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New gold(I) and silver(I) complexes with organophosphorus ligands with SPNSO skeleton. Crystal and molecular structures of monomeric $[Au\{(SPPh_2)(O_2SR)N\}(PPh_3)]$ (R = Me, C_6H_4Me-4) and dimeric $[Ag\{(SPPh_2)(O_2SPh)N\}(PPh_3)]_2{\cdot}2CH_2Cl_2$

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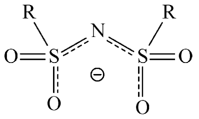
ABSTRACT

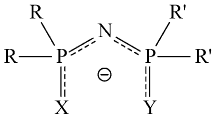
The reaction between gold(I) and silver(I) starting materials with anionic organophosphorus ligands of type $[(SPPh_2)(O_2SR)N]^-$ resulted in new group 11 complexes of the type $[Au\{(SPPh_2)(O_2SR)N\}(tht)]$ (tht = tetrahydrothiophene), $[Au\{(SPPh_2)(O_2SR)N\}(PPh_3)]$, PPN$[Au\{(SPPh_2)(O_2SR)N\}_2]$ [PPN = bis(triphenylphosphine)iminium], $[Ag\{(SPPh_2)(O_2SR)N\}]$ and $[Ag\{(SPPh_2)(O_2SR)N\}(PPh_3)]$ (R = Me, Ph, $C_6H_4CH_3$-4). The new derivatives were structurally characterized by ^1H and ^{31}P NMR spectroscopy, as well as infrared and mass spectrometry. Single-crystal X-ray diffraction studies revealed monomeric structures for the gold(I) species $[Au\{(SPPh_2)(O_2SMe)N\}(PPh_3)]$ (**4**) and $[Au\{(SPPh_2)(O_2SC_6H_4Me\text{-}4)N\}(PPh_3)]$ (**6**), while a dimeric association was found for the silver(I) compound $[Ag\{(SPPh_2)(O_2SPh)N\}(PPh_3)]_2{\cdot}2CH_2Cl_2$ (**14**$\cdot 2CH_2Cl_2$). The organophosphorus(V) ligand units have different coordination patterns, *i.e. S*-monometallic monoconnective in **4**, *S,O*-monometallic biconnective in **6** and *S,S,O*-bimetallic triconnective in **14**, respectively.

1. Introduction

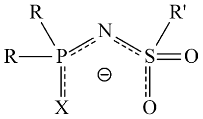
Silver(I) [1,2] and gold(I) [3,4] complexes attracted an increased interest during last years due both to their structural features and their potential applications. Silver(I) complexes with oxo- or thio ligands proved to be valuable candidates for catalysis [5], material science [6,7], or CVD techniques [8]. Gold(I) complexes containing ligands with N, P or S donor atoms already proved to be valuable candidates in medicine [9–11], catalysis [12–14] and material science [15–17]. Polydentate ligands should offer different coordination sites, thus dictating different coordination geometries around the metal centre and the possibility to obtain monomeric or polymeric species. Gold(I) diorganodithiophosphinates and -phosphonates were intensively investigated in last years related to their expected metal–metal interactions, thus resulting in dimeric or polymeric solids with optical properties [18–20]. The dithiolato ligands act mostly bimetallic biconnective, bridging the neighboring gold(I) centres, except the complex $[Au\{S_2P(OMe)(C_6H_4OEt\text{-}4)\}(PPh_3)]$, where the ligand acts monodentate [21]. In the silver(I) analogues the dithioato ligands act either as bidentate chelating moieties [22,23] or bridging groups [21]. Group 11 metal complexes with bis(diorganosulfonyl)amido ligands of type **A**, as well as of tetraorganodichalcogenoimidodiphosphinato ligands of type **B**, were also described.



A



B



C

Both in silver(I) and gold(I) complexes the ligand of type **A** is primarily attached to the metal centre through nitrogen. Gold(I) complexes $[Au\{(O_2SR)_2N\}(PPh_3)]$ (R = Me, C_6H_4Cl-4, $C_6H_4NO_2$-4 [24], C_6H_4F-4, $C_6H_4CH_3$-4 [25]) have monomeric structures with a linear coordination geometry around the metal center. For the silver(I) $[Ag\{(O_2SR)_2N\}_2]^-$ (R = Me, C_6H_4F-4) anionic species a linear N–Ag–N core is achieved, but the coordination number of the silver(I) ion is extended to [2 + 6] by four internal and two external Ag···O secondary interactions [26,27]. The dimeric species $[Ag\{(O_2SPh)_2N\}]_2(H_2O)$ and $[Ag\{(O_2SC_6H_4Me\text{-}4)_2N\}]_2$ [28] are based on (*N,O*)-bridging ligands. In the crystal of the water-free derivative the dimer units are further associated into infinite strands through two external dative Ag···O bonds per silver atom. Several gold(I) and silver(I) complexes with ligands of type **B**,

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[(XPR$_2$)(YPR′$_2$)N]$^-$ (X, Y = O, S, Se), were investigated as well and were found to display different coordination patterns [29–31]. A tetrahedral environment is realized by the *S,S*-bidentate coordinated protonated ligand in the mononuclear [Ag{(SPPh$_2$)$_2$NH}$_2$]$^+$ cation [32]. The tetranuclear species [Ag{(OPPh$_2$)$_2$N}]$_4$·2EtOH contains both (*N,O*)-bridging ligands and (*N,O,O′O′*)-trimetallic tetraconnective ligands [33]. In gold(I) complexes the metal center retains the expected linear geometry, the imidodiphosphinato ligands acting in most of the described derivatives as a *S*-monodentate moiety, *i.e.* in [Au{(SPPh$_2$)(OPPh$_2$)N}{(SPPh$_2$)(OPPh$_2$)NH}] [34], [Au{(SPPh$_2$)(OPPh$_2$)N}(Ph$_2$PC$_6$H$_4$NH$_2$)] [35], or [Au{(SPPh$_2$)(OPPh$_2$)N}{*P*-(Ph$_2$P)(OPPh$_2$)NH}] [36]. In the derivative [Au{(SPPh$_2$)$_2$N}(PPh$_3$)] both sulfur atoms are involved in coordination to the gold(I) center [37].

