atoms were refined anisotropically. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1539591 (**1**), 1539592 (**2**), 1539593 (**4**) and 1539594 (**7**).

## 3. Results and Discussion

### 3.1 Synthesis and complexation reactions

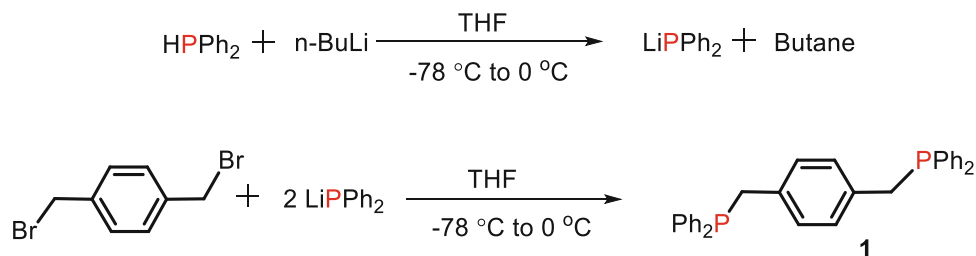
The compound **1** was prepared from modified procedure reported by Imhof *et al.*<sup>18</sup> Lithium diphenylphosphide (LiPPh<sub>2</sub>), generated *in situ* by the reaction of diphenylphosphine (HPPh<sub>2</sub>) and *n*-BuLi at  $-78^\circ\text{C}$ , was treated with  $\alpha,\alpha'$ -dibromo-*p*-xylene [1,4-dibromomethylbenzene) to afford 1,4-bis((diphenylphosphino)methyl)benzene (**1**) (Scheme 1). The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **1** shows singlet at -10 ppm and the mass

spectrum shows the molecular ion peak at  $m/z = 474.1$  [M + H]<sup>+</sup>. The reaction of **1** with two equivalents of H<sub>2</sub>O<sub>2</sub> in tetrahydrofuran (THF) at room temperature resulted in the oxidation of both the phosphorus atoms to afford bis(oxide) **2** in good yield. Similar reaction of **1** with elemental sulfur in toluene under refluxing conditions furnished bis(sulfide) **3**. The <sup>31</sup>P{<sup>1</sup>H} NMR spectra of bischalcogenides **2** and **3** showed single resonances at 30 and 42 ppm, respectively. Mass spectra of **2** and **3** showed the cationic species [M + Na]<sup>+</sup> at ( $m/z$ ): = 529.1 and 561.1, respectively. The structures of **1** and **2** were further confirmed by single crystal X-ray analysis.

Reaction between **1** and [Pd( $\eta^3$ -allyl)Cl]<sub>2</sub> in 1:1 molar ratio yielded [{Pd( $\eta^3$ -allyl)Cl]<sub>2</sub>( $\mu$ -Ph<sub>2</sub>PCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>PPh<sub>2</sub>)] (**4**) with bisphosphine exhibiting bridging mode of coordination. In the reaction of **1** with copper halides (X = Cl, Br or I), tricoordinated dicopper complexes of the type [{(CuX)( $\mu$ -Ph<sub>2</sub>PCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>PPh<sub>2</sub>)]<sub>2</sub> (**5**, X = Cl; **6**, X = Br; **7**, X = I) were obtained (Chart 1). The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **4** showed a single resonance at 24.8 ppm, with a coordination shift of 34.7 ppm. The copper complexes **5–7** also showed single resonances at -4.2, -3.9 and -3.3 ppm, respectively.

### 3.2 Molecular structures of **1**, **2**, **4** and **7**

Molecular structures of **1**, **2**, **4** and **7** were confirmed by single crystal X-ray analysis. Crystals of **1**, **2** and **4** were grown from a mixture of dichloromethane and



Scheme 1. Preparation of bisphosphine 1.

