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Differing Coordination Modes of (O-Alkyl)-*p*-Ethoxyphenyldithiophosphonato Ligands in Copper(I), Silver(I) and Gold(I) Triphenylphosphine Complexes

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Dedicated to Professor Herbert W. Roesky on the Occasion of his 70th Birthday

Abstract. The three (O-methyl)-*p*-ethoxyphenyldithiophosphonato triphenylphosphine complexes of copper, silver and gold, $[(Ph_3P)_nM\{S_2P(OMe)C_6H_4OEt\text{-}p\}]$ (M = Cu, n = 2; M = Ag, Au, n = 1) investigated structurally by X-ray diffraction exhibit remarkable structural differences. The copper compound is a four-coordinate chelate monomer with Cu−S 2.4417(6) and 2.5048(6) Å; P−Cu−S 104.24(2)−114.01(2)°; Cu−S−P 82.49(3)° and 80.85(2)°. The silver compound is a cyclic dimer with bridging dithiophosphonato ligands and three-coordinate silver atoms [Ag−S 2.5371(5) and 2.6867(5) Å; P−Ag−S 122.88(2)° and 122.17(2)°; Ag−S−P 89.32(2)° and 103.56(2)°]. The gold compound is monomeric with linear dicoordinate gold [Au−S 2.3218(6) Å; P−Au−S 177.72(2)°, Au−S−P 100.97(3)°].

Keywords: Copper; Silver; Gold; Dithiophosphonates; Phosphor-1,1-dithiolates; Crystal structure

Introduction

Phosphor-1,1-dithiolato ligands [1] are versatile metal complex forming reagents and include O,O-dialkyl-dithiophosphates, $(RO)_2PS_2^-$, dithiophosphinates, $R_2PS_2^-$ and the hybrid (O-alkyl)-aryldithiophosphonates, $R(R'O)PS_2^-$. An extensive coordination chemistry of dithiophosphates [2] has been developed, but dithiophosphinates [3] received relatively less attention, whereas dithiophosphonates have been almost neglected until recently. This was mainly caused by the differing availability of the ligands.

(O-alkyl)aryldithiophosphonato proligands can be conveniently prepared as dithiophosphonic acid O-monoesters from the cyclic phosphine disulfide dimers (diphosphetane disulfides), $[RP(S)S]_2$, by ring cleavage with alcohols (under anhydrous conditions). Although this reaction was known for a long time [4] and some metal dithiophosphonato complexes were investigated in various laboratories [5−8] only in recent years it received due attention as a source of (O-alkyl)aryldithiophosphonato ligands [9−11]. In most cases the so-called Lawesson’s reagent [12], $[p\text{-MeOC}_6H_4PS_2]_2$, readily obtained from anisole and tetraphosphorus decasulfide, has been used. Alternatively, dithiophosphonato complexes can be prepared by the reaction of Lawesson’s reagent with metal and non-metal alkoxides and this procedure is best suited for the synthesis of main group derivatives [13].

Results

We report here some copper(I), silver(I) and gold(I) triphenylphosphine complexes of $[p\text{-EtOC}_6H_4P(OR')S_2]^-$ ligands (R′ = Me, Et, *iso*-Pr) obtained from phenetole, $C_6H_5OC_2H_5$. Introduction of a *para*-ethoxy substituent improves the solubility of the derived metal complex (O-alkyl)aryldithiophosphonates and facilitates their crystallization from organic solvents. The derivatives with R′ = Me have been investigated structurally by single crystal X-ray diffraction and showed differing bonding modes of the ligands. The copper(I) complex is a monomeric four-coordinate chelate **1**, containing an isobidentate (symmetrical) dithiophosphonato ligand. Silver(I) forms a dimeric, eight-membered ring, containing two bridging dithiophosphonato ligands, **2**. The gold(I) compound is again monomeric, but with a monodentate (unsymmetrical) dithiophosphonato ligand, with a long nonbonding intramolecular Au···S distance *(vide infra)*, **3**.

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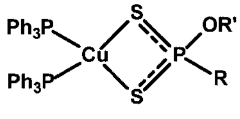

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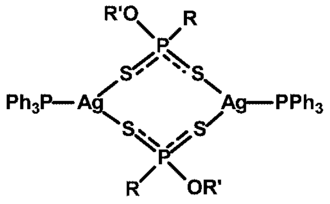

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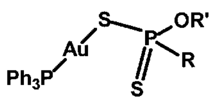

3

R = *p*-EtOC$_6$H$_4$, R' = Me, Et, *iso*-Pr

The copper(I) complex, **1**, R = Me, was prepared by reacting [(Ph$_3$P)$_2$CuNO$_3$], dissolved in nitrobenzene, with a solution of (O-methyl)-*p*-ethoxyphenyldithiophosphonic acid obtained *in situ* by dissolving the dimeric sulfide in methanol. The ethyl (**1**, R′ = Et) and isopropyl (**1**, R′ = *iso*-Pr) derivatives were obtained by reacting CuSO$_4$·5H$_2$O, dissolved in methanol, with the ammonium salt NH$_4$[S$_2$P(OR′)C$_6$H$_4$OEt-*p*] and triphenylphosphine, dissolved in ethanol. Similarly prepared were the silver complexes, **2** (R′ = Me, Et, *iso*-PrO) by reacting AgNO$_3$ and PPh$_3$ with the ammonium salts of the (O-alkyl)aryldithiophosphonic acid monoesters in methanolic solution. The gold(I) compounds, **3** (R′ = Me, Et, *iso*-Pr) were obtained from [(Ph$_3$P)AuCl] and the ammonium salts in acetone solution. In all cases the yields were good or very good (see Experimental Part).