Recently we have reported a new class of organophosphorus(V) ligands of type **C** [38,39] and their copper(I) complexes [CuL(PPh$_3$)$_2$] [39]. Here we report on the synthesis and structural characterization of some new gold(I) and silver(I) complexes of type [MLL^1], [AuL$_2$]$^-$ or [AgL] (M = Au, Ag, L^1 = tht, PPh$_3$, L = ligand of type **C**).

2. Experimental

2.1. General methods

Starting materials, *i.e.* K[(SPPh$_2$)(O$_2$SR)N] (R = Me, Ph, C$_6$H$_4$Me-4) [38,39], the gold(I) complexes [AuCl(tht)] [40], [AuCl(PPh$_3$)] [41], PPN[AuCl$_2$] [42] and silver(I) derivatives [Ag(OTf)(PPh$_3$)] [43] were prepared according to literature methods or used as purchased (Ag(OTf) – Aldrich). The solvents were dried and freshly distilled under argon prior to use. Elemental analyses were performed on a Perkin–Elmer 2400 analyser and melting points were measured on an Electrothermal 9200 apparatus and are not corrected. Infrared spectra were recorded in the range 4000–400 cm^{-1} as KBr pellets on a Jasco FTIR-615 machine, while mass spectra (ESI MS) were performed on an Agilent 6320 Ion Trap instrument. ^{1}H and ^{31}P NMR spectra were recorded on a BRUKER Avance DRX 400 instrument. The chemical shifts are reported in δ units (ppm) relative to the residual peak of the deuterated solvent (Ref. CHCl$_3$: ^{1}H 7.26 ppm, DMSO: ^{1}H 2.50 ppm and H$_3$PO$_4$ 85%, respectively).

2.2. Syntheses

2.2.1. Preparation of [Au{(SPPh$_2$)(O$_2$SMe)N}(tht)] (**1**)

Stoichiometric amounts of K[(SPPh$_2$)(O$_2$SMe)N] (0.035 g, 0.1 mmol) and [AuCl(tht)] (0.032 g, 0.1 mmol) were stirred in CH$_2$Cl$_2$ (50 mL) for 1 h at room temperature. KCl was removed by filtration and the solution was concentrated under reduced pressure to approximately 2 mL. The title compound was precipitated with *n*-hexane, separated by filtration and dried in vacuum. Yield: 0.05 g (84%). M.p. 130 °C (dec.). *Anal.* Calc. for C$_{17}$H$_{21}$AuNO$_2$PS$_3$ (MW 595.49): C, 34.29; H, 3.55; N, 2.35; S, 16.15. Found: C, 34.42; H, 3.61; N, 2.25; S, 16.34%. ^{1}H NMR (CDCl$_3$): δ 1.93s, br. (4H, tht), 3.01s (3H, O$_2$S–C*H*$_3$), 3.22s, br. (4H, tht); 7.43m [6H, P(S)–C$_6$H$_5$-meta + para], 8.01m [4H, P(S)–C$_6$*H*$_5$-*ortho*]; ^{31}P NMR (CDCl$_3$): δ 29.9. ESI+ (*m*/*z*, %): 895 (62) [(tht)$_2$Au$_2$L+Me]$^+$, 880 (100) [(tht)$_2$Au$_2$L]$^+$, 865 (93) [(tht)$_2$Au$_2$L–Me]$^+$, 508 (34) [AuL+H]$^+$. ESI– (*m*/*z*, %): 817 (43) [AuL$_2$]$^-$, 533 (100) [AuL+CN]$^-$, 310 (15) [L]$^-$. FT-IR (cm^{-1}): ν_{as}(SO$_2$) 1241s; ν_{as}(PNS) 1180s; ν_s(SO$_2$) 1142vs, 1109vs; ν(P–S) 568s.

Compounds **2**–**6** were prepared similarly:

[Au{(SPPh$_2$)(O$_2$SPh)N}(tht)] (**2**), from K[(SPPh$_2$)(O$_2$SPh)N] (0.041 g, 0.1 mmol) and [AuCl(tht)] (0.032 g, 0.1 mmol). Yield: 0.06 g (92%). M.p. 65 °C (dec). *Anal.* Calc. for C$_{22}$H$_{23}$AuNO$_2$PS$_3$ (MW 657.56): C, 40.18; H, 3.52; N, 2.13; S, 14.63. Found: C, 39.96; H, 3.46; N, 2.14; S, 14.22%. ^{1}H NMR (CDCl$_3$): δ 1.96s, br. (4H, tht), 3.24s, br. (4H, tht), 7.32 m [6H, O$_2$S–C$_6$*H*$_5$-*meta*, P(S)–C$_6$*H*$_5$-*meta*], 7.40m [3H, O$_2$S–C$_6$*H*$_5$-*para*, P(S)–C$_6$*H*$_5$-*para*], 7.91m [6H, SO$_2$–C$_6$*H*$_5$-*ortho*, P(S)–C$_6$*H*$_5$-*ortho*], ^{31}P NMR (CDCl$_3$): δ 31.2. ESI+ (*m*/*z*, %): 1019 (100) [(tht)$_2$Au$_2$L+Ph]$^+$, 1003 (92), [(tht)$_2$Au$_2$L+Ph–O]$^+$, 680 (12) [AuL+Na]$^+$. ESI– (*m*/*z*, %): 941 (20) [AuL$_2$]$^-$, 595 (100) [AuL+CN]$^-$, 372 (12) [L]$^-$. FT-IR (cm^{-1}): ν_{as}(SO$_2$) 1256s; ν_{as}(PNS) 1185s; ν_s(SO$_2$) 1137vs; ν(P–S) 570s.

