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Group 11 Metal Complexes of the Mesocyclic Thioether Aminophosphonites [-OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O-]PNC$_4$H$_8$E (E = O, NMe)

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Group 11 metal complexes of the mesocyclic thioether aminophosphonites [-OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O-]PNC$_4$H$_8$E {**2a**: E = O; **2b**: E = NMe; IUPAC names: 4-(dinaphtho[2,1-*d*:1′,2′-*g*][1,3,6,2]dioxathiaphosphocin-4-yl)morpholine (**2a**), 1-(dinaphtho[2,1-*d*:1′,2′-*g*][1,3,6,2]dioxathiaphosphocin-4-yl)-4-methylpiperazine (**2b**)} are reported. Thioether aminophosphonites **2a** and **2b** react with CuX (X = Cl, Br, and I) in a 1:1 molar ratio to give the tricoordinate, dimeric complexes [{[{-OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O-}PNC$_4$H$_8$E-κ*P*]Cu(μ-X)}$_2$] (**4a**: E = O, X = Cl; **4b**: E = NMe, X = Cl; **5a**: E = O, X = Br; **5b**: E = NMe, X = Br; **6a**: E = O, X = I; **6b**: E = NMe, X = I), whereas with 2:1 molar ratios monomeric complexes of the type [{[-OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O-]PNC$_4$H$_8$O-κ*P*}$_2$CuX] (**7a**: E = O, X = Cl; **7b**: E = NMe, X = Cl; **8a**: E = O, X = Br; **8b**: E = NMe, X = Br; **9a**: E = O, X = I; **9b**: E = NMe, X = I) are obtained in excellent yield. The P,S-chelated cationic complexes [{[-OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O-]PNC$_4$H$_8$E-κ*P*,κ*S*}$_2$Cu]BF$_4$ (**10a**: E = O; **10b**: E = NMe) are obtained when **2a** and **2b** are treated with half an equivalent of [(MeCN)$_4$Cu]BF$_4$. Similarly, the silver complexes [{[{-OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O-}PNC$_4$H$_8$E-κ*P*,κ*S*]-AgCF$_3$SO$_3$}$_2$] (**11a**: E = O: **11b**: E = NMe) and [{[-OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O-]PNC$_4$H$_8$E-κ*P*,κ*S*}Ag(PPh$_3$)]CF$_3$SO$_3$ (**12a**: E = O; **12b**: E = NMe) are synthesized by the treatment of thioether aminophosphonites **2a** and **2b** with AgOTf and [Ag(PPh$_3$)][OTf], respectively. Reactions of **2a** and **2b** with [AuCl(SMe$_2$)] produce the simple monomeric gold(I) complexes [{[-OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O-]PNC$_4$H$_8$E-κ*P*}AuCl] (**13a**: E = O; **13b**: E = NMe). The iodo derivatives [{[-OC$_{10}$H$_6$(μ-S)-C$_{10}$H$_6$O-]PNC$_4$H$_8$E-κ*P*}AuI] (**14a**: E = O; **14b**: E = NMe) are obtained by the halide-exchange reaction of **13a** and **13b** with CuI at room temperature. The structures of complexes **5a**, **7a**, **8a**, **13a**, **13b**, and **14a** are confirmed by single-crystal X-ray diffraction studies. In all of these complexes, the sulfur atom in the mesocyclic ring shows coordinative interaction towards the phosphorus atom, and in **5a**, **7a**, **8a**, and **14a** towards the metal center as well.

Introduction

In recent years, complexes of mixed-donor ligands have been found to be more advantageous than those of ligands having only one type of donor atom because of their catalytic potential in various organic transformations.[1] In principle, those ligands containing donor atoms with different binding abilities are ideally suited to provide temporary coordinative saturation to the metal center via chelation until it is required to furnish an active site at the metal center prior to oxidative addition, an important step in homogeneous catalysis. Among various mixed-donor ligands of the type P,O,[2] P,N,[3] and P,S,[4] ligands combining phosphorus and sulfur centers are especially interesting. Both phosphorus and sulfur are excellent donor atoms for a wide range of metals while the low ionization energy of sulfur and the existence of several lone pairs of electrons (three in the case of a thiolate anion) offer the possibility of a rich sulfur-based chemistry of the complexes. Although, the coordination chemistry of P,S ligands with various transition metal derivatives has been well studied and some complexes have proved to be active catalysts,[5] P,S ligand chemistry with the group 11 metals is limited. Of the few complexes of mixed P,S donor ligands with group 11 metal derivatives that are known, some show excellent catalytic activity and offer interesting structural features (only P or both P and S coordination), and some bimetallic complexes show metallophilic interactions that can make them ideal candidates for luminescence studies.[6]

We recently reported the synthesis of the mesocyclic mixed P,S ligands **2a** and **2b**, which exhibit an interesting coordination behavior towards palladium and platinum derivatives that results in cationic, anionic (**3a**, **3b**), and neutral complexes (Scheme 1).[7] In all compounds, the sulfur atom present as part of an eight-membered thioether aminophosphonite ring system shows a coordinative interaction with phosphorus, which creates a pseudo trigonal bipyramidal (TBP) geometry at the phosphorus center. All the palladium complexes synthesized are promising catalysts for Suzuki cross-coupling reactions, with the anionic complexes **3a** and **3b** being particularly active (TONs of up to 92000). Since group 11 metal complexes of P,S ligands are

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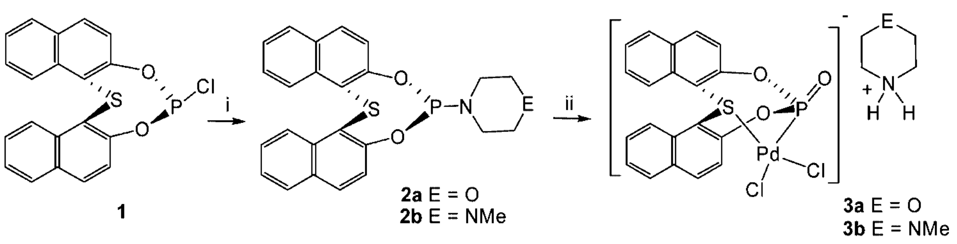


i: morpholine or *N*-methylpiperazine; ii: $(PhCN)_2PdCl_2/H_2O$(trace)

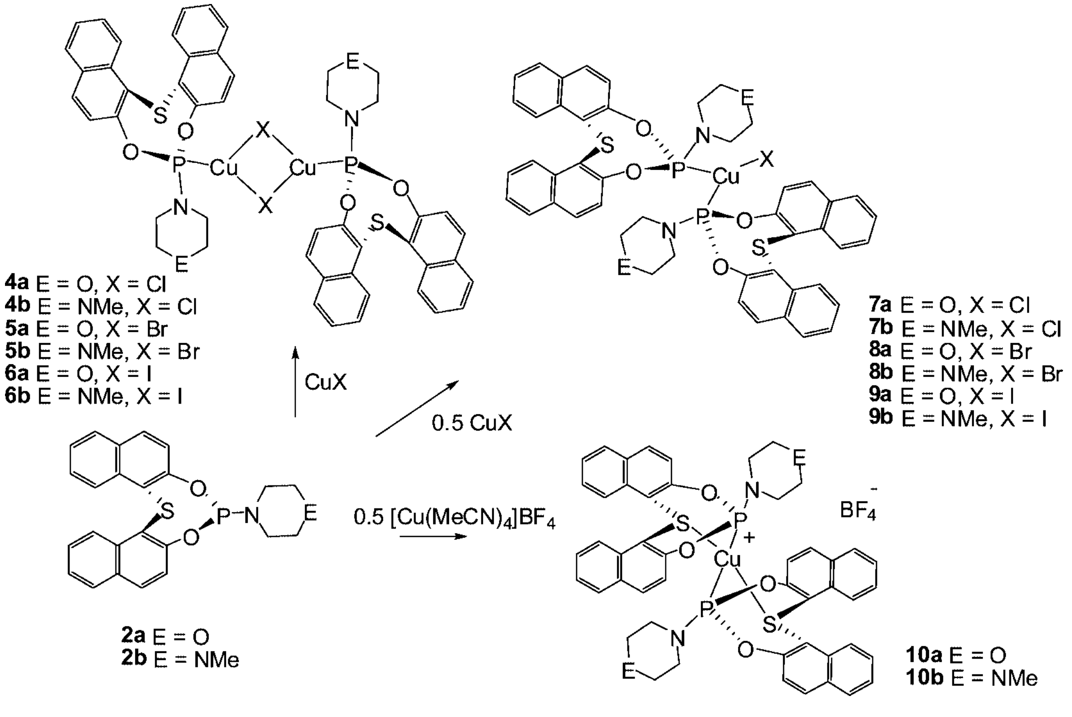
Scheme 1.

few in number, we sought to examine the reactivity of these thioether aminophosphonites with the group 11 metals. As part of our interest in organometallic chemistry[8] and catalytic investigations,[7,9] we report here on the reactivity of the mesocyclic thioether aminophosphonites **2a** and **2b** with group 11 metal centers as well as halide-exchange reactions of gold(I) complexes. X-ray structures of copper(I) (**5a**, **7a**, **8a**) and gold(I) (**13a**, **13b**, **14a**) complexes are also described.

