



Large-bite bisphosphite, 1,3-C₆H₄{OPOC₁₀H₆(μ-S)C₁₀H₆O}₂: Synthesis, copper(I), and gold(I) complexes

Maravanji S. Balakrishna^{a,*}, Pawan Kumar^a, B. Punji^a, Joel T. Mague^b

^a Phosphorus Laboratory, Department of Chemistry, Indian Institute of Technology Bombay, Mumbai 400076, India

^b Department of Chemistry, Tulane University, New Orleans, LA 70118, USA

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ABSTRACT

Large-bite bisphosphite ligand 1,3-C₆H₄{OPOC₁₀H₆(μ-S)C₁₀H₆O}₂ (**3**), is obtained by reacting chlorophosphonite {OC₁₀H₆(μ-S)C₁₀H₆O}P(Cl) (**2**) with resorcinol in the presence of triethylamine. Treatment of **3** with CuCl in 1:1 molar ratio produces a 1D-coordination polymer [CuCl{(-OC₁₀H₆(μ-S)C₁₀H₆O-)P(-OC₆H₄O-)P(-OC₁₀H₆(μ-S)C₁₀H₆O-)-κP,κP}]_∞ (**4**) in good yield. Similar reaction of **3** with two equivalents of AuCl(SMe₂) affords a dinuclear complex, [Au₂Cl₂{(-OC₁₀H₆(μ-S)C₁₀H₆O-)P(-OC₆H₄O-)P(-OC₁₀H₆(μ-S)C₁₀H₆O-)-κP,κP}] (**5**). Single crystal X-ray structures of the ligand **3** and the complexes **4** and **5** are reported. The gold complex **5** shows dimeric structure supported by strong Au...Au aurophilic interactions.

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1. Introduction

The bisphosphine ligands appended with donor functionalities are found to be more advantageous than those of ligands having only one type of donor atoms because of their versatile and often unexpected coordination behavior. Further, this type of bisphosphines with additional donor atoms and different donor abilities are ideally suited to provide temporary coordinative saturation to the metal center via chelation until it is required to furnish a vacant site at the metal center prior to the oxidative addition, an important step in homogeneous catalysis [1]. Among mixed donor ligands of the type P=O [2], P=N [3] and P=S [4], ligands combining phosphorus and sulfur are especially interesting. Both phosphorus and sulfur are excellent donor atoms for a wide range of transition metals, in particular group 11 metals, while the low ionization energy of sulfur and the existence of several lone pair of electrons (three in the case of a thiolate anion) offer the possibility of a rich sulfur based chemistry of the complexes [5]. Recently we have reported the syntheses of both large-bite and short-bite bisphosphonite ligands containing mesocyclic thioether functionalities and reported their reactivity towards platinum and group 11 metals where it exhibits interesting coordination behavior produc-

ing neutral, cationic and anionic complexes [6–10]. The Pd^{II}, Rh^I and Ru^{II} complexes have shown excellent catalytic activities towards various cross coupling reactions (Suzuki-Miyaura, Mizoraki-Heck and amination reactions) and hydrogenation of olefins. As a continuation of our research in organometallic chemistry and catalytic investigation of phosphorus-based ligands, we report in this paper the copper(I) and gold(I) complexes of a new resorcinol based thioether-functionalized bisphosphonite, 1,3-C₆H₄{OPOC₁₀H₆(μ-S)C₁₀H₆O}₂ (**1**).

2. Results and discussion

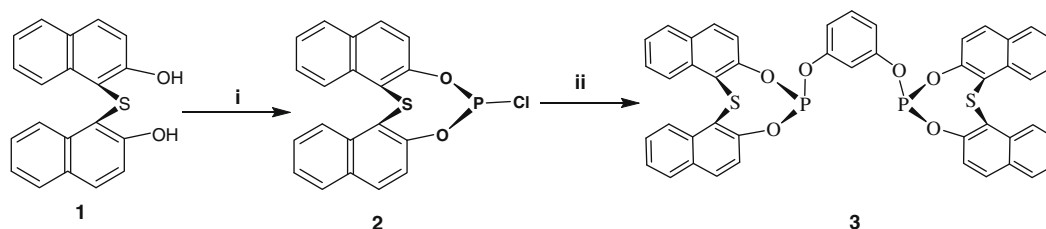
2.1. Synthesis of ligand and its chalcogen derivative