[Au{(SPPh$_2$)(O$_2$SC$_6$H$_4$Me-4)N}(tht)] (**3**), from K[(SPPh$_2$)(O$_2$SC$_6$H$_4$Me-4)N] (0.0425 g, 0.1 mmol) and [AuCl(tht)] (0.032 g, 0.1 mmol). Yield: 0.065 g (97%). M.p. 153 °C (dec). *Anal.* Calc. for C$_{23}$H$_{25}$AuNO$_2$PS$_3$ (MW 671.59): C, 41.13; H, 3.75; N, 2.08; S, 14.32. Found: C, 40.82; H, 3.57; N, 2.37; S, 14.48%. ^{1}H NMR (DMSO-d$_6$): δ 1.85s, br. (4H, tht), 2.30s (3H, O$_2$S–C$_6$H$_4$C*H*$_3$), 2.75s, br. (4H, tht), 7.15d [2H, O$_2$S–C$_6$*H*$_4$CH$_3$-*meta*, ^{3}*J*(HH) 8.0 Hz], 7.42m [4H, P(S)–C$_6$*H*$_5$-*meta*], 7.48m [2H, P(S)–C$_6$*H*$_5$-*para*], 7.65d [2H, O$_2$S–C$_6$*H*$_4$CH$_3$-*ortho*, ^{3}*J*(HH) 8.0 Hz]′ 7.83m [4H, P(S)–C$_6$*H*$_5$-*ortho*]. ^{31}P NMR (DMSO-d$_6$): δ 31.0. ESI+ (*m*/*z*, %): 1047 (10) [(tht)$_2$Au$_2$L+Tol]$^+$, 1031 (48), [(tht)$_2$Au$_2$L+Tol–O]$^+$, 1015 (100) [(tht)$_2$Au$_2$L+Tol–2O]$^+$, 694 (17) [AuL+Na]$^+$. ESI– (*m*/*z*, %): 969 (41) [AuL$_2$]$^-$, 609 (100) [AuL+CN]$^-$, 386 (38) [L]$^-$. FT-IR (cm^{-1}): ν_{as}(SO$_2$) 1266s, 1252s; ν_{as}(PNS) 1190m; ν_s(SO$_2$) 1143vs; ν(P–S) 568s.

[Au{(SPPh$_2$)(O$_2$SMe)N}(PPh$_3$)] (**4**), from K[(SPPh$_2$)(O$_2$SMe)N] (0.035 g, 0.1 mmol) and [AuCl(PPh$_3$)] (0.050 g, 0.1 mmol). Yield: 0.070 g (91%). M.p. 187 °C. *Anal.* Calc. for C$_{31}$H$_{28}$AuNO$_2$P$_2$S$_2$ (MW 769.61): C, 48.38; H, 3.67; N, 1.82; S, 8.33. Found: C, 48.34; H, 3.74; N, 2.08; S, 8.75%. ^{1}H NMR (CDCl$_3$): δ 2.94s (3H, O$_2$S–C*H*$_3$); 7.33m [19H, P(S)–C$_6$*H*$_5$-*meta*, P(C$_6$*H*$_5$)$_3$-*ortho* + *meta* + *para*], 7.49m [2H, P(S)–C$_6$*H*$_5$-*para*], 8.05ddd [4H, P(S)–C$_6$*H*$_5$-*ortho*, ^{3}*J*(HH) 7.1, ^{4}*J*(HH) 1.2, ^{3}*J*(PH) 13.9 Hz]. ^{31}P NMR (CDCl$_3$): δ 31.6s (*P*Ph$_3$); 37.2s [*P*(S)–C$_6$H$_5$]. ESI+ (*m*/*z*, %): 792 (12) [M+Na]$^+$, 721 (100) [(PPh$_3$)$_2$Au]$^+$, 508 (22) [AuL+H]$^+$. ESI– (*m*/*z*, %): 817 (57) [AuL$_2$]$^-$, 533 (60) [AuL+CN]$^-$, 310 (100) [L]$^-$. FT-IR (cm^{-1}): ν_{as}(SO$_2$) 1268s; ν_{as}(PNS) 1180m; ν_s(SO$_2$) 1140vs, 1121vs; ν(P–S) 557s, 538s.

[Au{(SPPh$_2$)(O$_2$SPh)N}(PPh$_3$)] (**5**), from K[(SPPh$_2$)(O$_2$SPh)N] (0.041 g, 0.1 mmol) and [AuCl(PPh$_3$)] (0.050 g, 0.1 mmol). Yield: 0.074 g (89%). M.p. 125 °C (dec.). *Anal.* Calc. for C$_{36}$H$_{30}$AuNO$_2$P$_2$S$_2$ (MW 831.67): C, 51.99; H, 3.63; N, 1.68; S, 7.71. Found: C, 51.83; H, 3.34; N, 1.51; S, 7.21%. ^{1}H NMR (CDCl$_3$): δ 7.14m (3H, O$_2$S–C$_6$*H*$_5$-*meta* + *para*), 7.24–7.55m [21H, P(S)–C$_6$*H*$_5$-*meta* + *para*, P(C$_6$*H*$_5$)$_3$-*ortho* + *meta* + *para*], 7.88d [2H, O$_2$S–C$_6$*H*$_5$-*ortho*, ^{3}*J*(HH) 7.3 Hz], 8.00dd [4H, P(S)–C$_6$*H*$_5$-*ortho*, ^{3}*J*(HH) 8.0, ^{3}*J*(PH) 13.9 Hz]. ^{31}P NMR (CDCl$_3$): δ 31.7d [*P*Ph$_3$, ^{3}*J*(PP) 8.2 Hz], 37.1d [*P*(S)–C$_6$H$_5$, ^{3}*J*(PP) 8.4 Hz]. ESI+ (*m*/*z*, %): 854 (10) [M+Na]$^+$, 832 (10) [M+H]$^+$, 721 (100) [(PPh$_3$)$_2$Au]$^+$. ESI– (*m*/*z*, %): 941 (36) [AuL$_2$]$^-$, 595 (48) [AuL+CN]$^-$, 372 (100) [L]$^-$. FT-IR (cm^{-1}): ν_{as}(SO$_2$) 1266s; ν_{as}(PNS) 1185s; ν_s(SO$_2$) 1138vs; ν(P–S) 538s.