Results and Discussion

Synthesis of Copper(I) Complexes

Treatment of thioether aminophosphonites **2a** and **2b** with one equivalent of CuX (X = Cl, Br, and I) in dichloromethane/acetonitrile mixtures leads to the formation of the halide-bridged dinuclear Cu^I complexes $[\{[\{\text{-}OC_{10}H_6(\mu\text{-}S)\text{-}C_{10}H_6O\text{-}\}PNC_4H_8E\text{-}\kappa P]Cu(\mu\text{-}X)\}_2]$ (**4a**: E = O, X = Cl; **4b**: E = NMe, X = Cl; **5a**: E = O, X = Br; **5b**: E = NMe, X = Br; **6a**: E = O, X = I; **6b**: E = NMe, X = I) in good yields, as shown in Scheme 2. Both the chloro derivatives (**4a** and **4b**) and iodo derivative **6b** precipitated from the reaction mixture as white insoluble solids, whereas the remaining complexes (**5a**, **5b**, and **6a**) crystallize from the mother liquor either at –25 °C or at room temperature. Most of the complexes (except for **4a** and **6b**) are soluble only in DMSO, which allows us to carry out spectroscopic studies. The ^{31}P NMR spectra of complexes **4b**, **5a**, **5b**, and **6a** show single resonances at δ = 114.4, 113.3, 110.5, and 110.4 ppm, respectively. In the ^1H NMR spectra of these complexes, two broad singlets are observed in the region δ = 2.49–3.71 ppm for the CH_2 protons of the morpholine and piperazine moieties. The mass spectrum of complex **5a** shows two peaks at *m*/*z* 576.0 and 496.0 for the ions corresponding to $[M^+ - (\mathbf{2a} + CuBr)]$ and $[M^+ - (\mathbf{2a} + CuBr_2)]$, respectively. Spectroscopic studies on complexes **4a** and **6b** could not be carried out because of their poor solubility in most organic solvents; however, their chemical compositions were established by elemental analysis. The molecular structure of complex **5a** was confirmed by a single-crystal X-ray diffraction study.



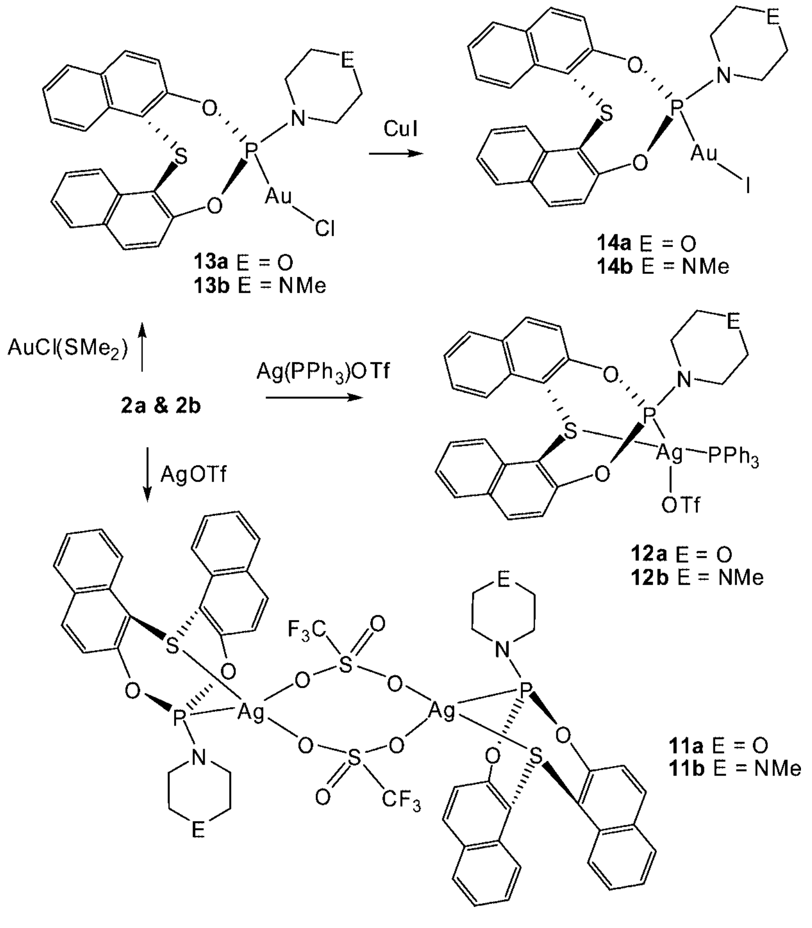
Scheme 2.

The reactions of **2a** with CuX (X = Cl, Br, and I) in a 2:1 ratio in dichloromethane afford the tricoordinate mononuclear complexes $[\{[\text{-OC}_{10}\text{H}_6(\mu\text{-S})\text{C}_{10}\text{H}_6\text{O-}]\text{PNC}_4\text{H}_8\text{O-}\kappa P\}_2\text{CuX}]$ (**7a**: X = Cl; **8a**: X = Br; **9a**: X = I; Scheme 2). The ^{31}P NMR spectra of complexes **7a**, **8a**, and **9a** show single resonances at δ = 115.8, 112.3, and 111.8 ppm, respectively. In the ^{1}H NMR spectra of these complexes, two broad singlets are observed in the region δ = 3.29–3.66 ppm for the CH_2 protons of the morpholine moiety, although two distinct triplets (δ = 3.41 and 3.79 ppm) are observed for ligand **2a**. Similarly, the reactions of **2b** with half an equivalent of CuX (X = Cl, Br, and I) produce the mononuclear complexes $[\{[\text{-OC}_{10}\text{H}_6(\mu\text{-S})\text{C}_{10}\text{H}_6\text{O-}]\text{PNC}_4\text{H}_8\text{NCH}_3\text{-}\kappa P\}_2\text{CuX}]$ (**7b**: X = Cl; **8b**: X = Br; **9b**: X = I) in good yields The chloro and bromo derivatives precipitate during the course of reaction while the iodo derivative crystallizes from the mother liquor. The ^{31}P NMR spectra of complexes **7b**, **8b**, and **9b** show single resonances at δ = 112.2, 113.4, and 116.9 ppm, respectively. Further support for the structural composition of these complexes comes from their ^{1}H NMR spectra and elemental analyses, while single-crystal X-ray structure determinations established the structures of complexes **7a** and **8a**.

Surprisingly, ligands **2a** and **2b** in the above complexes (**4a**–**9b**) are monodentate with only phosphorus coordination and do not form chelate rings with the P and S centers despite these centers being in close proximity [P···S nonbonding distances in **2a** and **2b** are 3.089(1) and 3.040(1) Å, respectively].[7] However, the P,S-chelated cationic complexes $[\{[\text{-OC}_{10}\text{H}_6(\mu\text{-S})\text{C}_{10}\text{H}_6\text{O-}]\text{PNC}_4\text{H}_8\text{O-}\kappa P,\kappa S\}_2\text{Cu}]\text{BF}_4$ (**10a**) and $[\{[\text{-OC}_{10}\text{H}_6(\mu\text{-S})\text{C}_{10}\text{H}_6\text{O-}]\text{PNC}_4\text{H}_8\text{NCH}_3\text{-}\kappa P,\kappa S\}_2\text{Cu}]\text{BF}_4$ (**10b**) are formed when ligands **2a** and **2b** are treated with half an equivalent of $[\text{Cu(MeCN)}_4]\text{BF}_4$, as shown in Scheme 2. Both these complexes are moderately stable in the solid state but decompose slowly in solution. The ^{31}P NMR spectra of complexes **10a** and **10b** show single resonances at δ = 112.2 and 113.7 ppm, respectively. The mass spectrum of complex **10a** shows peaks at *m*/*z* 929.1 and 496.0 for the ions $[\text{M}^+ - \text{BF}_4]$ and $[\text{M}^+ - (\textbf{2a} + \text{BF}_4)]$, respectively. Similarly, for complex **10b** peaks are observed at *m*/*z* 955.2 and 509.1 for the ions $[\text{M}^+ - \text{BF}_4]$ and $[\text{M}^+ - (\textbf{2b} + \text{BF}_4)]$, respectively.

Synthesis of Silver(I) Complexes

Treatment of thioether aminophosphonites **2a** and **2b** with one equivalent of AgOTf gives complexes with the composition [(**2a**)Ag(OTf)] (**11a**) and [(**2b**)Ag(OTf)] (**11b**), respectively. These complexes are highly light sensitive in solution, whereas they are moderately stable in the solid state. In the room-temperature ^{31}P NMR spectrum of com-



Scheme 3.

plex **11b**, two broad resonances separated by about 594 Hz are observed centered at δ = 123.3 ppm, while one broad singlet is observed at δ = 118.8 ppm for complex **11a**. Previous ^{31}P NMR studies of phosphane and phosphite complexes of Ag^{I} salts involving both coordinating and noncoordinating anions[6d,10] have shown the existence of ligand dissociation and/or exchange processes at or below room temperature that lead to broad resonances due to the loss of the expected $^{1}J_{Ag,P}$ couplings. Typically, the low-temperature limiting spectra consist of two doublets for each group of chemically equivalent phosphorus nuclei due to coupling with both ^{109}Ag and ^{107}Ag. Unfortunately, due to the poor solubility and stability of **11a** and **11b**, low-temperature NMR studies could not be carried out, so that while with **11a** there is probably only one phosphorus environment, in the case of **11b** it is not clear whether there are two different phosphorus environments or simply one where the dynamic process occurring is sufficiently slow that an average $^{1}J_{Ag,P}$ coupling is observed. Structural studies of the silver complexes of another P,S ligand [Fc(PPh$_2$)(SPh)] show a preference for a four-coordinate tetrahedral geometry.[6d] Although only tentatively because of the limited data available, we suggest that complexes **11a** and **11b** contain a chelating P,S ligand and are either monomeric with a bidentate trifluoromethanesulfonate or dinuclear with bridging trifluoromethanesulfonate ligands. Similarly, the P,S chelated complexes [{[-OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O-]-PNC$_4$H$_8$E-κ*P*,κ*S*}Ag(PPh$_3$)]CF$_3$SO$_3$ (**12a**: E = O; **12b**: E = NMe) can be synthesized by treatment of **2a** and **2b** with [Ag(PPh$_3$)][OTf] in a 1:1 molar ratio. The ^{31}P NMR spectrum of complex **12a** shows two sets of broad doublets centered at δ = 123.9 and 9.7 ppm with $^{1}J_{Ag,P}$ coupling constants of about 512 and 394 Hz for coordinated **2a** and PPh$_3$, respectively. However, the ^{31}P NMR spectrum of complex **12b** shows broad singlets at δ = 130.3 and 8.2 ppm for coordinated **2b** and PPh$_3$, respectively. In the mass spectra of complexes **12a** and **12b**, peaks are observed at *m*/*z* 803.1 and 816.9, respectively, for the ion [M^{+} – CF$_3$SO$_3$]. By analogy with the complex [Ag(PPh$_3$){Fc(PPh$_2$)-(SPh)}(OTf)],[6d] which contains a chelating P,S ligand and coordinated triflate, we propose that **12a** and **12b** are monomeric, four-coordinate species with chelating P,S ligands and monodentate trifluoromethanesulfonate. Further support for the composition of these complexes comes from their ^{1}H NMR spectra and elemental analysis data (Scheme 3).