The new compounds were characterized by elemental analysis, infrared and NMR spectra. For each of the three metals one derivative has been subjected to single crystal X-ray analysis.

Infrared spectra

The ν_{sym}PS$_2$ and ν_{as}PS$_2$ group frequencies of the new compounds compared with those of the ammonium salt are given in Table 1.

Table 1 Phosphorus-sulfur group vibration frequencies /cm^{-1} in **1**−**3**

Compound	ν_{sym}PS$_2$	ν_{as}PS$_2$
NH$_4$[S$_2$P(OMe)(C$_6$H$_4$OEt-*p*]	568	632
1, R′ = Me	520	643
1, R′ = Et	519	642
1, R′ = *iso*-Pr	518	642
2, R′ = Me	520	650
2, R′ = Et	520	650
2, R′ = *iso*-Pr	518	650
3, R′ = Me	510	647
3, R′ = Et	512	648

The frequencies were assigned by comparison with literature data [8b, 14]. It is obvious that in a given series (Me/Et/*iso*-Pr) the ν_{as}PS$_2$ frequency is practically constant, whereas ν_{sym}PS$_2$ decrease with increasing size of the R′ group, in agreement with the inductive electron repulsion effects of these groups.

NMR spectra

Multinuclear (^{1}H, ^{13}C and ^{31}P) NMR spectra of the metal complexes were recorded, and the values of chemical shifts and coupling constants are given in the Experimental Part.

In the ^{1}H NMR spectra signals are observed in the following ranges: 1.1−1.5 ppm (OCH$_2$C$\underline{\mathrm{H}}_3$), 3.3−4.3 ppm (-OC$\underline{\mathrm{H}}_2$-), 6.7−6.9 ppm (*meta*-C$_6\underline{\mathrm{H}}_4$OEt), 7.8−8.1 ppm (*ortho*-C$_6\underline{\mathrm{H}}_4$OEt) and 7.1−7.6 (P-C$_6\underline{\mathrm{H}}_5$).

The ^{13}C NMR spectra exhibit signals in the following ranges: 14.6−16.4 ppm (OCH$_2\underline{\mathrm{C}}$H$_3$), 51.0−63.6 ppm (-O$\underline{\mathrm{C}}$H$_2$), 113.4−113.8 ppm (*meta*-$\underline{\mathrm{C}}_6$H$_4$OEt), 128.1−134.3 ppm (*ipso*- and *ortho*-$\underline{\mathrm{C}}_6$H$_4$OEt), and carbon atoms from metal coordinated P($\underline{\mathrm{C}}_6$H$_5$)$_3$ (*ipso, meta and para*), 160.7−161.1 ppm (*para*-$\underline{\mathrm{C}}_6$H$_4$OEt)

In the ^{31}P NMR spectra the signals in the range 100−110 ppm were assigned to the dithiophosphonato ligand and those in the range −3 to −38 ppm to the coordinated triphenylphosphine. Free triphenylphosphine displays a ^{31}P chemical shift at −6 ppm. The ^{31}P NMR shifts of coordinated triphenylphosphine in the copper (−3 ppm), silver (+7 ppm) and gold (+38 ppm) complexes are determined by the electron back donation from metal *d*-orbital into vacant *d*-orbitals of phosphorus. In the case of the gold compounds the shielding is more dramatic due to relativistic effects.

Crystal structures

(Ph$_3$P)$_2$Cu[S$_2$P(OMe)C$_6$H$_4$OEt-*p*] (1)

Crystals of **1, R′ = Me**, were obtained by layering an acetonitrile solution with hexane. The crystal retains a molecule of solvent which is lost on storage. The compound crystallizes in the monoclinic space group P2$_1$/c and is monomeric. The molecular structure with the atomic numbering scheme is shown in Fig. 1, and the parameters are listed in Table 2. The compound contains a CuS$_2$P four-membered chelate ring, and the coordination geometry of copper is basically tetrahedral, with a distortion caused by the small bite of the PS$_2$ group, S1−Cu−S2 84.(7)°. The ligand is isobidentate, as shown by P−S1 1.9933(8) Å and P3−S2 1.9946(8) Å and Cu−S1 2.4417(6) and Cu−S2 2.5048(6) Å. The Cu−P bonds differ only slightly with 2.2852(6) and 2.2786(6) Å.