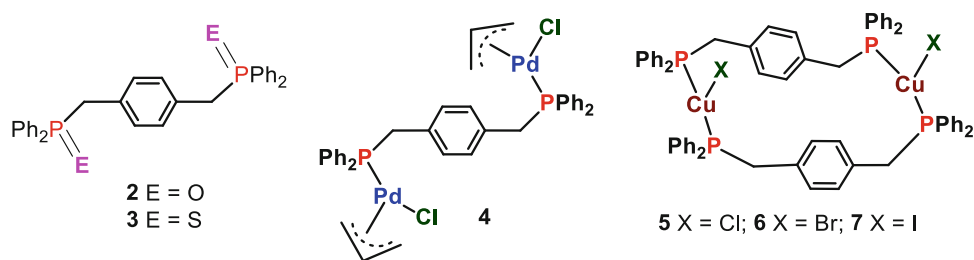
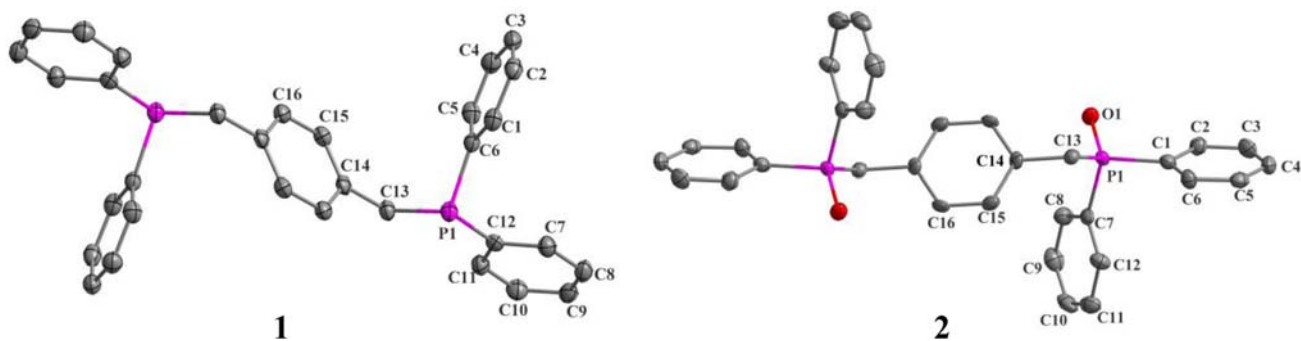
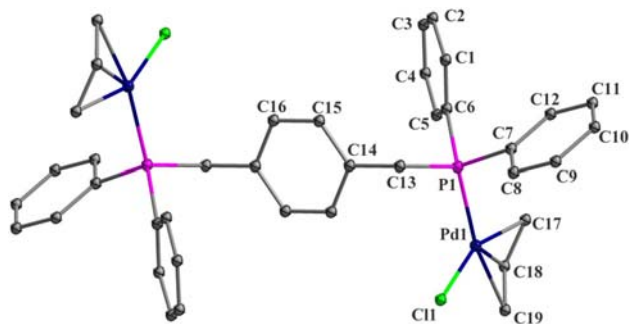


Chart 1. Bischalcogenides, palladium(II) and copper(I) complexes of bisphosphine 1.



**Figure 1.** Molecular structures of **1** and **2**. All hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and bond angles (°): Compound **1**: P1-C6 1.836(3), P1-C12 1.832(3), P1-C13 1.851(3), C6-P1-C12 100.1(12), C6-P1-C13 102.6(13), C12-P1-C13 102.9(13). Compound **2**: P1-C1 1.818(3), P1-C7 1.816(4), P1-C13 1.807(4), P1-O1 1.498(3), C1-P1-C7 104.48(16), C1-P1-C13 107.43(17), C7-P1-C13 106.31(16), C1-P1-O1 111.44(15), C7-P1-O1 111.99(16).

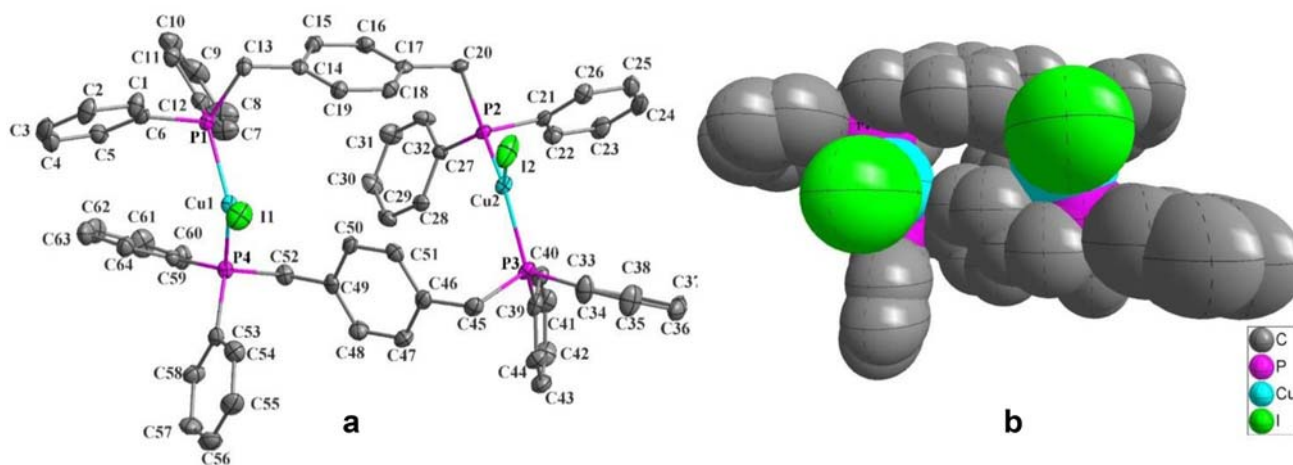


**Figure 2.** Molecular structure of **4**. All hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and bond angles (°): P1-C6 1.839(10), P1-C7 1.828(9), P1-C13 1.845(8), Pd1-C17 2.152(11), Pd1-C18 2.158(11), Pd1-C19 2.152(11), P1-Pd1 2.300(2), Pd1-C11 2.416(2), C6-P1-C7 105.5(4), P1-Pd1-C11 95.54(8), C13-P1-Pd1 115.5(3), C17-Pd1-C11 160.0(4), C19-Pd1-C11 94.3(4).