Reaction of thiobisnaphthol **1** with PCl₃ in the presence of triethyl amine gives chlorophosphonite, {(-OC₁₀H₆(μ-S)C₁₀H₆O-)}P(Cl) (**2**) in good yield (Scheme 1) [6]. The chlorophosphonite **2** is a moderately air stable white crystalline solid soluble in most of the organic solvents. The ³¹P NMR spectrum of **2** consists of a single resonance at 172.3 ppm. The EI mass spectrum of **2** shows molecular ion peak (*m/z*) at 347.2 corresponding to [M⁺-Cl].

Treatment of two equivalents of **2** with resorcinol in the presence of triethyl amine at 0 °C afforded the bisphosphite [(-OC₁₀H₆(μ-S)C₁₀H₆O-)P(-OC₆H₄O-)P(-OC₁₀H₆(μ-S)C₁₀H₆O-)] (**3**) in almost quantitative yield (Scheme 1). The ³¹P NMR spectrum of **3** shows a single resonance at 118.6 ppm. The structure and

* Corresponding author. Tel.: +91 22 2576 7181; fax: +91 22 2576 7152x2572 3480.

E-mail addresses: krishna@chem.iitb.ac.in, iitb_msb@yahoo.com (M.S. Balakrishna).



Scheme 1. Conditions: (i) PCl_3 , Et_3N , THF; (ii) Resorcinol, Et_3N , THF.

molecular composition of ligand **3** was further confirmed by ^1H NMR data, elemental analysis and single crystal X-ray structure determination.

2.2. Copper and gold derivatives

Treatment of bisphosphite **3** with one equivalent of CuCl in a mixture of dichloromethane/acetonitrile resulted in the formation of a Cu^{I} coordination polymer $[\text{CuCl}\{(-\text{OC}_{10}\text{H}_6(\mu\text{-S})\text{C}_{10}\text{H}_6\text{O}-)\text{P}(-\text{OC}_6\text{H}_4\text{O}-)\text{P}(-\text{OC}_{10}\text{H}_6(\mu\text{-S})\text{C}_{10}\text{H}_6\text{O}-))\text{-}\kappa\text{P},\kappa\text{P}}]_{\infty}$ (**4**) as an insoluble white solid. Spectroscopic studies could not be carried out because of the poor solubility of **4** in most of the organic solvents; however, the structural composition was established by elemental analysis data and further confirmed by single crystal X-ray diffraction study. The reaction between **3** and two equivalents of $\text{AuCl}(\text{SMe}_2)$ in dichloromethane at room temperature produced the binuclear complex, $[\text{Au}_2\text{Cl}_2\{(-\text{OC}_{10}\text{H}_6(\mu\text{-S})\text{C}_{10}\text{H}_6\text{O}-)\text{P}(-\text{OC}_6\text{H}_4\text{O}-)\text{P}(-\text{OC}_{10}\text{H}_6(\mu\text{-S})\text{C}_{10}\text{H}_6\text{O}-))\text{-}\kappa\text{P},\kappa\text{P}}]$ (**5**) with ligand exhibiting the bridged bidentate mode of coordination (Scheme 2). The ^{31}P NMR spectrum of complex **5** shows a single resonance at 107 ppm. Further evidence for the molecular composition of complex **5** comes from the elemental analysis, ^1H NMR data and single crystal X-ray structure.

2.3. Crystal structures of compounds 3–5

Perspective views of ligand **3** and complexes **4**, **5** with atom numbering schemes are shown in Figs. 1–3, respectively. The crystallographic data and the details of the structure determinations are given in Table 1, while the selected bond lengths and bond angles appear in Table 2.