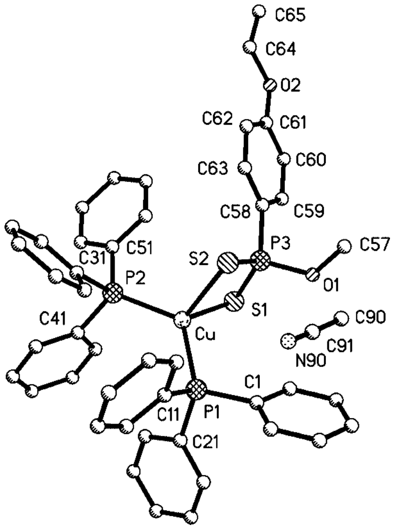

Fig. 1 Molecular structure of compound **1·MeCN**

Table 2 Bond lengths /Å and angles /° for compound **1·MeCN**, R′ = Me

Cu−P(2)	2.2786(6)	O(2)−C(64)	1.431(3)
Cu−P(1)	2.2852(6)	P(2)−Cu−P(1)	124.68(2)
Cu−S(1)	2.4417(6)	P(2)−Cu−S(1)	110.59(2)
Cu−S(2)	2.5048(6)	P(1)−Cu−S(1)	114.01(2)
S(1)−P(3)	1.9933(8)	P(2)−Cu−S(2)	111.32(2)
S(2)−P(3)	1.9946(8)	P(1)−Cu−S(2)	104.24(2)
P(1)−C(11)	1.827(2)	S(1)−Cu−S(2)	84.17(2)
P(1)−C(21)	1.829(2)	P(3)−S(1)−Cu	82.49(3)
P(1)−C(1)	1.829(2)	P(3)−S(2)−Cu	80.85(2)
P(2)−C(31)	1.824(2)	O(1)−P(3)−S(1)	105.79(7)
P(2)−C(41)	1.827(2)	C(58)−P(3)−S(1)	111.12(8)
P(2)−C(51)	1.830(2)	O(1)−P(3)−S(2)	112.22(7)
P(3)−O(1)	1.609(2)	C(58)−P(3)−S(2)	111.30(8)
P(3)−C(58)	1.800(2)	S(1)−P(3)−S(2)	112.49(3)
O(1)−C(57)	1.444(3)	C(57)−O(1)−P(3)	119.3(2)
O(2)−C(61)	1.366(3)	C(61)−O(2)−C(64)	117.0(2)

[(Ph$_3$P)Ag{S$_2$P(OMe)C$_6$H$_4$OEt-*p*}]

Single crystals of **2, R′ = Me,** were grown from dichloromethane layered with hexane. The compound crystallizes in the triclinic space group P$\bar{1}$ and is a centrosymmetric dimer based upon an eight-membered Ag$_2$S$_4$P$_2$ ring formed *via* bridging coordination of the ligands. The molecular structure with the atom numbering scheme is shown in Figure 2, and the structural parameters are listed in Table 3. The silver atoms are trigonally coordinated. The Ag−S bond lengths differ slightly, Ag−S2 2.6867 (5) Å and Ag−S1# 2.5371(5) Å, as well as the P−S bonds, P2−S1 2.0199(7) Å and P2−S1 1.9890(7) Å, suggesting that one of the P−S bonds retains some double bond character. The Ag−P1 bond length is 2.4314(5) Å, longer than the Cu−P bond length measured in **1**, R′ = Me.

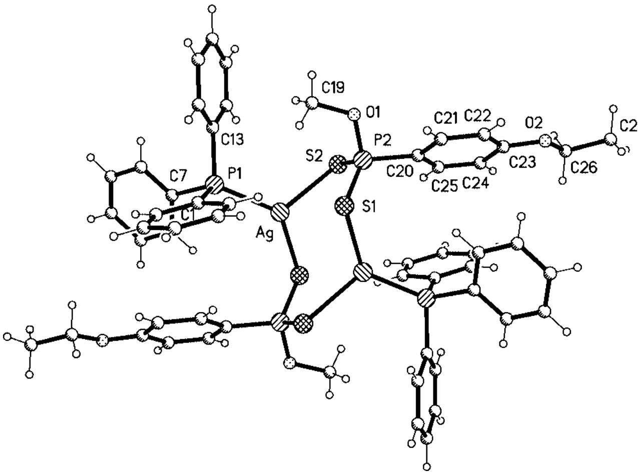

Fig. 2 Molecular structure of compound **2**

Table 3 Bond lengths /Å and angles /° for compound **2**, R′ = Me

Ag−P(1)	2.4314(5)	P(1)−C(1)	1.831(2)
Ag−S(1)#1	2.5371(5)	P(1)−C(7)	1.832(2)
Ag−S(2)	2.6867(5)	P(1)−C(13)	1.838(2)
S(1)−P(2)	2.0199(7)	P(2)−O(1)	1.6182(15)
S(1)−Ag#1	2.5371(5)	P(2)−C(20)	1.806(2)
S(2)−P(2)	1.9890(7)	O(1)−C(19)	1.444(2)
O(2)−C(23)	1.374(2)	O(1)−P(2)−C(20)	97.33(8)
O(2)−C(26)	1.426(3)	O(1)−P(2)−S(2)	112.61(6)
		C(20)−P(2)−S(2)	112.32(7)
P(1)−Ag−S(1)#1	132.88(2)	O(1)−P(2)−S(1)	107.08(6)
P(1)−Ag−S(2)	122.17(2)	C(20)−P(2)−S(1)	112.36(7)
S(1)#1−Ag−S(2)	98.01(2)	S(2)−P(2)−S(1)	113.88(3)
P(2)−S(1)−Ag#1	103.56(2)	C(19)−O(1)−P(2)	119.96(12)
P(2)−S(2)−Ag	89.32(2)	C(23)−O(2)−C(26)	119.0(2)