[Au{(SPPh$_2$)(O$_2$SC$_6$H$_4$Me-4)N}(PPh$_3$)] (**6**), from K[(SPPh$_2$)(O$_2$SC$_6$H$_4$Me-4)N] (0.0425 g, 0.1 mmol) and [AuCl(PPh$_3$)] (0.050 g, 0.1 mmol). Yield: 0.072 g (86%). M.p. 193 °C (dec.). *Anal.* Calc. for C$_{37}$H$_{32}$AuNO$_2$P$_2$S$_2$ (MW 845.69): C, 52.55; H, 3.81; N, 1.65; S, 7.58. Found: C, 52.35; H, 3.84; N, 1.73; S, 7.65%. ^{1}H NMR (CDCl$_3$): δ 2.17s (3H, O$_2$S–C$_6$H$_4$C*H*$_3$), 6.88d [2H, O$_2$S–C$_6$*H*$_4$CH$_3$-*meta*, ^{3}*J*(HH) 7.8 Hz], 7.21–7.51m [21H, P(C$_6$*H*$_5$)$_3$-*ortho* + *meta* + *para*, P(S)–C$_6$*H*$_5$-*meta* + *para*], 7.76d [2H, O$_2$S–C$_6$*H*$_4$CH$_3$-*ortho*, ^{3}*J*(HH) 7.9 Hz], 7.98dd [4H, P(S)–C$_6$*H*$_5$-*ortho*, ^{3}*J*(HH) 7.5, ^{3}*J*(PH) 13.8 Hz]. ^{31}P NMR (CDCl$_3$): δ 31.4s, br. (*P*Ph$_3$), 37.1s [*P*(S)–C$_6$H$_5$]. ESI+ (*m*/*z*, %): 868 (37) [M+Na]$^+$, 721 (100) [(PPh$_3$)$_2$Au]$^+$. ESI– (*m*/*z*, %): 969 (28) [AuL$_2$]$^-$, 609 (20) [AuL+CN]$^-$, 386 (100) [L]$^-$. FT-IR (cm^{-1}): ν_{as}(SO$_2$) 1250vs; ν_{as}(PNS) 1181m; ν_s(SO$_2$) 1155vs, 1131vs; ν(P–S) 566s.

2.2.2. Preparation of PPN[Au{(SPPh$_2$)(O$_2$SMe)N}$_2$] (**7**)

Stoichiometric amounts of K[(SPPh$_2$)(O$_2$SMe)N] (0.070 g, 0.2 mmol) and PPN[AuCl$_2$] (0.080 g, 0.1 mmol) were stirred in CH$_2$Cl$_2$ (50 mL) for 1 h at room temperature. KCl was removed by filtration and the solution was concentrated under reduced pressure to approximately 2 mL. The title compound was precipitated with *n*-hexane, separated by filtration and dried in vacuum. Yield: 0.126 g (93%). M.p. 88–90 °C. *Anal.* Calc. for $C_{62}H_{56}AuN_3O_4P_4S_4$ (MW 1356.27): C, 54.91; H, 4.16; N, 3.10; S, 9.46. Found: C, 54.79; H, 4.60; N, 3.48; S, 9.06. ^{1}H NMR ($CDCl_3$): δ 2.93s (6H, O_2S–CH_3); 7.28m [8H, P(S)–C_6H_5-*meta*], 7.34m [4H, P(S)–C_6H_5-*para*]; 7.45m [24H, $N(PPh_3)_2$-*ortho* + *meta*], 7.65m [6H, $N(PPh_3)_2$-*para*], 7.97ddd [8H, P(S)–C_6H_5-*ortho*, ^{3}J(HH) 7.0, ^{4}J(HH) 1.4, ^{3}J(PH) 13.7 Hz]. ^{31}P NMR ($CDCl_3$): δ 21.2s [$N(PPh_3)_2$]; 32.6s [*P*(S)–C_6H_5]. ESI+ (*m*/*z*, %): 538 (100) $[PPN]^+$. ESI− (*m*/*z*, %): 817 (100) $[AuL_2]^-$, 310 (12) $[L]^-$. FT-IR (cm^{-1}): $\nu_{as}(SO_2)$ 1264vs; ν_{as}(PNS) 1180m; $\nu_s(SO_2)$ 1117vs; ν(P–S) 565s, 548s.