Synthesis of Gold(I) Complexes

The reactions of thioether aminophosphonites **2a** and **2b** with [AuCl(SMe$_2$)] in dichloromethane afford the mononuclear P-coordinated complexes [{[-OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O-]-PNC$_4$H$_8$E-κ*P*}AuCl] (**13a**: E = O; **13b**: E = NMe). Both complexes are white, crystalline solids and are light sensitive while in solution. Attempt to synthesize three-coordinate gold complexes akin to [(PPh$_3$)$_2$AuCl][11] were unsuccessful and resulted in the formation of complexes **13a** and **13b**. This may be due to the bulkiness of the ligand, with the closeness of the sulfur atom to the gold center (vide infra) preventing another ligand from approaching the gold center. The ^{31}P NMR spectra of complexes **13a** and **13b** show single resonances at δ = 113.1 and 115.3 ppm, respectively. When these complexes are treated with CuI in dichloromethane at room temperature, they undergo halide exchange to form the iodo derivatives [{[-OC$_{10}$H$_6$(μ-S)-C$_{10}$H$_6$O-]PNC$_4$H$_8$E-κ*P*}AuI] (**14a**: E = O; **14b**: E = NMe). The ^{31}P NMR spectra of complexes **14a** and **14b** show singlets at δ = 118.1 and 118.9 ppm, which are considerably deshielded compared to their chloro analogs. The molecular compositions of these complexes (**13a**,**b** and **14a**,**b**) were further confirmed by their ^{1}H NMR spectra, elemental analysis data, and X-ray diffraction studies for complexes **13a**, **13b**, and **14a**. Other groups have also reported similar halogen-exchange reactions of gold complexes with KI at elevated temperature,[12] although halogen exchange of gold(I) complexes with CuI is not known in the literature.

Crystals Structures of Complexes 5a, 7a, 8a, 13a, 13b, and 14a

Perspective views of the molecular structures of compounds **5a**, **7a**, **8a**, **13a**, **13b**, and **14a** with the atom-numbering schemes are shown in Figures 1, 2, 3, 4, 5, and 6, respectively. Selected bond lengths and bond angles for complexes **5a**, **7a**, and **8a** appear in Table 1, whereas those of complexes **13a**, **13b**, and **14a** are listed in Table 2. Crystal data and the details of the structure determinations are given in the Experimental Section.

In the molecular structure of complex **5a**, each of the copper centers is coordinated to one phosphorus center and two bromine atoms and exists as a centrosymmetric dimer. The morpholine rings adopt a chair conformation and the sulfur atoms connecting the naphthalene groups face towards the Cu$_2$Br$_2$ ring with a Cu···S separation of 3.0901(14) Å. As this is less than the sum of the van der Waals radii for copper and sulfur (3.20 Å),[13] there may be a weak Cu···S interaction. The backbones of two aminophosphonite ligands are in the staggered conformation, while the PCu(μ-Br)$_2$CuP unit is almost planar. Several trigonal planar dinuclear copper complexes of this type containing monophosphanes have been well characterized,[14] however those of aminophosphonites or phosphites are rare. The Cu–P bond length [2.171(1) Å] in complex **5a** is comparable with that in the tetrahedral copper complex of the monophosphite 4-nitro,2,6,7-trioxa-1-phosphabicyclo-[2.2.2]octane [Cu–P 2.1683(6) Å].[15] The Cu···Cu and Br···Br distances are 3.108 and 3.758 Å, respectively, indicating a possible weak Cu···Cu interaction. The core angles Cu–Br–Cu$_a$ [79.17(2)°] and Br–Cu–Br$_a$ [100.83(2)°] are significantly distorted from those of the above-mentioned monophosphite complex [Cu–Br–Cu$_a$ 75.183(12); Br–Cu–Br$_a$ 104.817(12)°].[15]

Interestingly, the sulfur atom also appears to show a weak coordinative interaction with phosphorus, as indi-

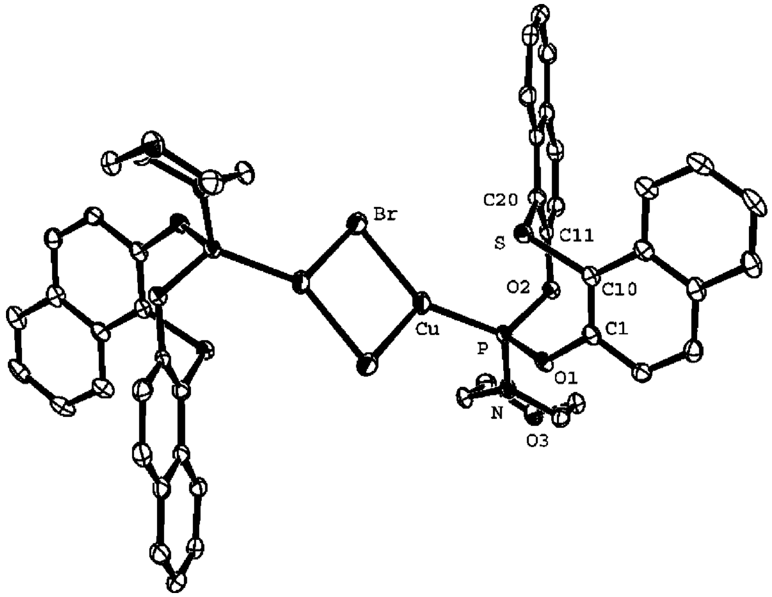


Figure 1. Molecular structure of **5a**. All hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

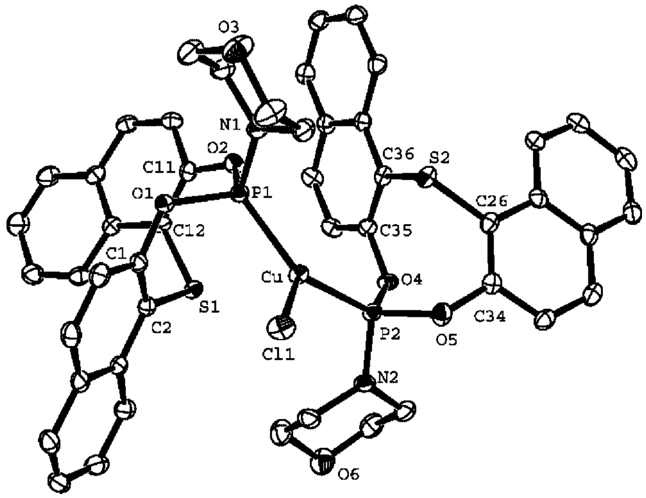


Figure 2. Molecular structure of **7a·CH$_2$Cl$_2$**. Solvent molecules and all hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

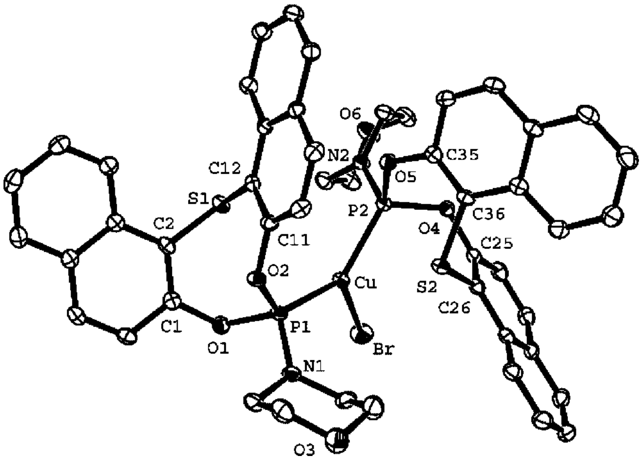


Figure 3. Molecular structure of **8a**. Solvent molecules and all hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

cated by the P···S distance [3.098(2) Å]. This P···S distance is comparable to that observed in our previous report[7] and that of others[16] (see Table 3). While considerably greater than the sum of the covalent radii for sulfur and phosphorus (2.12 Å),[17] this distance is less than the sum of van der Waals radii (3.65 Å)[13] for these two elements. This interaction leads to the structural displacement of phosphorus from pyramidal to a pseudo TBP. The degree to which the TBP is approached can be seen from the axial S–P–R angle and can be quantified by the procedure of Holmes and coworkers.[18] In this procedure, the degree of displacement from pyramidal toward TBP can be calculated by noting how far the P···S distance departs from the sum of the van der Waals radii (3.65 Å) toward the sum of the covalent radii (2.12 Å). For complex **5a** the %TBP displacement is calculated to be 36.1% (Table 3).