Symmetry transformations used to generate equivalent atoms:
#1 −x+1,−y,−z+1

[(Ph$_3$P)Au{S$_2$P(OMe)C$_6$H$_4$OEt-*p*}]

Crystals of compound **3**, R′ = Me, were obtained directly from the synthesis and belong to the monoclinic space group P2$_1$/c. The compound is monomeric. The molecular structure with the atom numbering scheme is shown in Figure 3, and the structural parameters are listed in Table 4. The gold atom is dicoordinate with a nearly linear arrangement: P1−Au−S1 177.72(2)°. The Au−P bond length is 2.2599(6) Å, shorter than the Ag−P bond in **2**, R′ = Me, and even the Cu−P bond in **1**, R′ = Me, due to relativistic effects which enhance the Au−P bond strength, as suggested also by the ^{31}P NMR spectra. The primary Au−S bond is 2.3218(6) Å, again shorter than the Cu−S and Ag−S bonds in **1** and **2**, R′ = Me. The second sulfur atom is far from the metal atom and the Au···S distance of 3.645 Å is too large even for a secondary gold-sulfur bond. Therefore, the dithiophosphonato ligand is monodentate, with P2−S1 2.0606(9) Å (single P−S bond) and P2−S2 1.9510(9) Å (double P=S bond).

No intermolecular aurophilic interactions were observed in the crystal, the shortest Au···Au distance being very large (6.548 Å). The intermolecular Au···S distances of 3.8670 Å are also too large for a secondary bond interaction, since the sum of the van der Waals radii for the Au/S pair is 3.50 Å.

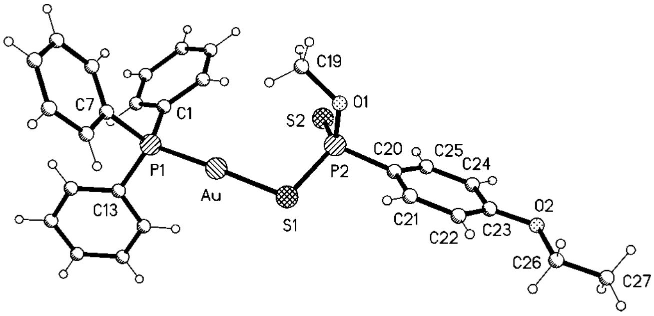

Fig. 3 Molecular structure of compound **3**

Table 4 Bond lengths /Å and angles /° for compound **3**, R′ = Me

Au−P(1)	2.2599(6)	P(2)−S(1)−Au	100.97(3)
Au−S(1)	2.3218(6)	C(1)−P(1)−Au	112.79(8)
Au−S(2)#1	3.8670(7)	C(13)−P(1)−Au	114.62(8)
S(1)−P(2)	2.0606(9)	C(7)−P(1)−Au	113.94(8)
S(2)−P(2)	1.9510(9)	O(1)−P(2)−C(20)	98.27(10)
P(2)−O(1)	1.607(2)	O(1)−P(2)−S(2)	112.19(8)
O(1)−C(19)	1.433(3)	C(20)−P(2)−S(2)	114.60(9)
O(2)−C(23)	1.356(3)	O(1)−P(2)−S(1)	106.48(8)
O(2)−C(26)	1.434(3)	C(20)−P(2)−S(1)	105.39(8)
		S(2)−P(2)−S(1)	117.83(4)
P(1)−Au−S(1)	177.72(2)	C(19)−O(1)−P(2)	119.6(2)
P(1)−Au−S(2)#1	97.11(2)	C(23)−O(2)−C(26)	118.2(2)
S(1)−Au−S(2)#1	82.27(2)		

Symmetry transformations used to generate equivalent atoms:
#1 x,−y+1/2,z+1/2

Conclusions

The three related compounds [$(Ph_3P)_nM\{S_2P(OMe)C_6H_4OEt$-*p*}] of copper (n = 2), silver (n = 1) and gold (n = 1) investigated structurally by X-ray diffraction exhibit remarkable structural differences. The metals are: four-coordinate tetrahedral in monomeric **1** (M = Cu), tri-coordinate trigonal planar in dimeric **2** (M = Ag) and di-coordinate linear in monomeric **3** (M = Au), reflecting different bonding properties, enhanced by the relativistic effects in the case of gold. Similar contrasting bonding modes in the Cu(I)−Ag(I)−Au(I) triad were reported in the triphenylphosphine metal complexes of these metals with another dithioligand, namely dithiotetraphenylimidodiphosphinato anion, $[SPPh_2NPPh_2S]^-$, and the difference is supported by DFT calculations for these compounds [15].

Experimental Part

All commercially available reagents were used as received. Some, including [$S(S)PC_6H_4OEt$-*p*]$_2$ [16], [$(Ph_3P)_2CuNO_3$] [17], and [$(Ph_3P)AuCl$] [18] were prepared according to published procedures. Solvents were purified and dried by standard techniques [19]. Elemental analyses were performed on a LECO CHNS-932 analyzer. Infrared and NMR spectra were recorded on Perkin Elmer 2000 FT-IR and Bruker DPX-400 instruments, respectively. Melting points were measured on an Electrothermal IA9100 apparatus and are reported without correction.