Compounds **8** and **9** were prepared similarly:

PPN[Au{$(SPPh_2)(O_2SPh)N\}_2$] (**8**), from K[$(SPPh_2)(O_2SPh)N$] (0.082 g, 0.2 mmol) and PPN[$AuCl_2$] (0.080 g, 0.1 mmol). Yield: 0.133 g (94%). M.p. 94–95 °C. *Anal.* Calc. for $C_{72}H_{60}AuN_3O_4P_4S_4$ (MW 1480.39): C, 58.42; H, 4.09; N, 2.84; S, 8.66. Found: C, 58.52, H, 4.11; N, 3.02; S, 8.92%. ^{1}H NMR ($CDCl_3$): δ 7.12–7.31m [18H, P(S)–C_6H_5-*meta* + *para*, O_2S–C_6H_5-*meta* + *para*], 7.44m [24H, $N(PPh_3)_2$-*ortho* + *meta*], 7.63dt [6H, $N(PPh_3)_2$-*para*, ^{3}J(HH) 7.0, ^{4}J(HH) 1.9 Hz], 7.82dd [8H, P(S)–C_6H_5-*ortho*, ^{3}J(HH) 7.6, ^{3}J(PH) 10.8 Hz], 7.84d [4H, O_2S–C_6H_5-*ortho*, ^{3}J(HH) 7.6 Hz]. ^{31}P NMR ($CDCl_3$): δ 21.2s [$N(PPh_3)_2$], 33.4s [*P*(S)–C_6H_5]. ESI+ (*m*/*z*, %): 538 (100) $[PPN]^+$. ESI− (*m*/*z*, %): 941 (100) $[AuL_2]^-$, 372 (10) $[L]^-$. FT-IR (cm^{-1}): $\nu_{as}(SO_2)$ 1266vs; ν_{as}(PNS) 1180m; $\nu_s(SO_2)$ 1140vs, 1115vs; ν(P–S) 534m.

PPN[Au{$(SPPh_2)(O_2SC_6H_4Me\text{-}4)N\}_2$] (**9**), from K[$(SPPh_2)(O_2SC_6H_4Me\text{-}4)N$] (0.0852 g, 0.2 mmol) and PPN[$AuCl_2$] (0.080 g, 0.1 mmol). Yield: 0.128 g (89%). M.p. 84–85 °C. *Anal.* Calc. for $C_{74}H_{64}AuN_3O_4P_4S_4$ (MW 1507.24): C, 58.92; H, 4.28; N, 2.79; S, 8.50. Found: C, 58.88; H, 4.20; N, 2.71; S, 8.41%. ^{1}H NMR ($CDCl_3$): 2.26s (6H, O_2S–$C_6H_4CH_3$); 6.96d [4H, O_2S–$C_6H_4CH_3$-*meta*, ^{3}J(HH) 7.9 Hz], 7.15m [8H, P(S)–C_6H_5-*meta*], 7.25t [4H, P(S)–C_6H_5-*para*, ^{3}J(HH) 7.2 Hz], 7.44m [24H, $N(PPh_3)_2$-*ortho* + *meta*], 7.62m (6H, $N(PPh_3)_2$-*para*], 7.71d [2H, O_2S–$C_6H_4CH_3$-*ortho*, ^{3}J(HH) 8.0 Hz], 7.81dd [4H, P(S)–C_6H_5-*ortho*, ^{3}J(HH) 7.4, ^{3}J(PH) 13.7 Hz]. ^{31}P NMR ($CDCl_3$): δ 21.2s [$N(PPh_3)_2$], 33.0s [*P*(S)–C_6H_5]. ESI+ (*m*/*z*, %): 538 (100) $[PPN]^+$. ESI− (*m*/*z*, %): 969 (100) $[AuL_2]^-$, 386 (10) $[L]^-$. FT-IR (cm^{-1}): $\nu_{as}(SO_2)$ 1265s; ν_{as}(PNS) 1181m; $\nu_s(SO_2)$ 1138vs, 1114vs; ν(P–S) 569s.

2.2.3. Preparation of [Ag{$(SPPh_2)(O_2SMe)N$}] (**10**)

Stoichiometric amounts of K[$(SPPh_2)(O_2SMe)N$] (0.035 g, 0.1 mmol) and Ag(OTf) (0.0256 g, 0.1 mmol) were stirred in acetone (50 mL) for 1 h at room temperature, in a flask covered with tin foil. KOTf was removed by filtration and the solution was concentrated under reduced pressure to approximately 2 mL. The title compound was precipitated with *n*-hexane, separated by filtration and dried in vacuum. Yield: 0.037 g (88%). M.p. 177 °C (dec.). *Anal.* Calc. for $C_{13}H_{13}AgNO_2PS_2$ (MW 418.22): C, 37.33; H, 3.13; N, 3.34; S, 15.33. Found: C, 37.62; H, 3.23; N, 3.25; S, 15.02%. ^{1}H NMR ($CDCl_3$): δ 2.63s (3H, O_2S–CH_3); 7.37m [4H, P(S)–C_6H_5-*meta*], 7.43m [2H, P(S)–C_6H_5-*para*], 7.88dd [4H, P(S)–C_6H_5-*ortho*, ^{3}J(HH) 7.2, ^{3}J(PH) 13.9 Hz]. ^{31}P NMR ($CDCl_3$): δ 36.8. ESI+ (*m*/*z*, %): 626 (100) $[Ag_2L{+}MeSO_2{+}Na]^+$ ESI− (*m*/*z*, %): 729 (100) $[AgL_2]^-$, 310 (82) $[L]^-$. FT-IR (cm^{-1}): $\nu_{as}(SO_2)$ 1266vs, 1230s, 1216s; ν_{as}(PNS) 1165vs; $\nu_s(SO_2)$ 1111s, 1095s, 1040s; ν(P=S) 645s; ν(P–S) 597s.