The molecular structures of the chloride (**7a**) and bromide (**8a**) complexes are isomorphous; they crystallize in the monoclinic space group $P2_1/n$. In both structures the copper centers are coordinated through two aminophosphonite ligands and a halide ion and exist as monomers. The geometries around the copper center are almost planar. The Cu–P bond lengths in complex **7a** [Cu–P1 2.2062, Cu–P2 2.1897(7) Å] and complex **8a** [Cu–P1 2.1884(6), Cu–P2 2.2063(5) Å] are almost identical. As seen in complex **5a**, the sulfur atoms in complexes **7a** and **8a** show coordinative interaction towards the phosphorus centers [**7a**: S1–P1 3.088(1), S2–P2 3.199(1) Å; **8a**: S1–P1 3.1918(8), S2–P2 3.0874(8) Å], which forces the phosphorus centers to as-

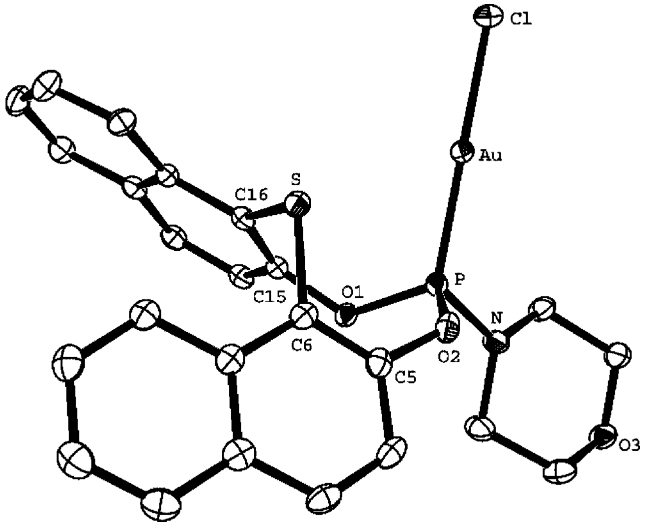


Figure 4. Molecular structure of **13a**. All hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

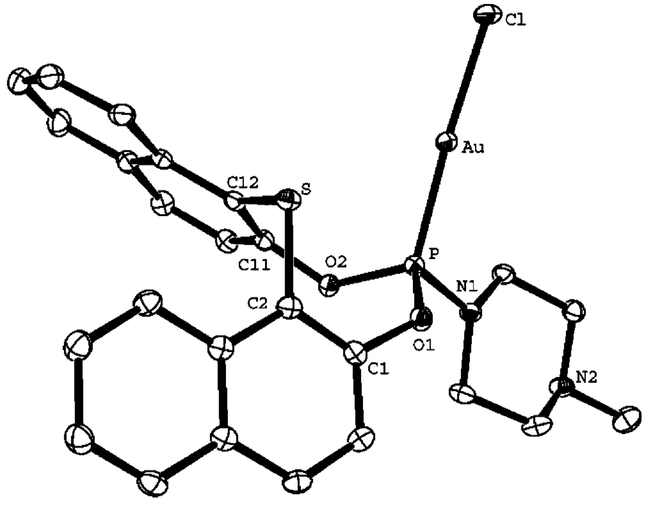


Figure 5. Molecular structure of **13b**. All hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

sume pseudo TBP geometries (Table 3). Although the sulfur atoms in both complexes are pointing towards the copper center, no sulfur to copper bonding interaction is observed as the Cu···S separations are 0.17–0.42 Å greater than the sum of the van der Waals radii. The P1–Cu–P2 bond angle in bromo derivative **8a** [130.20(2)°] is slightly greater than that of the chloro complex **7a** [128.61(3)°]. Structural data are available for a number of three-coordinate complexes of

Table 1. Selected bond lengths [Å] and bond angles [°] for complexes **5a**, **7a**, and **8a**. Symmetry operation: _a: 0.5 – *x*, 0.5 + *y*, 0.5 – *z*.

5a		**7a**		**8a**	
Br–Cu	2.3828(9)	Cu–Cl1	2.2307(8)	Br–Cu	2.3374(4)
Br–Cu_a	2.4931(9)	Cu–P1	2.2062(8)	Cu–P1	2.1884(6)
Cu–P	2.171(1)	Cu–P2	2.1897(7)	Cu–P2	2.2063(5)
S–C10	1.793(5)	S1–C2	1.774(2)	S1–C2	1.772(2)
S–C20	1.792(4)	S1–C12	1.768(2)	S1–C12	1.773(2)
P–O1	1.632(3)	P1–O2	1.636(2)	P1–O2	1.637(1)
P–O2	1.663(3)	P1–O1	1.650(2)	P1–O1	1.645(2)
P–N	1.639(4)	P1–N1	1.631(2)	P1–N1	1.636(2)
Cu–Br–Cu_a	79.17(2)	Cl1–Cu–P1	116.73(3)	Br–Cu–P1	114.13(2)
Br–Cu–P	142.15(4)	Cl1–Cu–P2	114.66(3)	Br–Cu–P2	115.66(2)
Br–Cu–Br_a	100.83(2)	P1–Cu–P2	128.61(3)	P1–Cu–P2	130.20(2)
Br_a–Cu–P	116.96(4)	C2–S1–C12	102.2(1)	C2–S1–C12	102.68(9)
C10–S–C20	102.8(2)	C26–S2–C36	102.7(1)	C26–S2–C36	102.46(9)
Cu–P–O1	110.9(1)	Cu–P1–O1	114.07(7)	Cu–P1–O1	115.52(6)
Cu–P–O2	120.2(1)	Cu–P1–O2	124.53(7)	Cu–P1–O2	120.95(5)
		Cu–P1–N1	113.80(8)	Cu–P1–N1	115.99(7)

Table 2. Selected bond lengths [Å] and bond angles [°] for complexes **13a**, **13b**, and **14a**.

13a		**13b**		**14a**	
Au–Cl	2.2725(7)	Au–Cl	2.2786(5)	Au–I	2.5603(3)
Au–P	2.2002(7)	Au–P	2.2038(5)	Au–P	2.2291(8)
S–C6	1.776(2)	S–C2	1.775(2)	S–C10	1.780(3)
S–C16	1.783(2)	S–C12	1.781(2)	S–C11	1.773(3)
P–O1	1.611(2)	P–O1	1.612(1)	P–O1	1.634(3)
P–O2	1.618(2)	P–O2	1.618(1)	P–O2	1.618(2)
P–N	1.628(2)	P–N1	1.630(2)	P–N	1.621(3)
Cl–Au–P	178.73(2)	Cl–Au–P	176.67(2)	I–Au–P	170.41(2)
C6–S–C16	101.3(1)	C2–S–C12	100.54(8)	C10–S–C11	102.8(2)
Au–P–O1	117.17(7)	Au–P–O1	116.93(5)	Au–P–O1	111.36(9)
Au–P–O2	117.07(8)	Au–P–O2	117.57(5)	Au–P–O2	119.69(9)
Au–P–N	114.44(8)	Au–P–N1	112.70(6)	Au–P–N	117.8(1)
O1–P–O2	100.78(8)	O1–P–O2	101.12(7)	O1–P–O2	99.9(1)

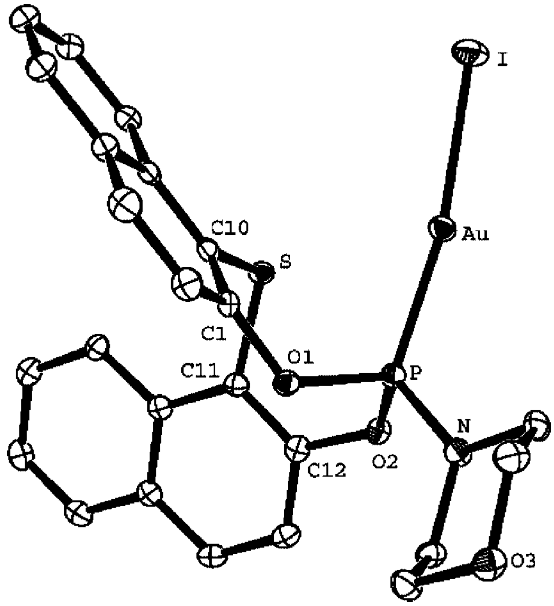
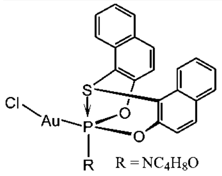
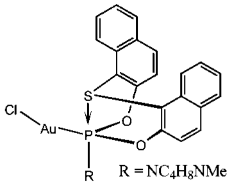
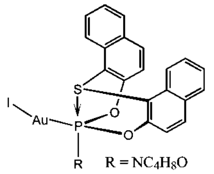
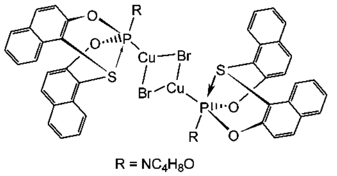
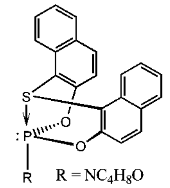
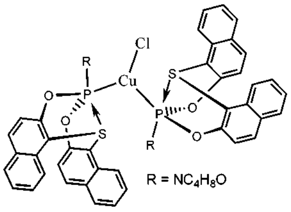
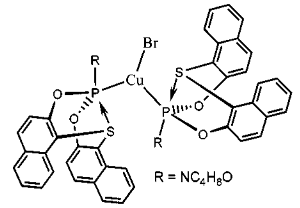
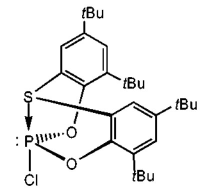
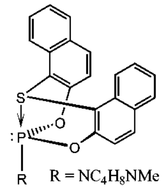
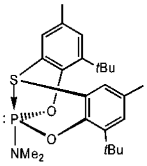
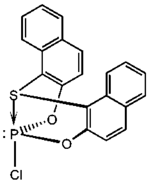
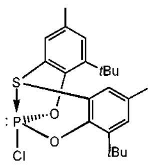


Figure 6. Molecular structure of **14a**. All hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

the type [CuX(PR$_3$)$_2$] containing tertiary phosphanes[14] but analogous complexes containing aminophosphonites or phosphites are not present in the literature.

Table 3. Comparison of P–S bond parameters and ring conformations obtained from the X-ray studies for cyclic phosphites (in increasing order of %TBP).