In the molecular structure of ligand **3** there is an intramolecular π - π interaction between the two naphthyl rings bonded through O_2 and O_4 atoms. Similar to the aminophosphonite and phosphonite ligands containing eight membered heterocycles reported by

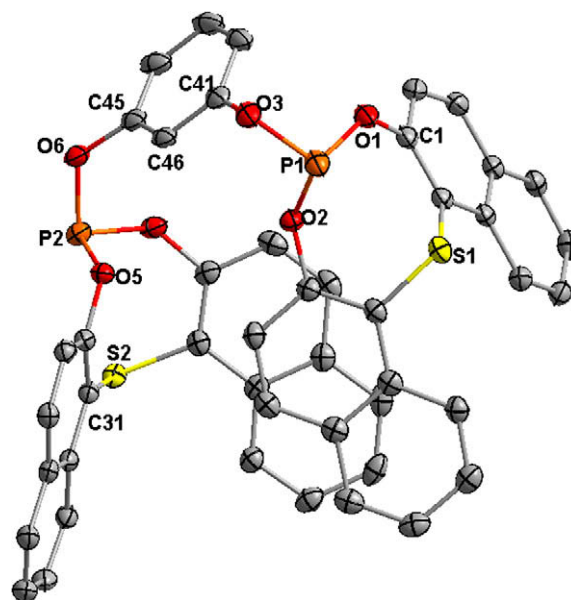
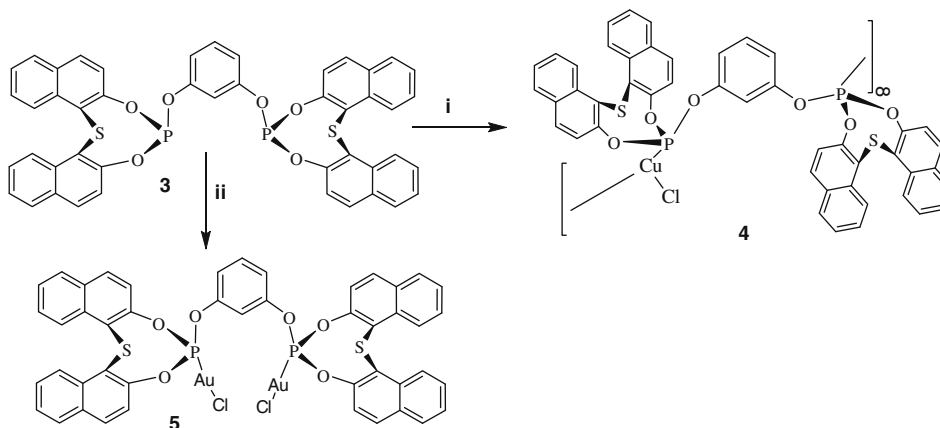


Fig. 1. Molecular structure of **3**. All hydrogen atoms have been omitted for clarity.

Punji et al., the ligand **3** contains two cyclic phosphite units in which because of P–S interaction the geometry around the phosphorus atoms displaces from pyramidal to a pseudotrigonal bipyramidal [6–9]. Very similar displacements were earlier observed, where varying degree of sulfur coordination to phosphorus resulted in structural displacements from square pyramidal to octahedral [11]. Both the eight membered rings contain phosphorus and sulfur atoms in a boat like *syn* conformation. The P...S distances 2.991(1) and 2.990(1) Å are comparable with those in similar structures, $\text{PhN}\{\text{P}(-\text{OC}_{10}\text{H}_6(\mu\text{-S})(\text{C}_{10}\text{H}_6\text{O}))_2\}_2$, $\{-\text{OC}_{10}\text{H}_6-$



Scheme 2. Conditions: (i) CuCl , $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$; (ii) $[\text{AuCl}(\text{SMe}_2)]$, CH_2Cl_2 .