Compounds **11** and **12** were prepared similarly:

[Ag{$(SPPh_2)(O_2SPh)N$}] (**11**), from K[$(SPPh_2)(O_2SPh)N$] (0.041 g, 0.1 mmol) and Ag(OTf) (0.0256 g, 0.1 mmol). Yield: 0.042 g (88%). M.p. 128–130 °C. *Anal.* Calc. for $C_{18}H_{15}AgNO_2PS_2$ (MW 480.29): C, 45.02; H, 3.15; N, 2.92; S, 13.35. Found: C, 44.89; H, 2.98; N, 2.80; S, 12.93%. ^{1}H NMR ($CDCl_3$): δ 7.16t [2H, O_2S–C_6H_5-*meta*, ^{3}J(HH) 7.8 Hz], 7.27m [5H, P(S)–C_6H_5-*meta*, SO_2–C_6H_5-*para*], 7.38t [2H, P(S)–C_6H_5-*para*, ^{3}J(HH) 7.4 Hz], 7.63d [2H, O_2S–C_6H_5-*ortho*, ^{3}J(HH) 7.5 Hz], 7.75dd [4H, P(S)–C_6H_5-*ortho*, ^{3}J(HH) 7.3, ^{3}J(PH) 14.1 Hz). ^{31}P NMR ($CDCl_3$): δ 37.3. ESI+ (*m*/*z*, %): 855 (80) $[Ag_2L_2{-}2SO_2{+}Na]^+$, 832 (100) $[Ag_2L_2{-}2SO_2]^+$. ESI− (*m*/*z*, %): 853 (100) $[AgL_2]^-$, 372 (10) $[L]^-$. FT-IR (cm^{-1}): $\nu_{as}(SO_2)$ 1253vs; ν_{as}(PNS) 1178s; $\nu_s(SO_2)$ 1134s, 1079m, 1051s; ν(P=S) 656s; ν(P–S) 591s.

[Ag{$(SPPh_2)(O_2SC_6H_4Me\text{-}4)N$}] (**12**), from K[$(SPPh_2)(O_2SC_6H_4Me\text{-}4)N$] (0.0425 g, 0.1 mmol) and Ag(OTf) (0.0256 g, 0.1 mmol). Yield: 0.038 g (77%). M.p. 170 °C (dec.). *Anal.* Calc. for $C_{19}H_{17}AgNO_2PS_2$ (MW 494.32): C, 46.17; H, 3.46; N, 2.83; S, 12.97. Found: C, 46.49; H, 3.35; N, 2.76; S, 13.19%. ^{1}H NMR ($CDCl_3$): δ 2.28s (3H, O_2S–$C_6H_4CH_3$), 6.95d [2H, O_2S–$C_6H_4CH_3$-*meta*, ^{3}J(HH) 7.7 Hz]; 7.25m [4H, P(S)–C_6H_5-*meta*]; 7.36t [2H, P(S)–C_6H_5-*para*, ^{3}J(HH) 7.1 Hz); 7.54d [2H, O_2S–$C_6H_4CH_3$-*ortho*, ^{3}J(HH) 7.8 Hz], 7.76dd [4H, P(S)–C_6H_5-*ortho*, ^{3}J(HH) 7.8, ^{3}J(PH) 13.8 Hz]. ^{31}P NMR ($CDCl_3$): δ 37.5. ESI+ (*m*/*z*, %): 883 (100) $[Ag_2L_2{-}2SO_2{+}Na]^+$, 860 (32) $[Ag_2L_2{-}2SO_2]^+$. ESI− (*m*/*z*, %): 881 (100) $[AgL_2]^-$, 386 (28) $[L]^-$. FT-IR (cm^{-1}): $\nu_{as}(SO_2)$ 1252vs; ν_{as}(PNS) 1175s; $\nu_s(SO_2)$ 1132s, 1079m, 1037s; ν(P=S) 655s; ν(P–S) 590s.

2.2.4. Preparation of [Ag{$(SPPh_2)(O_2SMe)N$}(PPh_3)] (**13**)

Stoichiometric amounts of K[$(SPPh_2)(O_2SMe)N$] (0.035 g, 0.1 mmol) and [Ag(OTf)(PPh_3)] (0.052 g, 0.1 mmol) were stirred in acetone (50 mL) for 1 h at room temperature, in a flask covered with tin foil. KOTf was removed by filtration and the solution was concentrated under reduced pressure to approximately 2 mL. The title compound was precipitated with *n*-hexane, separated by filtration and dried in vacuum. Yield: 0.059 g (87%). M.p. 211 °C (dec.). *Anal.* Calc. for $C_{31}H_{28}AgNO_2P_2S_2$ (MW 680.51): C, 54.71; H, 4.15; N, 2.06; S, 9.42. Found: C, 54.43; H, 3.98; N, 2.14; S, 8.84%. ^{1}H NMR ($CDCl_3$): δ 2.64s (3H, O_2S–CH_3), 7.29m [21H, $P(C_6H_5)_3$-*ortho* + *meta* + *para*, P(S)–C_6H_5-*meta* + *para*], 7.91dd [4H, P(S)–C_6H_5-*ortho*, ^{3}J(HH) 7.3, ^{3}J(PH) 13.5 Hz]. ^{31}P NMR ($CDCl_3$): δ 6.6s (PPh_3); 37.3s [*P*(S)–C_6H_5]. ESI+ (*m*/*z*, %): 631 (100) $[(PPh_3)_2Ag]^+$. ESI− (*m*/*z*, %): 1146 (5), $[Ag_2L_3]^-$, 729 (68) $[AgL_2]^-$, 310 (100) $[L]^-$. FT-IR (cm^{-1}): $\nu_{as}(SO_2)$ 1243s; ν_{as}(PNS) 1198s; $\nu_s(SO_2)$ 1156m; ν(P–S) 570s.