petroleum ether solutions, whereas the copper complex **7** was crystallized from a 1:1 mixture of acetonitrile and diethyl ether at room temperature. The molecular views of **1** and **2** with selected bond lengths and bond angles are depicted in Figure 1, whereas Figures 2 and 3 include, respectively, the structures of **4** and **7**, along with the selected bond lengths and bond angles. Crystallographic information and the details of the structure determination are summarized in Table 1.

Compounds **1**, **2** and **4** have crystallographically imposed center of symmetry. In both the compounds **1** and **2**, PPh<sub>2</sub> moieties are oriented in a mutually *trans*-disposition clearly indicating the conformational rigidity which is unperturbed even during the oxidation reaction, i.e., the mutual orientations of phosphorus lone pairs and the chalcogen atoms are essentially the same. The P—CH<sub>2</sub>—C bond angles at methyl carbon





**Figure 3.** (a) Molecular structure of **7**. All hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. (b) Space-filling representation of **7**. Selected bond lengths (Å) and bond angles (°): P1–C6 1.820(4), P1–C12 1.826(4), P1–C13 1.850(4), P1–Cu1 2.252(10), P4–Cu1 2.229(11), P2–Cu2 2.241(10), P3–Cu2 2.252(10), Cu1–I1 2.5115(7), Cu2–I2 2.511(7), P1–Cu1–P4 122.42(4), P1–Cu1–I1 111.00(3), P4–Cu1–I1 125.28(3), P2–Cu2–P3 132.13(4), P2–Cu2–I2 120.72(3), P3–Cu2–I2 107.11(3).

in both **1** and **2** are in the range of  $110^\circ$ , whereas the P1–C13 (bridging  $C_6H_4$ ) bond length (1.851(3) Å) is slightly longer than the same in bisoxide **2** (1.807(4) Å). The P1–O1 bond length of 1.498(3) Å in compound **2** is comparable with that in  $Ph_3P=O$  (1.479(2) Å).<sup>19</sup>

Orientation of  $[Pd(\eta^3-C_3H_5)Cl]$  moieties in compound **4** are similar to the orientations of phosphorus lone pairs in bisphosphine **1** and surprisingly the same orientations are retained in the case of dimeric copper(I) complex **7** as well. The palladium atoms are in a distorted square planar environment with  $\tau$  value equal to 0.22.<sup>20</sup> The Pd–P and Pd–Cl1 bond distances are 2.300(2) and 2.416(2) Å, respectively. The Pd–P bond distance is slightly shorter than the same in  $[(\eta^3-C_3H_5)Pd(2-(P^tBu)_2(C_{12}H_9)Br)]$  (2.372(3)) Å.<sup>21</sup> The C13–P1–Pd1 bond angle is  $115.5(3)^\circ$ . The orientation of bisphosphines and the P–CH<sub>2</sub>–C bond angles in copper complex **7** are very similar to those in palladium complex. In the dimeric structure of copper complex **7**, the *p*-xylyl moieties are almost orthogonal to each other with minimum distance that separates them, i.e., CH–C being 3.1 Å. The copper atoms are in a typical trigonal planar environment with sum of the angles at copper atoms is  $\sim 360^\circ$ . Similar dimeric tricoordinated copper(I) complexes have been reported in the literature.<sup>22</sup> The average Cu–P and Cu–I bond distances are 2.239(11) and 2.502(7) Å, respectively. The intramolecular Cu···Cu distance is 7.092 Å.

#### 4. Conclusions

In summary, wide angle bisphosphine was synthesized by modifying the reported procedure with improved yield and has been structurally characterized. Bisphosphine shows both monodentate and bridged bidentate modes of coordination. The ligand framework is found to be rigid and the original conformation is retained in bischalcogenides and metal complexes. It would be interesting to further investigate its coordination properties with other transition metals to get some insight into the structural flexibility as this type of ligands can be ideally suited to develop 2D or 3D-coordination polymers (MOFs) to examine their soft metal sensing abilities. The research work is in progress in this direction in our laboratory.

#### Supplementary information (SI)

NMR ( $^{31}P\{^1H\}$  and  $^1H$ ) and mass spectra for compounds **1–7** are provided in Supplementary Information which is available at [www.ias.ac.in/chemsci](http://www.ias.ac.in/chemsci).

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