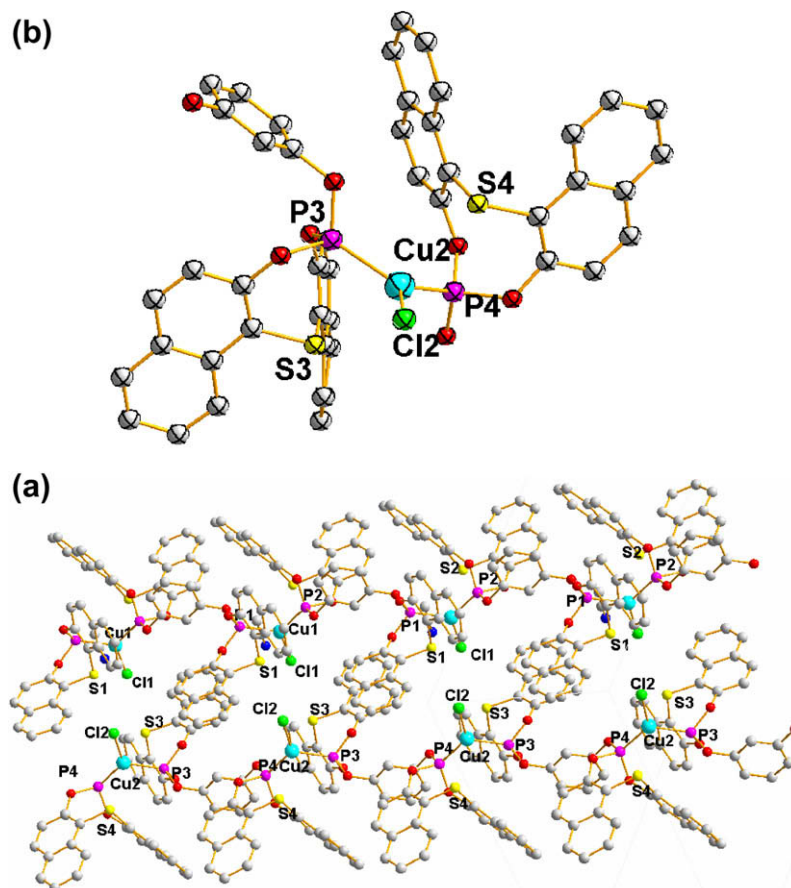


Fig. 2. Molecular structure of **4**. All hydrogen atoms have been omitted for clarity. (a) Single molecule; (b) parallel propagating chains.

(μ -S) $C_{10}H_6O$ -}PNC $_4H_8O$, and $\{-OC_{10}H_6(\mu$ -S) $C_{10}H_6O$ -}PNC $_4H_8NMe$, reported earlier [6,7]. These values are considerably less than the sum of van der Waals radii for phosphorus and sulfur (3.65 Å) but noticeably longer than the sum of their covalent radii (2.12 Å).

Molecular structure of complex **4** consists two chains of one dimensional coordination polymer with alternating ligand and Cu centers. Each of the copper centers is coordinated by two phosphorus atoms of different ligand molecules and one chlorine atom. The bridging mode of coordination is attributed to the bulkiness of the thioether moieties. The geometry around Cu is distorted trigonal planar with, Cl1–Cu1–P1, Cl1–Cu1–P2, Cl2–Cu2–P3, and Cl2–Cu2–P4 bond angles of 113.80(8), 126.19(8), 113.52(8), and 128.21(9)°, respectively. The sulfur atoms connecting the naphthalene groups are approaching towards the Cu center through axial positions with separation of 2.955(2), 3.039(2), 3.007(2) and 3.014(1) Å for Cu1–S1, Cu1–S2, Cu2–S3, and Cu2–S4, respectively. All these values are considerably less than the sum of van der Waals radii which clearly indicates the presence of strong Cu...S interactions. Here the intermolecular π - π interaction between the two naphthyl rings is probably responsible for the growth of polymeric chains parallel to each other. The P1...S1 (2.991(1) Å) and P2...S2 (2.990(1) Å) distances are comparable with those in the ligand **3**.

Similar to the ligand **3**, in complex **5**, the phosphorus and sulfur atoms in the eight membered rings adopt a boat like conformation with mentioned atoms *syn* to each other. The P...S distances of 3.113(1) Å (P₁–S₁) and 3.137(1) Å (P₂–S₂) are quite larger in comparison to those of the ligand. In gold complex, the P...P distance (6.336(1) Å) is found to be more compared to the same in bisphosphite ligand **3** (5.942(1) Å). The Au centers adopt approxi-

mately linear geometry with P–Au–Cl angle of 176.96(6)°. The structure depicts the intermolecular aurophilic interaction with a Au...Au distance 3.124 Å which is less than sum of the van der Waals radii (3.6 Å). This interaction resulted in the formation a dimeric 14-membered macrocycle as shown in Fig. 3. Several such reports are there for the self assembly of gold(I) compounds because of the existence of Au...Au aurophilic interactions, which is having strength comparable to Hydrogen bonding (7–11 kcal/mol) [12]. Theory suggests that these Au...Au interactions arise from the relativistic London forces, with relative strength predicted to increase with the softness of ligands [13].