Syntheses

$NH_4[S_2P(OMe)C_6H_4OEt$-*p*]: 7.92 g of [$S(S)PC_6H_4OEt$-*p*]$_2$ were added to a mixture of 50 ml anhydrous benzene and 1.8 ml anhydrous methanol. After stirring for 30 minutes at 40 − 60 °C, the solid dissolved and a clear, colourless solution was obtained. Excess dry NH_3 was bubbled through the ice-cooled solution, giving rise to a voluminous, white precipitate. The thick slurry was taken up into 50 ml anhydrous benzene, filtered, washed with benzene and dried in a vacuum dessicator. Yield: 9.47 g (97 %). Mp 152 − 158 °C (decomp.). For $C_9H_{16}NO_2PS_2$, calcd.: C 40.74, H 6.08, N 5.28; found C 40.54, H 6.53, N 5.43 %. $NH_4[S_2P(OMe)C_6H_4OEt$-*p*] is a white, non-hygroscopic powder, which is soluble in H_2O, alcohols, acetone, MeCN, THF and insoluble in benzene, Et_2O, CH_2Cl_2, $CHCl_3$, CCl_4.

$NH_4[S_2P(OEt)C_6H_4OEt$-*p*]: A similar procedure using 6.25 g [$S(S)PC_6H_4OEt$-*p*]$_2$ and 2.0 ml anhydrous EtOH. Yield: 7.43 g (92 %). Mp 157 − 160 °C (decomp.). For $C_{10}H_{18}NO_2PS_2$, calcd.: C 42.99, H 6.49, N 5.01; found C 42.67, H 6.11, N 5.07 %.

$NH_4[S_2P(OPr^i)C_6H_4OEt$-*p*]: A similar procedure using 7.23 g [$S(S)PC_6H_4OEt$-*p*]$_2$ and 2.8 ml anhydrous Pr^iOH. Yield: 9.34 g (95 %). Mp 166 − 169 °C (decomp.). For $C_{11}H_{20}NO_2PS_2$, calcd.: C 45.03, H 6.87, N 4.77; found C 44.51, H 7.35, N 4.78 %.

[$(Ph_3P)_2Cu\{S_2P(OMe)C_6H_4OEt$-*p*}]: The free acid $HS(S)P(OMe)C_6H_4OEt$-*p* was prepared in a 100 ml flask by dissolving 2.16 g of the disulfide [$S(S)P(OMe)C_6H_4OEt$-*p*]$_2$ in 40 ml anhydrous methanol under mild heating. The clear solution was treated with 3.25 g $(Ph_3P)_2CuNO_3$ and 20 ml nitrobenzene and the solution was refluxed for 30 minutes. The crystalline white precipitate which separated on cooling was filtered, washed with methanol and dried in vacuo. Yield 3.48 g (83 %), m.p. 182 °C (decomp). $C_{45}H_{42}O_2P_3S_2Cu$, calcd.: C 64.69; H 5.07, S 7.68; found C 64.66, H 5.66; S 7.67 %.

^1H NMR: $OCH_2C\underline{H}_3$ 1.41 t, 3H, $^3J(HH)$ 7.0 Hz; P-$OC\underline{H}_3$ 3.36 d, 3H, $^3J(PH)$ 15.1 Hz; $OC\underline{H}_2$ 4.04 q, 2H, $^3J(HH)$ 7.0 Hz; *meta*-$C_6\underline{H}_4OEt$ 6.76 dd, 2H, $^3J(HH)$ 8.8 Hz, $^4J(PH)$ 2.7 Hz; *ortho*-$C_6\underline{H}_4OEt$ 7.82 dd, 2H, $^3J(HH)$ 8.8 Hz, $^3J(PH)$ 14.2 Hz; CuP-$C_6\underline{H}_5$ 7.11−7.37 m, 30 H. **^{13}C NMR:** $OCH_2\underline{C}H_3$ 14.73 s, P-$O\underline{C}H_3$ 51.01 d, $^2J(PC)$ 6.6 Hz, $O\underline{C}H_2$ 63.44 s, *meta*-$\underline{C}_6H_4OEt$ 113.46 d, $^3J(PC)$ 15.4 Hz, *ortho*-$\underline{C}_6H_4OEt$ 131.56 d, $^2J(PC)$ 14.2 Hz, *para*-$\underline{C}_6H_4OEt$ 131.56 d, $^2J(PC)$ 14.2 Hz, CuP-$\underline{C}_6H_5$ *meta* 128.19 d, $^3J(PC)$ 8.6 Hz, *para* 129.26 s, *ortho* 133.91 d, $^2J(PC)$ 14.1 Hz; *para*-$\underline{C}_6H_4OEt$ 160.70 d, $^4J(PC)$ 2.9 Hz. **^{31}P NMR:** **P**Ph_3 −3.01s, **PS**$_2$ 100.88 s, $^3J(HP)$ 14.5 Hz.