Compounds **14** and **15** were prepared similarly:

[Ag{$(SPPh_2)(O_2SPh)N$}$(PPh_3)]_2$ (**14**), from K[$(SPPh_2)(O_2SPh)N$] (0.041 g, 0.1 mmol) and [Ag(OTf)(PPh_3)] (0.052 g, 0.1 mmol). Yield: 0.063 g (85%). M.p. 170–171 °C. *Anal.* Calc. for $C_{36}H_{30}AgNO_2P_2S_2$ (MW 742.58): C, 58.23; H, 4.07; N, 1.89; S, 8.64. Found: C, 58.09; H, 3.99; N, 1.81; S, 9.19%. ^{1}H NMR ($CDCl_3$): δ 7.08t [2H, O_2S–C_6H_5-*meta*, ^{3}J(HH) 7.1 Hz], 7.21m [5H, P(S)–C_6H_5-*meta*, O_2S–C_6H_5-*para*]; 7.32m [17H, $P(C_6H_5)_3$-*ortho* + *meta* + *para*, P(S)–C_6H_5-*para*], 7.67d [2H, O_2S–C_6H_5-*ortho*, ^{3}J(HH) 7.3 Hz], 7.84dd [4H, P(S)–C_6H_5-*ortho*, ^{3}J(HH) 7.4, ^{3}J(PH) 13.8 Hz), ^{31}P NMR ($CDCl_3$): δ 6.6s (PPh_3); 38.7s [*P*(S)–C_6H_5]. ESI+ (*m*/*z*, %): 631 (100) $[(PPh_3)_2Ag]^+$. ESI− (*m*/*z*, %): 1335 (10), $[Ag_2L_3]^-$, 853 (100) $[AgL_2]^-$, 372 (32) $[L]^-$. FT-IR (cm^{-1}): $\nu_{as}(SO_2)$ 1254vs; ν_{as}(PNS) 1162m; $\nu_s(SO_2)$ 1132vs; ν(P–S) 576s.

[Ag{$(SPPh_2)(O_2SC_6H_4Me\text{-}4)N$}$(PPh_3)$] (**15**), from K[$(SPPh_2)(O_2SC_6H_4Me\text{-}4)N$] (0.0425 g, 0.1 mmol) and [Ag(OTf)(PPh_3)] (0.052 g, 0.1 mmol). Yield: 0.071 g (96%). M.p. 162–163 °C. *Anal.* Calc. for $C_{37}H_{32}AgNO_2P_2S_2$ (MW 756.60): C, 58.73; H, 4.26; N, 1.85; S, 8.48. Found: C, 58.50; H, 4.04; N, 2.02; S, 7.83%. ^{1}H NMR ($CDCl_3$): δ 2.22s (3H, O_2S–$C_6H_4CH_3$); 6.82d [2H, O_2S–$C_6H_4CH_3$-*meta*, ^{3}J(HH) 8.0 Hz], 7.17dt [4H, P(S)–C_6H_5-*meta*, ^{3}J(HH) 7.4, ^{4}J(PH) 3.4 Hz], 7.27m [14H, $P(C_6H_5)_3$-*ortho* + *meta*, P(S)–C_6H_5-*para*], 7.37t [3H, $P(C_6H_5)_3$-*para*, ^{3}J(HH) 7.6 Hz], 7.53d [2H, O_2S–$C_6H_4CH_3$-*ortho*, ^{3}J(HH) 8.1 Hz], 7.76dd [4H, P(S)–C_6H_5-*ortho*, ^{3}J(HH) 7.2, ^{3}J(PH) 13.7 Hz], ^{31}P NMR ($CDCl_3$): δ 7.7s (PPh_3), 37.7s [*P*(S)–C_6H_5]. ESI+ (*m*/*z*, %): 631 (100) $[(PPh_3)_2Ag]^+$. ESI− (*m*/*z*, %): 1374 (5) $[Ag_2L_3]^-$, 881 (100) $[AgL_2]^-$, 386 (23) $[L]^-$. FT-IR (cm^{-1}): $\nu_{as}(SO_2)$ 1262vs; ν_{as}(PNS) 1183m; $\nu_s(SO_2)$ 1153vs, 1126vs; ν(P–S) 592vs.

Table 1
Crystallographic data for [Au{(SPPh$_2$)(O$_2$SMe)N}(PPh$_3$)] (**4**), [Au{(SPPh$_2$)(O$_2$SC$_6$H$_4$Me-4)N}(PPh$_3$)] (**6**) and [Ag{(SPPh$_2$)(O$_2$SPh)N}(PPh$_3$)]$_2$·2CH$_2$Cl$_2$ (**14**·2CH$_2$Cl$_2$).

Compound	**4**	**6**	**14**·2CH$_2$Cl$_2$
Empirical formula	$C_{31}H_{28}AuNO_2P_2S_2$	$C_{37}H_{32}AuNO_2P_2S_2$	$C_{74}H_{64}Ag_2Cl_4N_2O_4P_4S_4$
Formula weight	769.57	845.66	1654.97
Crystal size (mm)	0.26 × 0.15 × 0.15	0.32 × 0.23 × 0.18	0.23 × 0.22 × 0.19
Temperature (K)	297(2)	297(2)	297(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Trigonal	Triclinic
Space group	$C2/c$	$P3(2)$	$P\bar{1}$
a (Å)	27.499(2)	10.4687(4)	10.7507(13)
b (Å)	8.9413(7)	10.4687(4)	13.6911(17)
c (Å)	26.836(2)	27.184(2)	13.8693(17)
α (°)	90.00	90.00	103.806(2)
β (°)	116.591(1)	90.00	91.200(2)
γ (°)	90.00	120.00	112.646(2)
V (Å^3)	5900.3(8)	2580.1(2)	1815.0(4)
Z	8	3	1
D_{calc} (mg m^{-3})	1.733	1.633	1.514
μ (mm^{-1})	5.267	4.525	0.940
F (0 0 0)	3024	1254	840
θ Range for data collections (°)	1.66–26.37	2.25–25.02	1.94–25.00
Maximum and minimum transmission	0.454 and 0.403	0.443 and 0.298	0.8416 and 0.8128
Reflections collected	23090	18696	17655
Independent reflections	6023 [R_{int} = 0.0412]	6006 [R_{int} = 0.0401]	6379 [R_{int} = 0.0417]
Refinement method	Full-matrix least-squares on F^2		
Data/restraints/parameters	6023/0/353	6006/1/407	6379/0/424
Goodness-of-fit on F^2	1.074	0.989	1.095
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0330 wR_2 = 0.0670	R_1 = 0.0312 wR_2 = 0.0641	R_1 = 0.0522 wR_2 = 0.1050
R indices (all data)	R_1 = 0.0393 wR_2 = 0.0693	R_1 = 0.0330 wR_2 = 0.0648	R_1 = 0.0670 wR_2 = 0.1103
Final Λ-map (e Å^{-3})	1.061, −0.453	0.831, −1.063	0.557, −0.315