3. Conclusions

A resorcinol based new bisphosphite ligand (**2**) containing mesocyclicthioether groups is synthesized and its copper(I) and gold(I) complexes are reported. Surprisingly, the reaction between **2** and CuX gives exclusively the 1D-coordination polymer **4** with ligand involving two phosphorus atoms and one of the sulfur atoms in an alternating fashion. The dinuclear gold(I) complex **5** shows strong intermolecular Au...Au interactions with a Au...Au distance of 3.124 Å. The ligand **2** with 1,3-resorcinol moiety bridging the two phosphorus centers can also function as a pincer ligand through phenyl C–H activation. It would be interesting to make a pincer complex as there are four soft donor (2Ps and 2Ss) centers; with sulfur atoms functioning as switching ligands, such complexes may find useful application in organic synthesis. The work in this direction is in progress.

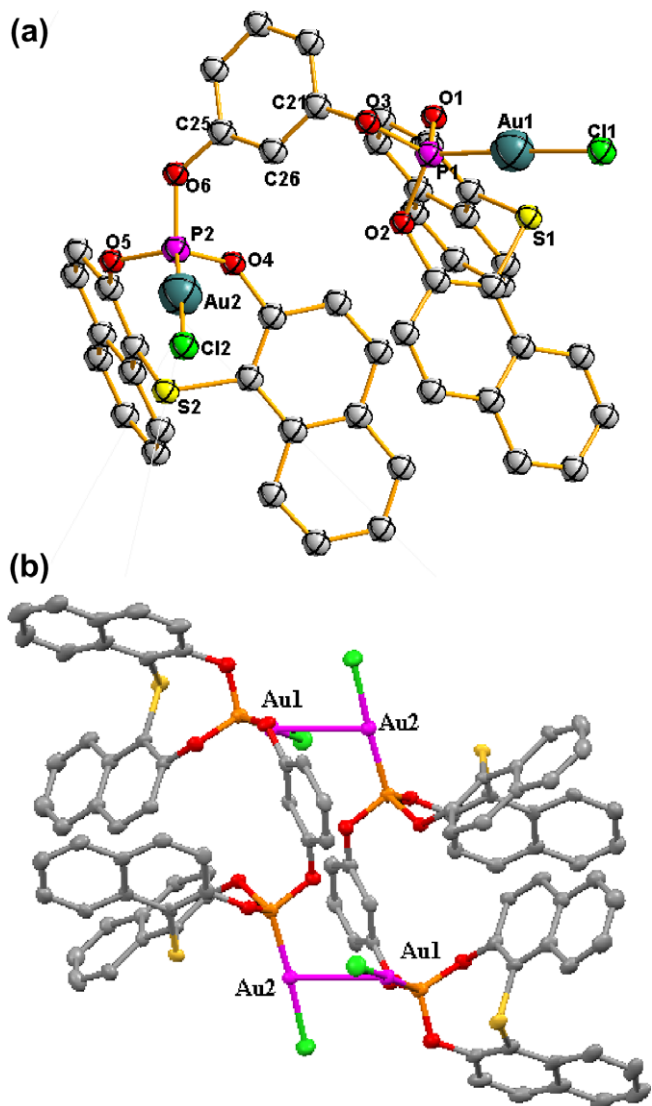


Fig. 3. (a) Molecular structure of **5**. All hydrogen atoms have been omitted for clarity. (b) Two molecules with intermolecular Au–Au interaction.

4. Experimental

All experimental manipulations were carried out under an atmosphere of dry nitrogen or argon using Schlenk techniques. Solvents were dried and distilled prior to use by conventional methods. The metal precursor $\text{AuCl}(\text{SMe}_2)$ [14] was prepared according to the published procedures. Other reagents were used as obtained from commercial sources. The ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR (δ in ppm) spectra were obtained on a Varian VRX 400 spectrometer operating at frequencies of 400 and 162 MHz, respectively. The spectra were recorded in CDCl_3 solutions with CDCl_3 as an internal lock; TMS and 85% H_3PO_4 were used as internal and external standards for ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR, respectively. Positive shifts lie downfield of the standard in all of the cases. Microanalyses were carried out on a Carlo Erba (Model 1106) elemental analyzer. Mass spectrum was recorded using Waters Q-ToF micro (YA-105) instrument. Melting points of all compounds were determined on Veego melting point apparatus and were uncorrected.