[$(Ph_3P)_2Cu\{S_2P(OEt)C_6H_4OEt$-*p*}]: An amount of 0.3 g $CuSO_4{\cdot}5H_2O$ was dissolved in 10 ml methanol. To this solution was added dropwise, under stirring, a solution obtained by dissolving 0.67 g $NH_4[S_2P(OEt)C_6H_4OEt$-*p*] and 0.63 g PPh_3 in 20 ml of hot ethanol. The mixture was stirred for 15 minute and the white precipitate formed was filtered, washed with methanol, water and finally with petroleum ether and was dried *in vacuo* over $CaCl_2$. Yield 0.84 g (82 %), m.p. 147−153 °C; decomp. *ca.* 170 °C.

[$(Ph_3P)_2Cu\{S_2P(OPr^i)C_6H_4OEt$-*p*}]: The compound was similarly prepared from 0.3 g $CuSO_4{\cdot}5H_2O$, 0.70 g $NH_4[S_2P(OPr^i)C_6H_4OEt$-*p*] and 0.63 g PPh_3. The viscous mass formed solidified on standing and cooling, Yield 0.86 g (83 %), m.p. 130−135 °C (decomp).

[(Ph$_3$P)Ag{S$_2$P(OMe)C$_6$H$_4$OEt-*p*}]: A solution of 0.5 g AgNO$_3$ and 0.77 g PPh$_3$ in 40 ml methanol was treated dropwise under stirring with a solution of 0.78 g NH$_4$[S$_2$P(OMe)C$_6$H$_4$OEt-*p*] in 5 ml methanol. The white precipitate formed was filtered after 15 minutes of stirring and washed with methanol and ether and dried. Yield 1.76 g (97 %), m.p. 182−184 °C (decomp.). $C_{27}H_{27}O_2P_2S_2Ag$, calcd: C 52.52, H 4.41, S 10.39; found: C 52.35, H 4.63, S 10.17 %.

^{1}H NMR (ppm): OCH$_2$C$\underline{\mathbf{H}}_3$ 1.37 t, 3H, ^3J(HH) 7.0 Hz; P-OC$\underline{\mathbf{H}}_3$ 3.49 d, 3H, ^3J(PH) 15.1 Hz; OC$\underline{\mathbf{H}}_2$ 3.96 q, 2H, ^3J(HH) 7.0 Hz; *meta*-C$_6\underline{\mathbf{H}}_4$OEt 6.70 dd, 2H, ^3J(HH) 8.7 Hz, ^4J(PH) 2.8 Hz; *ortho*-C$_6\underline{\mathbf{H}}_4$OEt 7.90 dd, 2H, ^3J(HH) 8.7 Hz, ^3J(PH) 13.8 Hz; P-C$_6\underline{\mathbf{H}}_5$ 7.24−7.43 m, 30 H;
^{13}C NMR: OCH$_2\underline{\mathbf{C}}$H$_3$ 14.69 s; P-O$\underline{\mathbf{C}}$H$_3$ 52.02 d, ^2J(PC) 7.3 Hz; O$\underline{\mathbf{C}}$H$_2$ 63.37 s; *meta*-$\underline{\mathbf{C}}_6$H$_4$OEt 113.52 d, ^3J(PC) 15.3 Hz; *ortho*-$\underline{\mathbf{C}}_6$H$_4$OEt 132.10 d, ^2J(PC) 14.2 Hz; *ipso*-$\underline{\mathbf{C}}_6$H$_4$OEt 131.24 d, ^1J(PC) 114.4 Hz; AgP-$\underline{\mathbf{C}}_6$H$_5$ *meta* 128.62 d, ^3J(PC) 8.6 Hz, *para* 129.93 s, *ortho* 134.03 d, ^2J(PC) 16.3 Hz, *ipso* 132.48 d, ^2J(PC) 26.2 Hz; *para*-$\underline{\mathbf{C}}_6$H$_4$OEt 160.86 d, ^4J(PC) 3.1 Hz;
^{31}P NMR: P Ph$_3$ 7.50 s, **PS**$_2$ 110.49 s, ^3J(HP) 14.6 Hz.

[(Ph$_3$P)Ag{S$_2$P(OEt)C$_6$H$_4$OEt-*p*}]: The compound was similarly prepared from 0.3 g AgNO$_3$, 0.49 g NH$_4$[S$_2$P(OEt)C$_6$H$_4$OEt-*p*] and 0.46 g PPh$_3$. Yield 1.03 g (93 %), m.p. 140−143 °C (decomp.).