Compound	d(P–S) /Å	% TBP[a]	S–P–R$_{ax}$ /° [b]	Ref.
 $R = NC_4H_8O$	3.1820(8)	30.6	166.94	this work
 $R = NC_4H_8NMe$	3.1673(7)	31.5	168.78	this work
 $R = NC_4H_8O$	3.1566(13)	32.2	168.22	this work
 $R = NC_4H_8O$	3.0978(17)	36.1	168.34	this work
 $R = NC_4H_8O$	3.089(1)	36.7	164.47	[7]
 $R = NC_4H_8O$	3.0879(10) 3.1992(10)	36.7 29.5	168.24 162.11	this work
 $R = NC_4H_8O$	3.0874(8) 3.1918(8)	36.8 29.9	168.79 162.75	this work
	3.043(2)	39.7	172.22(8)	[16a]
 $R = NC_4H_8NMe$	3.040(1)	39.8	166.68	[7]
	2.952(9)	47.1	173.3(9)	[16a]
	2.887(1)	49.9	165.55	[7]
	2.816(2)	54.5	169.24(7)	[16b]

[a] Percent geometrical displacement from a pyramid towards a TBP. [b] With reference to a TBP with sulfur in an axial site.

For complexes **13a** and **13b** the unit cell contains two molecules arranged in an anti-parallel manner with no intermolecular gold–gold interaction [a common feature among linear mononuclear gold(I) complexes][12b] present (Au···Au 5.017 and 5.511 Å, respectively). The Au–Cl [2.2725(7) and 2.2786(5) Å] and Au–P bond lengths [2.2002(7) and 2.2038(5) Å] in complexes **13a** and **13b** are comparable with those observed for [$(PhO)_3PAuCl$] [Au–Cl 2.273(5), Au–P 2.192(5) Å][19a] as well as for [{2,4,6-$t$$Bu_3C_6H_2P$=C(Cl)$PPh_2$}AuCl] [Au–Cl 2.283(1), Au–P 2.229(1) Å].[19b] The S···Au separations observed in **13a** and **13b** are 3.4876(6) and 3.4508(5) Å, respectively, which are comparable to the sum of the van der Waals radii for gold and sulfur (3.46 Å).[13] There is thus only a minimal Au···S interaction at best. As with the previous complexes, the sulfur atoms in **13a** and **13b** show a coordinative interaction towards phosphorus, with S···P separations of 3.1820(8) (for **13a**) and 3.1673(7) Å (for **13b**), which are markedly shorter than the sum of the van der Waals radii for sulfur and phosphorus (3.65 Å).[13] The geometries around gold are not quite linear, with Cl–Au–P bond angles of 178.73(2)° and 176.67(2)°, respectively, for **13a** and **13b**. Again, these are comparable with that found in [$(PhO)_3$-PAuCl] [Cl–Au–P 178.5(2)°].[19a]

The molecular structure of complex **14a** is shown in Figure 6. The unit cell contains two molecules that are somewhat more closely packed (Au···Au 4.285 Å) than is observed for the chloro derivative **13a**. The Au–P bond [2.2291(8) Å] is somewhat longer than that found in the chloro derivative **13a**, possibly reflecting the increased size and polarizability of iodine compared with chlorine. The sulfur shows weak interactions with the gold and phosphorus centers since the S···Au and S···P distances [3.2976(9) and 3.1566(13) Å, respectively] are less than the sum of the van der Waals radii (S···Au 3.46 and S···P 3.65 Å).[13] There is a C–H···I contact of 3.075 Å with a C17–H17–I angle of 139.82°. As this distance lies between the outer limits proposed by Steiner[20] and by Brammer et al.[21] for C–H···I hydrogen bonds, and as the C–H···I angle is rather small, this is a weak interaction at best. The coordination about the gold center is less linear, with an I–Au–P bond angle of 170.41(2)°.

Conclusions

Group 11 metal complexes of thioether aminophosphonite ligands have been synthesized. The aminophosphonites **2a** and **2b**, which contain a hemilabile thioether functionality, show versatile coordination properties. By choosing appropriate metal reagents and reaction conditions both mono- and chelating bidentate modes of coordination can be achieved. With copper halides both the mononuclear and dinuclear trigonal planar complexes are obtained. In these complexes only phosphorus takes part in coordination, leaving the sulfur center uncoordinated. The uncoordinated sulfur atom is pointing towards the metal center in all complexes, and in some cases there is an interaction with the metal. Structurally characterized dinuclear trigonal-planar copper complexes of phosphites or aminophosphonites of the type **5a** are rare. Silver and cationic copper complexes (**10a** and **10b**) have also been synthesized where sulfur is also involved in coordination. Gold complexes of both the thioether aminophosphonite ligands undergo halide exchange with copper(I) iodide to form the iodide derivatives in quantitative yield at room temperature. Generally, the halogen-exchange reactions of platinum metal derivatives are carried out at high temperature using an excess of NaI or KI. In all the complexes, the sulfur atom present in the eight-membered mesocycle shows a tendency to coordinate to phosphorus. As a consequence, the tricoordinate geometry of phosphorus is displaced towards TBP.

Experimental Section

Reagents and Technique: 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 thioether aminophosphonites (**2a** and **2b**) were prepared as reported previously.[7] The metal precursors CuX (X = Cl and Br),[22] [$Cu(MeCN)_4]BF_4$,[23] [AuCl-(SMe_2)][24] and [Ag(OTf)PPh_3][25] were prepared according to the published procedures. The ^1H and $^{31}P\{^1H\}$ NMR spectra (δ in ppm) were obtained with a Varian VXR 300 or VRX 400 spectrometer operating at frequencies of 300 or 400 (^1H) and 121 or 162 MHz (^{31}P), respectively. The spectra were recorded for $CDCl_3$ (or [D_6]DMSO or [D_6]acetone) solutions with $CDCl_3$ (or [D_6]-DMSO or [D_6]acetone) as an internal lock; TMS and 85% H_3PO_4 were used as internal and external standards for ^1H and $^{31}P\{^1H\}$ NMR, respectively. Positive shifts lie downfield of the standard in all cases. IR spectra were recorded with a Nicolet Impact 400 FTIR instrument as KBr disks. Microanalyses were carried out with a Carlo–Erba Model 1106 elemental analyzer. Q-Tof Micromass experiments were carried out with a Waters Q-Tof micro (YA-105). Melting points of all compounds were determined with a Veego melting point apparatus and are uncorrected.

Synthesis of [{[{-$OC_{10}H_6(\mu\text{-}S)C_{10}H_6O$-}$PNC_4H_8O$-κ*P*]Cu(μ-Cl)}$_2$] (4a): A solution of **2a** (0.087 g, 0.202 mmol) in dichloromethane (10 mL) was added dropwise to a solution of CuCl (0.02 g, 0.202 mmol) in acetonitrile (4 mL) and the reaction mixture was stirred for 1 h. The white precipitate formed was filtered and dried under vacuum. Yield: 85% (0.091 g); m.p. 208 °C (dec.). $C_{48}H_{40}Cl_2Cu_2N_2O_6P_2S_2$ (1064.9): calcd. C 54.14, H 3.79, N 2.63, S 6.02; found C 54.08, H 3.75, N 2.61, S 5.97.

Synthesis of [{[{-$OC_{10}H_6(\mu\text{-}S)C_{10}H_6O$-}$PNC_4H_8NCH_3$-κ*P*]Cu(μ-Cl)}$_2$] (4b): This compound was synthesized by a procedure similar to that for **4a** from **2b** (0.090 g, 0.202 mmol) and CuCl (0.02 g, 0.202 mmol). Yield: 83% (0.091 g); m.p. 186 °C (dec.). $C_{50}H_{46}Cl_2Cu_2N_4O_4P_2S_2$ (1091.0): calcd. C 55.04, H 4.25, N 5.14, S 5.88; found C 54.98, H 4.22, N 5.11, S 5.81. ^1H NMR (400 MHz, [D_6]DMSO): δ = 8.62 (d, $^3J_{H,H}$ = 8.8 Hz, 4 H, ArH), 7.92 (d, $^3J_{H,H}$ = 8.4 Hz, 8 H, ArH), 7.22–7.65 (m, 12 H, ArH), 3.33 (br. s, 8 H, CH_2), 2.49 (br. s, 8 H, CH_2), 2.06 (s, 6 H, CH_3) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, [D_6]DMSO): δ = 114.4 (s) ppm.

Synthesis of [{[{-$OC_{10}H_6(\mu\text{-}S)C_{10}H_6O$-}$PNC_4H_8O$-κ*P*]Cu(μ-Br)}$_2$] (5a): This compound was synthesized by a procedure similar to that for **4a** from **2a** (0.06 g, 0.139 mmol) and CuBr (0.02 g, 0.139 mmol). Yield: 85% (0.068 g); m.p. 228 °C (dec.). $C_{48}H_{40}Br_2Cu_2N_2O_6P_2S_2$ (1153.8): calcd. C 49.97, H 3.49, N 2.43, S 5.56; found C 49.92, H 3.45, N 2.41, S 5.51. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 8.67 (d, $^3J_{H,H}$ = 8.4 Hz, 4 H, ArH), 7.97 (t, $^3J_{H,H}$ = 9.2 Hz, 8 H, ArH), 7.67 (d, $^3J_{H,H}$ = 6.8 Hz, 4 H, ArH), 7.51 (d, $^3J_{H,H}$ = 6.8 Hz, 4 H, ArH), 7.37 (d, $^3J_{H,H}$ = 8.4 Hz, 4 H, ArH), 3.71 (br. s, 8 H, CH$_2$), 3.37 (br. s, 8 H, CH$_2$) ppm. ^{31}P{^{1}H} NMR (162 MHz, [D$_6$]DMSO): δ = 113.3 (s) ppm. MS (EI): *m/z* 576.0 [M$^+$ – (L + CuBr)], 496.0 [M$^+$ – (L + CuBr$_2$)].