4.1. Synthesis of chlorophosphite $\{-\text{OC}_{10}\text{H}_6(\mu\text{-S})\text{C}_{10}\text{H}_6\text{O}-\}\text{P}(\text{Cl})$ (**2**)

A solution of PCl_3 (0.65 ml, 7.5 mol) in 15 ml THF was added dropwise to a solution of thiobis(2,2'-naphthol) (**1**) (1.5 g,

4.7 mmol) in THF (40 ml) at -20°C , followed by the addition of Et_3N (1.96 ml, 14.1 mmol) and a catalytic amount of DMAP in THF (15 ml). The reaction mixture was warmed to room temperature and stirred for 14 h. The solvent was removed under reduced pressure and white residue obtained was dissolved in 30 ml of toluene and filtered through celite to remove $\text{Et}_3\text{N}\cdot\text{HCl}$ salt. The filtrate obtained was concentrated under reduced pressure and kept at -25°C to give white crystalline product of **2**. It was recrystallized from a mixture of CH_2Cl_2 /petroleum ether (bp $60\text{--}80^\circ\text{C}$) to give colorless crystals of X-ray quality at -25°C . Yield: 90% (1.62 g). m.p.: $138\text{--}140^\circ\text{C}$. *Anal.* Calc. for $\text{C}_{20}\text{H}_{12}\text{ClO}_2\text{PS}$: C, 62.75; H, 3.16; S, 8.38. Found: C, 62.55; H, 3.08; S, 8.29%. ^1H NMR (400 MHz, CDCl_3): δ 8.72 (d, 2H, Ar, $^3J_{\text{HH}} = 8.8$ Hz), 7.75 (t, 2H, Ar, $^3J_{\text{HH}} = 7.6$ Hz), 7.54–7.58 (m, 4H, Ar), 7.41 (t, 2H, Ar, $^3J_{\text{HH}} = 7.6$ Hz), 7.25 (d, 2H, Ar, $^3J_{\text{HH}} = 8.8$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ 172.3 (s). MS (EI): m/z 347.2 ($\text{M}^+ - \text{Cl}$).

4.2. Synthesis of bisphosphite

$2,6\text{-C}_6\text{H}_4\{\text{OP}(\text{OC}_{10}\text{H}_6(\mu\text{-S})\text{C}_{10}\text{H}_6\text{O}-)\}_2$ (**3**)

A solution of chlorophosphite **1** (1.5 g, 3.92 mmol) in THF (20 ml) was added dropwise to a solution of resorcinol (0.21 g, 1.96 mmol) in THF (20 ml) at 0°C . After 10 min of continuous stirring, Et_3N (0.59 ml, 4.31 mmol) in THF (10 ml) was added dropwise to the reaction mixture and the solution was warmed to room temperature and stirred for 14 h. The solvent was removed under reduced pressure and the white residue obtained was dissolved in 40 ml of toluene and $\text{Et}_3\text{N}\cdot\text{HCl}$ was removed by filtration. The clear solution was concentrated and cooled to -25°C to give analytically pure product of **2** as colorless crystals. Yield: 86% (1.35 g). m.p.: $183\text{--}185^\circ\text{C}$ (dec). *Anal.* Calc. for $\text{C}_{46}\text{H}_{28}\text{O}_6\text{P}_2\text{S}_2$: C, 68.82; H, 3.52; S, 7.99. Found: C, 67.92; H, 3.19; S, 7.05%. ^1H NMR (400 MHz, CDCl_3): δ 8.63 (d, 4H, Ar, $^3J_{\text{HH}} = 8.5$ Hz), 7.12–7.52 (m, 16H, Ar), 6.67 (d, 4H, Ar, $^3J_{\text{HH}} = 8.8$ Hz), 6.53 (d, 4H, CH_2 , $^3J_{\text{PH}} = 8.8$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ 118.6 (s).