^{1}H NMR (ppm): POCH$_2$C$\underline{\mathbf{H}}_3$ 1.11 t, 6H, ^3J(HH) 7.0 Hz; C$_6$H$_4$-OCH$_2$C$\underline{\mathbf{H}}_3$ 1.39 t, 6H, ^3J(HH) 6.9 Hz; C$_6$H$_4$OC$\underline{\mathbf{H}}_2$CH$_3$ and POC$\underline{\mathbf{H}}_2$CH$_3$ 3.95 m, 4H, 4H; *meta*-C$_6\underline{\mathbf{H}}_4$OEt 6.71 dd, 4H, ^3J(HH) 8.6 Hz, ^4J(PH) 2.7 Hz; *ortho*-C$_6\underline{\mathbf{H}}_4$OEt 7.94 dd, 4H, ^3J(HH) 8.8 Hz, ^3J(PH) 13.8 Hz; AgP-C$_6\underline{\mathbf{H}}_5$ 7.25−7.45 m, 30H. **^{13}C NMR:** C$_6$H$_4$OCH$_2\underline{\mathbf{C}}$H$_3$ 14.82 s; P-OCH$_2\underline{\mathbf{C}}$H$_3$ 16.21 d, ^2J(PC) 9.5 Hz; P-O$\underline{\mathbf{C}}$H$_2$CH$_3$ 61.74 d, ^2J(PC) 6.7 Hz; C$_6$H$_4$O$\underline{\mathbf{C}}$H$_2$CH$_3$ 63.45 s; *meta*-$\underline{\mathbf{C}}_6$H$_4$OEt 113.57 d, ^3J(PC) 15.1 Hz; *ortho*-$\underline{\mathbf{C}}_6$H$_4$OEt 132.16 d, ^2J(PC) 13.9 Hz; *ipso*-$\underline{\mathbf{C}}_6$H$_4$OEt 131.90 d, ^1J(PC) 114.4 Hz; AgP-$\underline{\mathbf{C}}_6$H$_5$ *ortho* 134.14 d, ^2J(PC) 16.4 Hz, *ipso* 132.60 d, ^2J(PC) 25.3 Hz; *para*-$\underline{\mathbf{C}}_6$H$_4$OEt 160.87 s **^{31}P NMR: P**Ph$_3$ 6.96 s, **PS**$_2$ 107.32 s.

[(Ph$_3$P)Ag{S$_2$P(OPr^i)C$_6$H$_4$OEt-*p*}]: The compound was similarly prepared from 0.3 g AgNO$_3$, 0.46 g PPh$_3$ and 0.52 g NH$_4$[S$_2$P(OPr^i)-C$_6$H$_4$OEt-*p*]. Yield 1.03 g (90 %), m.p. 165−168 °C (decomp.).

[(Ph$_3$P)Au{S$_2$P(OMe)C$_6$H$_4$OEt-*p*}]: A solution of 0.2 g (Ph$_3$P)AuCl in 10 ml acetone was tretaed with a solution of 0.11 g NH$_4$[S$_2$P(OMe)-C$_6$H$_4$OEt-*p*] in 5 ml acetone. The white precipitate of NH$_4$Cl was filtered and the clear filtrate was left in the refrigerator. The white, shiny crystals formed were filtered and washed with a small amount of acetone and dried in air. Yield 0.25 g (88 %), m.p. 114−116 °C, decomp. 170 °C. $C_{27}H_{27}O_2P_2S_2Au$, calcd.: 45.90, H 3.85, S 9.08; found: 46.14, H 4.26, S 9.05 %.

^{1}H NMR (ppm): OCH$_2$C$\underline{\mathbf{H}}_3$ 1.40 t, 3H, ^3J(HH) 7.0 Hz; P-OC$\underline{\mathbf{H}}_3$ 3.84 d, 3H, ^3J(PH) 15.3 Hz; OC$\underline{\mathbf{H}}_2$ 4.02 q, 2H, ^3J(HH) 7.0 Hz; *meta*-C$_6\underline{\mathbf{H}}_4$OEt 6.83 dd, 2H, ^3J(HH) 8.9 Hz, ^4J(PH) 2.8 Hz; *ortho*-C$_6\underline{\mathbf{H}}_4$OEt 8.07 dd, 2H, ^3J(HH) 8.9 Hz, ^3J(PH) 13.9 Hz; AuP-C$_6\underline{\mathbf{H}}_5$ 7.41−7.54 m, 30 H; **^{13}C NMR:** OCH$_2\underline{\mathbf{C}}$H$_3$ 14.67 s; P-O$\underline{\mathbf{C}}$H$_3$, 51.45 d, ^2J(PC) 6.7 Hz; OC$\underline{\mathbf{H}}_2$ 63.44 s; *meta*-C$_6\underline{\mathbf{H}}_4$OEt 113.69d, ^3J(PC) 15.5 Hz; *ortho*-C$_6\underline{\mathbf{H}}_4$OEt 131.92 d, ^2J(PC) 13.6 Hz; *para*-C$_6\underline{\mathbf{H}}_4$OEt 161.04 d, ^4J(PC) 3.3 Hz; *ipso*-C$_6\underline{\mathbf{H}}_4$OEt 133.06 d, ^1J(PC) 120.4 Hz; AuP-C$_6\underline{\mathbf{H}}_5$ *meta* 129.11 d, ^3J(PC) 11.7 Hz, *para* 131.68 s, *ortho* 134.14 d, ^2J(PC) 13.9 Hz, *ipso* 129.08 d, ^2J(PC) 58.5 Hz; **^{31}P NMR: P**Ph$_3$ 38.01 s; **PS**$_2$ 104.50 s, ^3J(HP) 14.7 Hz.

[(Ph$_3$P)Au{S$_2$P(OEt)C$_6$H$_4$OEt-*p*}]: The compound was similarly prepared from 0.2 g (Ph$_3$P)AuCl, 0.13 g NH$_4$[S$_2$P(OMe)-C$_6$H$_4$OEt-*p*]. Yield 0.24 g (83 %), mp. 106−108 °C, decomp. 165 °C. $C_{28}H_{29}O_2P_2S_2Au$, calcd.: C 46.67, H 4.06, S 8.90; found: C 46.14, H 4.37, S 8.74 %.