Synthesis of [{[{-$OC_{10}H_6(\mu\text{-}S)C_{10}H_6O$-}$PNC_4H_8NCH_3$-κ*P*]Cu(μ-Br)}$_2$] (5b): This compound was synthesized by a procedure similar to that for **4a** from **2b** (0.062 g, 0.139 mmol) and CuBr (0.02 g, 0.139 mmol). Yield: 83% (0.068 g); m.p. 196 °C (dec.). $C_{50}H_{46}Br_2Cu_2N_4O_4P_2S_2$ (1179.9): calcd. C 50.89, H 3.93, N 4.75, S 5.44; found C 50.82, H 3.89, N 4.71, S 5.42. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 8.75 (d, $^3J_{H,H}$ = 8.8 Hz, 4 H, ArH), 7.05 (d, $^3J_{H,H}$ = 8.4 Hz, 4 H, ArH), 7.36–7.99 (m, 16 H, ArH), 3.37 (br. s, 8 H, CH$_2$), 2.50 (br. s, 8 H, CH$_2$), 2.29 (s, 6 H, CH$_3$) ppm. ^{31}P{^{1}H} NMR (162 MHz, [D$_6$]DMSO): δ = 110.5 (s) ppm.

Synthesis of [{[{-$OC_{10}H_6(\mu\text{-}S)C_{10}H_6O$-}$PNC_4H_8O$-κ*P*]Cu(μ-I)}$_2$] (6a): This compound was synthesized by a procedure similar to that for **4a** from **2a** (0.068 g, 0.157 mmol) and CuI (0.03 g, 0.157 mmol) and was stirred for 2 h. Yield: 89% (0.087 g); m.p. 232 °C (dec.). $C_{48}H_{40}Cu_2I_2N_2O_6P_2S_2$ (1247.8): calcd. C 46.20, H 3.23, N 2.24, S 5.14; found C 46.15, H 3.21, N 2.22, S 5.11. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 8.67 (d, $^3J_{H,H}$ = 8.4 Hz, 4 H, ArH), 7.96 (t, $^3J_{H,H}$ = 7.2 Hz, 8 H, ArH), 7.39–7.67 (m, 12 H, ArH), 3.71 (br. s, 8 H, CH$_2$), 3.35 (br. s, 8 H, CH$_2$) ppm. ^{31}P{^{1}H} NMR (162 MHz, [D$_6$]DMSO): δ = 110.4 (s) ppm.

Synthesis of [{[{-$OC_{10}H_6(\mu\text{-}S)C_{10}H_6O$-}$PNC_4H_8NCH_3$-κ*P*]Cu(μ-I)}$_2$] (6b): This compound was synthesized by a procedure similar to that for **4a** from **2b** (0.07 g, 0.157 mmol) and CuI (0.03 g, 0.157 mmol). Yield: 88% (0.088 g); m.p. 192 °C (dec.). $C_{50}H_{46}Cu_2I_2N_4O_4P_2S_2$ (1273.9): calcd. C 47.14, H 3.64, N 4.39, S 5.03; found C 47.03, H 3.57, N 4.32, S 4.98.

Synthesis of [{[-$OC_{10}H_6(\mu\text{-}S)C_{10}H_6O$-]$PNC_4H_8O$-κ*P*}$_2$CuCl] (7a): CuCl (0.01 g, 0.101 mmol) was added to a solution of **2a** (0.09 g, 0.207 mmol) in dichloromethane (12 mL) and the reaction mixture was stirred for 3 h. The colorless solution obtained was concentrated (5 mL) under vacuum and 1 mL of acetonitrile was added. Slow evaporation of the solution at room temperature gave colorless crystals of **7a**. Yield: 88% (0.093 g); m.p. 218 °C (dec.). $C_{48}H_{40}ClCuN_2O_6P_2S_2\cdot CH_2Cl_2$ (1050.9): calcd. C 56.00, H 4.03, N 2.67, S 6.10; found C 55.96, H 4.01, N 2.59, S 5.96. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 8.60 (d, $^3J_{H,H}$ = 8.4 Hz, 4 H, ArH), 7.89 (d, $^3J_{H,H}$ = 8.8 Hz, 8 H, ArH), 7.62 (t, $^3J_{H,H}$ = 7.2 Hz, 4 H, ArH), 7.45 (t, $^3J_{H,H}$ = 7.2 Hz, 4 H, ArH), 7.23 (d, $^3J_{H,H}$ = 8.8 Hz, 4 H, ArH), 3.64 (br. s, 8 H, CH$_2$), 3.30 (br. s, 8 H, CH$_2$) ppm. ^{31}P{^{1}H} NMR (121.4 MHz, [D$_6$]DMSO): δ = 115.8 (s) ppm.

Synthesis of [{(-$OC_{10}H_6(\mu\text{-}S)C_{10}H_6O$-)$PNC_4H_8NCH_3$-κ*P*}$_2$CuCl] (7b): This compound was synthesized by a procedure similar to that for **7a** from **2b** (0.092 g, 0.207 mmol) and CuCl (0.01 g, 0.101 mmol). Yield: 87% (0.087 g); m.p. 188 °C (dec.). $C_{50}H_{46}ClCuN_4O_4P_2S_2$ (992.00): calcd. C 60.54, H 4.67, N 5.65, S 6.46; found C 60.49, H 4.63, N 5.61, S 6.40. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 8.65 (d, $^3J_{H,H}$ = 7.6 Hz, 4 H, ArH), 7.95 (d, $^3J_{H,H}$ = 8.4 Hz, 8 H, ArH), 7.67 (t, $^3J_{H,H}$ = 8.4 Hz, 4 H, ArH), 7.50 (t, $^3J_{H,H}$ = 8.4 Hz, 4 H, ArH), 7.31 (d, $^3J_{H,H}$ = 7.6 Hz, 4 H, ArH), 3.33 (br. s, 8 H, CH$_2$), 2.50 (br. s, 8 H, CH$_2$), 2.08 (s, 6 H, CH$_3$) ppm. ^{31}P{^{1}H} NMR (162 MHz, [D$_6$]DMSO): δ = 112.2 (s) ppm.

Synthesis of [{[-$OC_{10}H_6(\mu\text{-}S)C_{10}H_6O$-]$PNC_4H_8O$-κ*P*}$_2$CuBr] (8a): This compound was synthesized by a procedure similar to that for **7a** from CuBr (0.015 g, 0.105 mmol) and **2a** (0.093 g, 0.214 mmol). Yield: 90% (0.104 g); m.p. 242 °C (dec.). $C_{48}H_{40}BrCuN_2O_6P_2S_2\cdot CH_2Cl_2$ (1095.30): calcd. C 53.73, H 3.87, N 2.56, S 5.86; found C 53.65, H 3.82, N 2.51, S 5.82. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 8.71 (d, $^3J_{H,H}$ = 8.8 Hz, 4 H, ArH), 7.26–8.01 (m, 20 H, ArH), 3.65 (br. s, 8 H, CH$_2$), 3.31 (br. s, 8 H, CH$_2$) ppm. ^{31}P{^{1}H} NMR (162 MHz, [D$_6$]DMSO): δ = 112.3 (s) ppm.

Synthesis of [{[-$OC_{10}H_6(\mu\text{-}S)C_{10}H_6O$-]$PNC_4H_8NCH_3$-κ*P*}$_2$CuBr] (8b): This compound was synthesized by a procedure similar to that for **7a** from CuBr (0.015 g, 0.105 mmol) and **2b** (0.096 g, 0.214 mmol) and was stirred for 4 h. Yield: 85% (0.092 g); m.p. 196 °C (dec.). $C_{50}H_{46}BrCuN_4O_4P_2S_2$ (1036.5): calcd. C 57.94, H 4.47, N 5.41, S 6.19; found C 57.89, H 4.41, N 5.36, S 6.10. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 8.63 (d, $^3J_{H,H}$ = 8.4 Hz, 4 H, ArH), 7.92 (d, $^3J_{H,H}$ = 8.8 Hz, 8 H, ArH), 7.33–7.66 (m, 12 H, ArH), 3.34 (br. s, 8 H, CH$_2$), 2.52 (br. s, 8 H, CH$_2$), 2.09 (s, 6 H, CH$_3$) ppm. ^{31}P{^{1}H} NMR (121.4 MHz, [D$_6$]DMSO): δ = 113.4 (s) ppm.

Synthesis of [{[-$OC_{10}H_6(\mu\text{-}S)C_{10}H_6O$-]$PNC_4H_8O$-κ*P*}$_2$CuI] (9a): This compound was synthesized by a procedure similar to that for **7a** from CuI (0.02 g, 0.105 mmol) and **2a** (0.093 g, 0.215 mmol) and was stirred for 6 h. Yield: 81% (0.09 g); m.p. 220 °C (dec.). $C_{48}H_{40}CuIN_2O_6P_2S_2$ (1057.4): calcd. C 54.52, H 3.81, N 2.65, S 6.07; found C 54.49, H 3.78, N 2.62, S 5.98. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 8.71 (d, $^3J_{H,H}$ = 8.8 Hz, 4 H, ArH), 8.02 (d, $^3J_{H,H}$ = 8.4 Hz, 4 H, ArH), 7.96 (d, $^3J_{H,H}$ = 8.0 Hz, 4 H, ArH), 7.31–7.91 (m, 12 H, ArH), 3.66 (br. s, 8 H, CH$_2$), 3.29 (br. s, 8 H, CH$_2$) ppm. ^{31}P{^{1}H} NMR (121.4 MHz, [D$_6$]DMSO): δ = 111.8 (s) ppm.