4.3. Synthesis of

$[\text{CuCl}\{2,6\text{-C}_6\text{H}_4\{\text{OP}(\text{OC}_{10}\text{H}_6(\mu\text{-S})\text{C}_{10}\text{H}_6\text{O}-)\}_2\}\text{KP},\kappa\text{P},\kappa\text{S}]$ (**4**)

A solution of bisphosphite **2** (0.042 g, 0.052 mmol) in CH_2Cl_2 (7 ml) was added dropwise to a solution of CuCl (0.0051 g, 0.052 mmol) in CH_3CN (4 ml) and the mixture was stirred at room temperature for 1 h. The white product precipitated out was separated by filtration and dried under vacuum. The crystals suitable for X-ray analysis were grown by slow addition of a CH_2Cl_2 solution of **2** to CuCl in CH_3CN at room temperature without stirring over a period of 24 h. Yield: 88% (0.044 g). m.p.: 215°C (dec). *Anal.* Calc. for $\text{C}_{48}\text{H}_{36}\text{ClO}_6\text{P}_2\text{S}_2\text{Cu}$: C, 61.73; H, 3.89; S, 6.87. Found: C, 61.61; H, 3.79; S, 6.77%.

4.4. Synthesis of

$[\text{Au}_2\text{Cl}_2\{2,6\text{-C}_6\text{H}_4\{\text{OP}(\text{OC}_{10}\text{H}_6(\mu\text{-S})\text{C}_{10}\text{H}_6\text{O}-)\}_2\}\kappa\text{P},\kappa\text{P}]$ (**5**)

A solution of bisphosphite **2** (0.040 g, 0.049 mmol) in CH_2Cl_2 (8 ml) was added dropwise to a solution of $\text{AuCl}(\text{SMe}_2)$ (0.0293 g, 0.099 mmol) in CH_2Cl_2 (6 ml) and the mixture was stirred at room temperature for 3 h. The resulting solution was concentrated to 3 ml, layered with petroleum ether (0.5 mL), which on cooling to -25°C gave complex **5** as analytically pure colorless crystals. Yield: 88% (0.055 g). m.p.: 192°C (dec). *Anal.* Calc. for $\text{C}_{46}\text{H}_{28}\text{Cl}_2\text{O}_6\text{P}_2\text{S}_2\text{Au}_2$: C, 43.58; H, 2.23; S, 5.06. Found: C, 43.39; H, 2.25; S, 4.96%. ^1H NMR (400 MHz, CDCl_3): δ 8.70 (d, 4H, Ar, $^3J_{\text{HH}} = 8.5$ Hz), 7.64 (d, 1H, Ar, $^3J_{\text{HH}} = 1.5$ Hz), 7.30 (t, 1H, Ar, $^3J_{\text{HH}} = 1.5$ Hz), 7.61 (d, 1H, Ar, $^3J_{\text{HH}} = 1.5$ Hz), 7.49–7.34 (m, 13H, Ar), 7.17 (d, 4H, Ar, $^3J_{\text{HH}} = 8.8$ Hz), 6.69 (d, 4H, Ar, $^3J_{\text{HH}} = 8.8$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ 107.0 (s).

Table 1
Crystallographic Data for Compounds **3–5**.

Compound	3	4	5
Empirical formula	C ₄₆ H ₂₈ O ₆ P ₂ S ₂ ·C ₄ H ₈ O	C ₄₆ H ₂₈ ClCuO ₆ P ₂ S ₂ 0.25CH ₂ Cl ₂ , 1.5C ₂ H ₃ N	C ₄₆ H ₂₈ Au ₂ Cl ₂ O ₆ P ₂ S ₂
Formula weight	874.85	984.55	1267.58
Crystal system	Monoclinic	Orthorhombic	Triclinic
Crystal size (mm)	0.16 × 0.18 × 0.30	0.08 × 0.08 × 0.21	0.04 × 0.07 × 0.20
Space group	<i>P2₁/c</i> (no. 14)	<i>Pca2₁</i> (no. 29)	<i>P1</i> (no. 2)
<i>a</i> (Å)	7.285(1)	38.004(4)	10.069(2)
<i>b</i> (Å)	25.176(2)	10.453(1)	14.342(2)
<i>c</i> (Å)	22.492(2)	21.736(3)	18.586(3)
α (°)	90	90	70.976(2)
β (°)	98.935(1)	90	79.141(2)
γ (°)	90	90	75.290(2)
<i>V</i> (Å ³)	4075.0(6)	8635.0(2)	2437.8(7)
<i>Z</i>	4	8	2
ρ_{calc} (g cm ⁻³)	1.426	1.515	1.727
μ (Mo K α) (mm ⁻¹)	0.266	0.824	6.315
<i>F</i> (0 0 0)	1816	4028	1212
Temperature (K)	100	100	100
θ (minimum, maximum) (°)	2.5, 28.3	1.4, 26.4	2.1, 28.4
Goodness-of-fit (GOF) on (<i>F</i> ²)	1.08	1.09	1.06
Total number of reflections	10126	17718	11998
Number of independent reflections	8496 (<i>R</i> _{int} = 0.041)	13250 (<i>R</i> _{int} = 0.079)	9779 (<i>R</i> _{int} = 0.050)
<i>R</i> ₁ ^a	0.0396	0.0704	0.0473
<i>wR</i> ₂ ^b	0.0909	0.1610	0.1336