^{1}H NMR (ppm): POCH$_2$C$\underline{\mathbf{H}}_3$ 1.34 t, 3H, ^3J(HH) 6.9 Hz; C$_6$H$_4$OCH$_2$C$\underline{\mathbf{H}}_3$ 1.40 t, 3H, ^3J(HH) 6.8 Hz; C$_6$H$_4$OC$\underline{\mathbf{H}}_2$CH$_3$ 4.02 q, 2H, ^3J(HH) 6.7 Hz; POC$\underline{\mathbf{H}}_2$CH$_3$ 4.27 q, 2H, ^3J(HH/PH) 7.5 Hz; *meta*-C$_6\underline{\mathbf{H}}_4$OEt 6.83 dd, 2H, ^3J(HH) 7.9 Hz; AuP-C$_6\underline{\mathbf{H}}_5$ 7.47−7.51 m, 30 H; *ortho*-C$_6\underline{\mathbf{H}}_4$OEt 8.08 dd, 2H, ^3J(HH) 8.2 Hz, ^3J(PH) 13.6 Hz; **^{13}C NMR:** C$_6$H$_4$OCH$_2\underline{\mathbf{C}}$H$_3$ 14.82 s; P-OCH$_2\underline{\mathbf{C}}$H$_3$, 16.39 d, ^3J(PC) 8.9 Hz; PO$\underline{\mathbf{C}}$H$_2$CH$_3$ 61.16 s; C$_6$H$_4$OCH$_2$CH$_3$ 63.55 s, *meta*-$\underline{\mathbf{C}}_6$H$_4$OEt 113.77 d, ^3J(PC) 15.6 Hz; AuP($\underline{\mathbf{C}}_6$H$_5$)$_3$ *para*- and *ortho*, *ipso*-$\underline{\mathbf{C}}_6$H$_4$OEt 131.0−133.0 m, AuP-$\underline{\mathbf{C}}_6$H$_5$ *meta* 129.23 d, ^3J(PC) 11.5 Hz, AuP-$\underline{\mathbf{C}}_6$H$_5$ *ortho* 134.26 d, ^3J(PC) 14.1 Hz; **^{31}P NMR: P**Ph$_3$ 38.00 s; **PS**$_2$ 101.22 s.

Table 5 Crystallographic data for compounds **1**, **2** and **3**.

	1·MeCN	**2**	**3**
Empirical formula	$C_{47}H_{45}CuNO_2P_3S_2$	$C_{54}H_{54}Ag_2O_4P_4S_4$	$C_{27}H_{27}AuO_2P_2S_2$
Formula weight	876.41	1234.83	706.51
Temperature /K	173(2)	173(2)	173(2)
Wavelength /Å^3	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	monoclinic
Space group	P2$_1$/c (No. 14)	P$\bar{1}$ (No. 2)	P2$_1$/c (No. 14)
a /Å	13.0704(2)	10.8802(2)	9.4323(1)
b /Å	27.7424(3)	11.8510(1)	20.7062(1)
c /Å	12.7558(1)	12.7811(2)	13.4458(2)
α /°	90	113.595(1)	90
β /°	109.471(1)	106.742(1)	92.219(1)
γ /°	90	99.148(1)	90
Volume /Å^3	4360.79(9)	1373.76(4)	2624.09(5)
Z	4	1	4
D$_{calc}$ /g cm^{-3}	1.335	1.493	1.788
μ /mm^{-1}	0.745	1.024	5.911
F(000)	1824	628	1384
Crystal size /mm	0.65 × 0.12 × 0.06	0.45 × 0.40 × 0.10	0.50 × 0.35 × 0.30
θ range /°	1.47 − 28.29	1.89 − 28.26	1.81 − 28.28
Index ranges	$-17 \le h \le 16$	$-36 \le k \le 31$	$-16 \le l \le 16$
	$-14 \le h \le 12$	$-15 \le k \le 12$	$-8 \le l \le 17$
	$-12 \le h \le 4$	$-26 \le k \le 27$	$-17 \le l \le 17$
Reflections collected	28966	9172	17339
Unique reflections	10724 [R(int) = 0.0354]	6459 [R(int) = 0.0189]	6447 [R(int) = 0.0235]
Max. and min. transmission	1.00 / 0.86	1.00 / 0.76	1.00 / 0.70
Data/restraints/parameters	10723 / 0 / 508	6450 / 0 / 309	6441 / 0 / 309
Goodness-of-fit	1.090	1.018	1.084
Final R indices R1 / wR2 [I>2σ(I)]	0.0405 / 0.0762	0.0276; 0.0687	0.0210; 0.0446
R indices (all data) R1 / wR2	0.0663 / 0.0877	0.0344 / 0.0756	0.0257 / 0.0472
Max. peak/hole /e Å^{-3}	0.377 / −0.415	0.456 / −0.429	0.464 / −1.136

[(Ph$_3$P)Au{S$_2$P(OPr^i)C$_6$H$_4$OEt-*p*}]: A similar procedure with 0.2 g (Ph$_3$P)AuCl, 0.12 g NH$_4$[S$_2$P(OPr^i)C$_6$H$_4$OEt-*p*] gave a viscous oil which could not be solidified and was discarded.

Crystallography

The details of crystallographic determinations are given in Table 5.

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