Synthesis of [{[-$OC_{10}H_6(\mu\text{-}S)C_{10}H_6O$-]$PNC_4H_8NCH_3$-κ*P*}$_2$CuI] (9b): This compound was synthesized by a procedure similar to that for **7a** from CuI (0.02 g, 0.105 mmol) and **2b** (0.096 g, 0.215 mmol). Yield: 83% (0.095 g); m.p. 232 °C (dec.). $C_{50}H_{46}CuIN_4O_4P_2S_2$ (1083.5): calcd. C 55.43, H 4.28, N 5.17, S 5.92; found C 55.38, H 4.27, N 5.15, S 5.88. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 8.71 (d, $^3J_{H,H}$ = 8.4 Hz, 4 H, ArH), 7.76 (d, $^3J_{H,H}$ = 8.0 Hz, 4 H, ArH), 7.64 (d, $^3J_{H,H}$ = 9.2 Hz, 4 H, ArH), 7.61 (t, $^3J_{H,H}$ = 8.0 Hz, 4 H, ArH), 7.44 (t, $^3J_{H,H}$ = 7.2 Hz, 4 H, ArH), 6.94 (d, $^3J_{H,H}$ = 8.4 Hz, 4 H, ArH), 3.47 (br. s, 8 H, CH$_2$), 2.49 (br. s, 8 H, CH$_2$), 2.13 (s, 6 H, CH$_3$) ppm. ^{31}P{^{1}H} NMR (162 MHz, [D$_6$]DMSO): δ = 116.9 (s) ppm.

Synthesis of [{[-$OC_{10}H_6(\mu\text{-}S)C_{10}H_6O$-]$PNC_4H_8O$-κ*P*,κ*S*}$_2$Cu]BF$_4$ (10a): [Cu(MeCN)$_4$]BF$_4$ (0.025 g, 0.079 mmol) was added to a solution of **2a** (0.07 g, 0.162 mmol) in dichloromethane (15 mL) and the reaction mixture was stirred for 2 h. The resultant solution was concentrated to 5 mL under vacuum and layered with petroleum ether (1 mL) to give **10a** as a white crystalline product at –25 °C. Yield: 89% (0.072 g); m.p. 170–172 °C (dec.). $C_{48}H_{40}BCuF_4N_2O_6P_2S_2$ (1017.3): calcd. C 56.67, H 3.96, N 2.75, S 6.30; found C 56.59, H 3.92, N 2.73, S 6.26. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.52 (d, $^3J_{H,H}$ = 7.6 Hz, 4 H, ArH), 7.77 (d, $^3J_{H,H}$ = 8.4 Hz, 8 H, ArH), 7.26–7.54 (m, 8 H, ArH), 7.12 (d, $^3J_{H,H}$ = 8.0 Hz, 4 H, ArH), 3.74 (br. s, 8 H, CH$_2$), 3.37 (br. s, 8 H, CH$_2$) ppm. ^{31}P{^{1}H} NMR (121.4 MHz, CDCl$_3$): δ = 112.2 (s) ppm. MS (EI): *m/z* 929.1 [M$^+$ – BF$_4$], 496.0 [M$^+$ – (L + BF$_4$)].

Synthesis of [{[-$OC_{10}H_6(\mu\text{-}S)C_{10}H_6O$-]$PNC_4H_8NCH_3$-κ*P*,κ*S*}$_2$-Cu]BF$_4$ (10b): This compound was synthesized by a procedure similar to that for **10a** from **2b** (0.072 g, 0.162 mmol) and [Cu(MeCN)$_4$]BF$_4$ (0.025 g, 0.079 mmol). Yield: 90% (0.075 g); m.p. 158–160 °C (dec.). $C_{50}H_{46}BCuF_4N_4O_4P_2S_2$ (1043.35): calcd. C 57.56, H 4.44, N 5.37, S 6.15; found C 57.48, H 4.41, N 5.32, S 6.09. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.55 (d, $^3J_{H,H}$ = 8.4 Hz, 4 H, ArH), 7.59

(d, $^3J_{\mathrm{H,H}}$ = 8.0 Hz, 8 H, ArH), 6.88–7.56 (m, 12 H, ArH), 3.35 (br. s, 8 H, CH$_2$), 2.52 (br. s, 8 H, CH$_2$), 2.01 (s, 6 H, CH$_3$) ppm. ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): δ = 113.7 (s) ppm. MS (EI): *m*/*z* 955.2 [M$^+$ – BF$_4$], 509.1 [M$^+$ – (L + BF$_4$)].

Synthesis of [{[{-OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O-}PNC$_4$H$_8$O-κ*P*,κ*S*]Ag(CF$_3$SO$_3$)}$_2$] (11a): AgOTf (0.04 g, 0.156 mmol) was added to a solution of **2a** (0.067 g, 0.156 mmol) in dichloromethane (12 mL) and the reaction mixture was stirred for 3 h. The resultant solution was concentrated to 3 mL under vacuum and petroleum ether (5 mL) was added to precipitate **11a** as a white crystalline product, which was then filtered off and dried under high vacuum. Yield: 91% (0.097 g); m.p. 138 °C (dec.). C$_{25}$H$_{20}$AgF$_3$NO$_6$PS$_2$ (690.39): calcd. C 43.49, H 2.92, N 2.03, S 9.29; found C 43.41, H 2.89, N 1.99, S 9.21. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.79 (d, $^3J_{\mathrm{H,H}}$ = 8.4 Hz, 2 H, ArH), 7.15–8.32 (m, 10 H, ArH), 3.91 (br. s, 4 H, CH$_2$), 3.28 (br. s, 4 H, CH$_2$) ppm. ^{31}P{^{1}H} NMR (121.4 MHz, CDCl$_3$): δ = 118.8 (br. s) ppm.

Synthesis of [{[{-OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O-}PNC$_4$H$_8$NCH$_3$-κ*P*,κ*S*]Ag(CF$_3$SO$_3$)}$_2$] (11b): This compound was synthesized by a procedure similar to that for **11a** from **2b** (0.069 g, 0.156 mmol) and AgOTf (0.04 g, 0.156 mmol). Yield: 89% (0.097 g); m.p. 192 °C (dec.). C$_{26}$H$_{23}$AgF$_3$N$_2$O$_5$PS$_2$ (703.44): calcd. C 44.39, H 3.29, N 3.98, S 9.12; found C 44.31, H 3.22, N 3.91, S 9.03. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.52 (d, $^3J_{\mathrm{H,H}}$ = 8.8 Hz, 4 H, ArH), 8.28 (d, $^3J_{\mathrm{H,H}}$ = 8.4 Hz, 8 H, ArH), 6.86–7.58 (m, 12 H, ArH), 3.19 (br. s, 8 H, CH$_2$), 2.67 (br. s, 8 H, CH$_2$), 2.33 (s, 6 H, CH$_3$) ppm. ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): δ = 123.3 (2 br. s, $^1J_{\mathrm{Ag,P}} \approx$ 594 Hz, 2 P) ppm.

Synthesis of [{[-OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O-]PNC$_4$H$_8$O-κ*P*,κ*S*}Ag(PPh$_3$)]CF$_3$SO$_3$ (12a): [Ag(PPh$_3$)][OTf] (0.05 g, 0.096 mmol) was added to a solution of **2a** (0.042 g, 0.096 mmol) in dichloromethane (12 mL), and the reaction mixture was stirred for 2 h. The solution was concentrated under vacuum and diethyl ether (5 mL) was added to precipitate a white crystalline product. This was filtered off and dried under vacuum. Yield: 82% (0.075 g); m.p. 140–142 °C (dec.). C$_{43}$H$_{35}$AgF$_3$NO$_6$P$_2$S$_2$ (952.69): calcd. C 54.21, H 3.70, N 1.47, S 6.73; found C 54.16, H 3.64, N 1.44, S 6.69. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.76 (d, $^3J_{\mathrm{H,H}}$ = 8.4 Hz, 2 H, ArH), 7.09–8.34 (m, 10 H, ArH, 15 H, PPh$_3$), 3.89 (br. s, 4 H, CH$_2$), 3.24 (br. s, 4 H, CH$_2$) ppm. ^{31}P{^{1}H} NMR (121.4 MHz, CDCl$_3$): δ = 123.9 (2 br. d, $J_{\mathrm{Ag,P}} \approx$ 512 Hz, 1 P), 9.7 (2 br. d, $J_{\mathrm{Ag,P}} \approx$ 394 Hz, 1 P, PPh$_3$) ppm. MS (EI): *m*/*z* 803.1 [M$^+$ – OTf].

Synthesis of [{[-OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O-]PNC$_4$H$_8$NCH$_3$-κ*P*,κ*S*}Ag(PPh$_3$)]CF$_3$SO$_3$ (12b): This complex was synthesized by a procedure similar to that for **12a** from **2b** (0.0043 g, 0.096 mmol) and [Ag(PPh$_3$)][OTf] (0.05 g, 0.096 mmol). Yield: 78% (0.073 g); m.p. 144 °C (dec.). C$_{44}$H$_{38}$AgF$_3$N$_2$O$_5$P$_2$S$_2$ (965.73): calcd. C 54.72, H 3.97, N 2.90, S 6.64; found C 54.68, H 3.92, N 2.88, S 6.59. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.64 (d, $^3J_{\mathrm{H,H}}$ = 8.4 Hz, 2 H, ArH), 7.04–7.75 (m, 10 H, ArH, 15 H, PPh$_3$), 3.45 (br. s, 4 H, CH$_2$), 2.61 (br. s, 4 H, CH$_2$), 2.36 (s, 3 H, CH$_3$) ppm. ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): δ = 130.3 (br. s, 1 P), 8.2 (br. s, 1 P, PPh$_3$) ppm. MS (EI): *m*/*z* 816.9 [M$^+$ – OTf].