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$.^b $R_w = \{[\sum w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2\}^{1/2}$ $w = 1/[\sigma^2(F_o^2) + (AP)^2]$ where $P = (F_o^2 + F_c^2)/3$.**Table 2**
Selected bond distances (Å) and bond angles (°) for compounds **3–5**.

3	4	5			
P1–O3	1.641(1)	Au1–Cl1	2.279(2)	Cu1–Cl1	2.218(2)
P2–O6	1.632(1)	Au2–Cl2	2.273(1)	Cu1–S1	2.955(2)
S1–C10	1.770(2)	Au1–P1	2.197(11)	Cu1–P1	2.196(2)
S1–C20	1.776(2)	Au2–P2	2.194(1)	Cu1–S2	3.039(2)
S2–C22	1.778(2)	Au1–Au2	3.124(5)	Cu1–P2	2.200(2)
S2–C40	1.770(2)	S1–C20	1.794(6)	Cu2–Cl2	2.209(2)
O3–P1–O2	96.50(7)	S1–C10	1.766(6)	Cu2–S3	3.007(2)
O3–P1–O1	96.60(7)	S2–C46	1.773(7)	Cu2–P3	2.222(2)
O6–P2–O4	96.57(6)	S2–C36	1.788(6)	Cu2–S4	3.014(2)
O6–P2–O5	97.48(6)	P2–Au2–Cl2	176.64(6)	Cu2–P4	2.204(2)
C41–O3–P1	122.82(11)	P1–Au1–Cl1	176.96(6)	P1–Cu1–Cl1	113.80(8)
C45–O6–P2	125.65(11)	O3–P1–O1	100.9(2)	P2–Cu1–Cl1	126.19(8)
		O3–P1–O2	101.2(2)	P3–Cu2–Cl2	113.52(8)
		O6–P2–O4	98.2(2)	P4–Cu2–Cl2	128.21(9)
		O6–P2–O5	98.8(2)	Cu1–P1–O3	118.4(2)
		C25–O6–P2	126.6(3)	Cu1–P2–O6	118.0(2)
		C21–O3–P1	120.8(3)	Cu2–P3–O9	117.2(2)
				Cu2–P4–O12	117.2(2)

5. X-ray crystallography

Crystals of **3**, **4**, and **5** were mounted in a Cryoloop with a drop of Paratone oil and placed in the cold nitrogen stream of the Kryoflex attachment of the Bruker APEX charge-coupled device (CCD) diffractometer. A full sphere of data was collected using 606 scans in ω (0.3° per scan) at $\phi = 0, 120$, and 240° using the SMART software package [15]. The raw data were reduced to *F*² values using the SAINT+ software [16], and a global refinement of unit cell parameters using 3832–9997 reflections chosen from the full data set was performed. Multiple measurements of equivalent reflections provided the basis for an empirical absorption correction as well as a correction for any crystal deterioration during the data collection (SADABS) [17]. The structures were solved by direct methods and refined by full-matrix least-squares procedures using the SHELXTL program package [18]. Hydrogen atoms were placed in calculated positions and included as riding contributions with isotropic displacement parameters tied to those of the attached non-hydrogen atoms.

Supplementary material

CCDC 749084, 749086 and 749085 contain the supplementary crystallographic data for **3**, **4** and **5**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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