Synthesis of [{[-OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O-]PNC$_4$H$_8$O-κ*P*}AuCl] (13a): A solution of **2a** (0.051 g, 0.119 mmol) in CH$_2$Cl$_2$ (8 mL) was added dropwise to a dichloromethane (5 mL) solution of [AuCl(SMe$_2$)] (0.035 g, 0.119 mmol) and the reaction mixture was stirred for 3 h at room temperature. The solution was concentrated to 3 mL and layered with petroleum ether to give colorless crystals of **13a** on cooling to –25 °C. Yield: 90% (0.071 g); m.p. 178–180 °C (dec.). C$_{24}$H$_{20}$AuClNO$_3$PS (665.88): calcd. C 43.29, H 3.03, N 2.10, S 4.82; found C 43.19, H 2.99, N 2.08, S 4.79. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.77 (d, $^3J_{\mathrm{H,H}}$ = 8.4 Hz, 2 H, ArH), 7.63–7.87 (m, 6 H, ArH), 7.51 (t, $^3J_{\mathrm{H,H}}$ = 7.2 Hz, 2 H, ArH), 7.24 (d, $^3J_{\mathrm{H,H}}$ = 8.0 Hz, 2 H, ArH), 3.84 (t, $^3J_{\mathrm{H,H}}$ = 4.8 Hz, 4 H, CH$_2$), 3.65 (t, $^3J_{\mathrm{H,H}}$ = 5.2 Hz, 4 H, CH$_2$) ppm. ^{31}P{^{1}H} NMR (121.4 MHz, CDCl$_3$): δ = 113.1 (s) ppm.

Synthesis of [{[-OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O-]PNC$_4$H$_8$NCH$_3$-κ*P*}AuCl] (13b): This was synthesized by a procedure similar to that for **13a** from **2b** (0.053 g, 0.119 mmol) and [AuCl(SMe$_2$)] (0.035 g, 0.119 mmol). Yield: 89% (0.072 g); m.p. 158 °C (dec.). C$_{25}$H$_{23}$AuClN$_2$O$_2$PS (678.92): calcd. C 44.23, H 3.41, N 4.13, S 4.72; found C 44.18, H 3.37, N 4.09, S 4.69. ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 8.84 (d, $^3J_{\mathrm{H,H}}$ = 8.0 Hz, 2 H, ArH), 8.08 (d, $^3J_{\mathrm{H,H}}$ = 8.8 Hz, 2 H, ArH), 7.99 (d, $^3J_{\mathrm{H,H}}$ = 8.0 Hz, 2 H, ArH), 7.52–7.76 (m, 4 H, ArH), 7.49 (d, $^3J_{\mathrm{H,H}}$ = 7.6 Hz, 2 H, ArH), 3.72 (br. s, 4 H, CH$_2$), 2.91 (br. s, 4 H, CH$_2$), 2.37 (s, 3 H, CH$_3$) ppm. ^{31}P{^{1}H} NMR (121.4 MHz, [D$_6$]acetone): δ = 115.3 (s) ppm.

Synthesis of [{[-OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O-]PNC$_4$H$_8$O-κ*P*}AuI] (14a): A solution of CuI (0.014 g, 0.075 mmol) in acetonitrile (5 mL) was added dropwise to a solution of **13a** (0.05 g, 0.075 mmol) in dichloromethane (8 mL) and the reaction mixture was stirred for 3 h. The solution obtained was concentrated to 5 mL to give a crystalline product on cooling to –25 °C. Yield: 74% (0.042 g); m.p. 208–210 °C (dec.). C$_{24}$H$_{20}$AuINO$_3$PS (757.33): calcd. C 38.06, H 2.66, N 1.85, S 4.23; found C 37.98, H 2.63, N 1.81, S 4.19. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.78 (d, $^3J_{\mathrm{H,H}}$ = 8.0 Hz, 2 H, ArH), 7.43–7.81 (m, 8 H, ArH), 7.28 (d, $^3J_{\mathrm{H,H}}$ = 8.4 Hz, 2 H, ArH), 3.85 (br. s, 4 H, CH$_2$), 3.68 (br. s, 4 H, CH$_2$) ppm. ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): δ = 118.1 (s) ppm.

Synthesis of [{[-OC$_{10}$H$_6$(μ-S)C$_{10}$H$_6$O-]PNC$_4$H$_8$NCH$_3$-κ*P*}AuI] (14b): This complex was synthesized by a procedure similar to that for **14a** from CuI (0.014 g, 0.075 mmol) and **13b** (0.051 g, 0.075 mmol). Yield: 69% (0.04 g); m.p. 192–194 °C (dec.). C$_{25}$H$_{23}$AuIN$_2$O$_2$PS (770.37): calcd. C 38.98, H 3.01, N 3.64, S 4.16; found C 38.92, H 2.97, N 3.59, S 4.12. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.76 (d, $^3J_{\mathrm{H,H}}$ = 8.4 Hz, 2 H, ArH), 7.80–7.85 (m, 4 H, ArH), 7.64 (t, $^3J_{\mathrm{H,H}}$ = 7.6 Hz, 2 H, ArH), 7.48 (t, $^3J_{\mathrm{H,H}}$ = 7.6 Hz, 2 H, ArH), 7.22 (d, $^3J_{\mathrm{H,H}}$ = 8.8 Hz, 2 H, ArH), 3.67 (br. s, 4 H, CH$_2$), 2.55 (br. s, 4 H, CH$_2$), 2.39 (s, 3 H, CH$_3$) ppm. ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): δ = 118.9 (s) ppm.

X-ray Crystallography: Crystals of **5a**, **7a**, **8a**, **13a**, **13b**, and **14a** were mounted in a Cryoloop™ with a drop of Paratone oil and placed in the cold nitrogen stream of the Kryoflex™ attachment of a Bruker APEX CCD diffractometer. A full sphere of data was collected using 606 scans in ω (0.3° per scan) at ϕ = 0, 120, and 240° (for **5a**, **7a**, and **14a**) or 400 scans in ω (0.5° per scan) at ϕ = 0, 90, and 180° plus 800 scans in ϕ (0.45° per scan) at ω = 0 and 210° (for **8a**, **13a**, and **13b**) using the SMART software package.[26] The raw data were reduced to F^2 values using the SAINT+ software[27] and global refinements of unit cell parameters using 4630–9050 reflections chosen from the full data sets were performed. Multiple measurements of equivalent reflections provided the basis for empirical absorption corrections as well as corrections for any crystal deterioration during the data collection (SADABS[28]). The structures were solved by direct methods (for **5a**, **7a**, **8a**, **13a**, and **13b**) or the position of the metal atoms was obtained from a sharpened Patterson function (for **14a**) and refined by full-matrix least-squares procedures using the SHELXTL program package.[29] 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. Pertinent crystallographic data and other experimental details are summarized in Tables 4 and 5.

Table 4. Crystallographic data for complexes **5a**, **7a**, and **8a**.

	5a	**7a**	**8a**
Formula	$C_{48}H_{40}Br_2Cu_2N_2O_6P_2S_2$	$C_{48}H_{40}ClCuN_2O_6P_2S_2{\cdot}CH_2Cl_2$	$C_{48}H_{40}BrCuN_2O_6P_2S_2{\cdot}CH_2Cl_2$
Molecular weight	1153.80	1050.83	1095.26
Crystal system	triclinic	monoclinic	monoclinic
Crystal size [mm]	0.11 × 0.11 × 0.14	0.17 × 0.17 × 0.32	0.14 × 0.15 × 0.28
Space group	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
a [Å]	9.574(2)	13.638(1)	13.582(1)
b [Å]	11.357(2)	21.690(2)	21.839(2)
c [Å]	11.462(2)	16.002(2)	16.042(1)
α [°]	98.769(2)	90	90
β [°]	108.777(2)	103.633(2)	103.437(1)
γ [°]	101.580(2)	90	90
V [Å^3]	1123.8(4)	4600.1(8)	4628.1(7)
Z	1	4	4
ρ_{calcd} [g cm^{-3}]	1.705	1.517	1.572
μ(Mo-K_α) [mm^{-1}]	2.941	0.863	1.663
F(000)	1160	2160	2232
Temp. [K]	100	100	100
$\theta_{min,max}$ [°]	2.4, 28.4	2.2, 28.2	2.4, 28.3
GOF (F^2)	0.99	1.03	1.04
R_1[a]	0.0504	0.0444	0.0352
wR_2[b]	0.1371	0.1220	0.0931

[a] $R_1 = \Sigma|F_o| - |F_c|/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma w[(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table 5. Crystallographic data for complexes **13a**, **13b**, and **14a**.

	13a	**13b**	**14a**
Formula	$C_{24}H_{20}AuClNO_3PS$	$C_{25}H_{23}AuClN_2O_2PS$	$C_{24}H_{20}AuINO_3PS$
Molecular weight	665.86	678.90	757.32
Crystal system	triclinic	triclinic	triclinic
Crystal size [mm]	0.09 × 0.14 × 0.21	0.14 × 0.17 × 0.21	0.12 × 0.15 × 0.22
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a [Å]	9.9857(9)	9.945(1)	9.5688(8)
b [Å]	10.817(1)	10.500(1)	11.2775(9)
c [Å]	11.704(1)	13.220(1)	11.648(1)
α [°]	76.089(1)	103.775(1)	99.422(1)
β [°]	67.262(1)	95.073(1)	99.004(1)
γ [°]	71.899(1)	104.354(1)	106.991(1)
V [Å^3]	1097.8(2)	1282.9(2)	1157.7(2)
Z	2	2	2
ρ_{calcd} [g cm^{-3}]	2.014	1.757	2.172
μ(Mo-K_α) [mm^{-1}]	7.019	6.006	7.874
F(000)	644	660	716
Temp. [K]	100	100	100
$\theta_{min,max}$ [°]	2.6, 28.3	2.9, 28.3	2.3, 28.2
GOF (F^2)	1.05	1.05	1.05
R_1[a]	0.0164	0.0141	0.0236
wR_2[b]	0.0399	0.0356	0.0568

[a] $R_1 = \Sigma|F_o| - |F_c|/\Sigma|F_o|$. [b]$wR_2 = \{\Sigma w[(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

CCDC-622054 (for **5a**), -622055 (for **7a**), -622056 (for **8a**), -622057 (for **13a**), -622058 (for **13b**), and -622059 (for **14a**) contain the supplementary crystallographic data for this paper. 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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