2.3. Crystal structure determination of compounds **4**, **6** and **14**·2CH$_2$Cl$_2$

Colorless crystals of compounds **4**, **6** and **14**·2CH$_2$Cl$_2$ were grown by slow diffusion in CH$_2$Cl$_2$/*n*-hexane (1/5, v/v) systems. The crystals were attached with epoxy glue on cryoloops. Data collection and processing was carried on a Bruker SMART APEX system (Babes-Bolyai University, Cluj-Napoca) using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Details of the crystal structure determination and refinement for compounds **4**, **6** and **14**·2CH$_2$Cl$_2$ are given in Table 1.

Scan type ω and Φ. Absorption corrections: multi-scan [44]. The structures were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a riding model and a mutual isotropic thermal parameter. For structure solving and refinement the software package SHELX-97 was used [45]. The drawings were created with the DIAMOND program [46].

3. Results and discussion

3.1. Preparation and solution NMR characterization

The gold(I) and silver(I) complexes were obtained by salt metathesis reactions between the potassium salt of the appropriate organophosphorus acid and the corresponding gold- or silver-containing starting material, according to Eqs. (1)–(4)

$$\begin{aligned}&[\mathrm{AuClL}] + \mathrm{K}[(\mathrm{SPPh_2})(\mathrm{O_2SR})\mathrm{N}]\\ &\quad\rightarrow [\mathrm{Au}\{(\mathrm{SPPh_2})(\mathrm{O_2SR})\mathrm{N}\}\mathrm{L}] + \mathrm{KCl}\\ &\qquad \mathrm{L} = \mathrm{tht}, \mathrm{R} = \mathrm{Me}\ (\mathbf{1}), \mathrm{Ph}\ (\mathbf{2}), \mathrm{C_6H_4Me\text{-}4}\ (\mathbf{3})\\ &\qquad \mathrm{L} = \mathrm{PPh_3}, \mathrm{R} = \mathrm{Me}\ (\mathbf{4}), \mathrm{Ph}\ (\mathbf{5}), \mathrm{C_6H_4Me\text{-}4}\ (\mathbf{6})\end{aligned} \tag{1}$$

$$\begin{aligned}&\mathrm{PPN}[\mathrm{AuCL_2}] + 2\mathrm{K}[(\mathrm{SPPh_2})(\mathrm{O_2SR})\mathrm{N}]\\ &\quad\rightarrow \mathrm{PPN}[\mathrm{Au}\{(\mathrm{SPPh_2})(\mathrm{O_2SR})\mathrm{N}\}_2] + 2\mathrm{KCl}\\ &\qquad \mathrm{R} = \mathrm{Me}\ (\mathbf{7}), \mathrm{Ph}\ (\mathbf{8}), \mathrm{C_6H_4Me\text{-}4}\ (\mathbf{9})\end{aligned} \tag{2}$$

$$\begin{aligned}&[\mathrm{AgOTf}] + \mathrm{K}[(\mathrm{SPPh_2})(\mathrm{O_2SR})\mathrm{N}]\\ &\quad\rightarrow [\mathrm{Ag}\{(\mathrm{SPPh_2})(\mathrm{O_2SR})\mathrm{N}\}] + \mathrm{KOTf}\\ &\qquad \mathrm{R} = \mathrm{Me}\ (\mathbf{10}), \mathrm{Ph}\ (\mathbf{11}), \mathrm{C_6H_4Me\text{-}4}\ (\mathbf{12})\end{aligned} \tag{3}$$

$$\begin{aligned}&n[\mathrm{AgOTf}(\mathrm{PPh_3})] + n\mathrm{K}[(\mathrm{SPPh_2})(\mathrm{O_2SR})\mathrm{N}]\\ &\quad\rightarrow [\mathrm{Ag}\{(\mathrm{SPPh_2})(\mathrm{O_2SR})\mathrm{N}\}(\mathrm{PPh_3})]_n + n\mathrm{KOTf}\\ &\qquad n = 1, \mathrm{R} = \mathrm{Me}\ (\mathbf{13}), \mathrm{C_6H_4Me\text{-}4}\ (\mathbf{15})\\ &\qquad n = 1, \mathrm{R} = \mathrm{Ph}\ (\mathbf{14})\end{aligned} \tag{4}$$

All compounds described in this paper are colorless crystalline solids. NMR data and elemental analysis are consistent with the desired compounds.

For the phenyl groups attached to phosphorus the ^{1}H NMR spectra showed resonances with the expected pattern due to the proton–proton and phosphorus–proton couplings, respectively. The ^{31}P NMR spectra of the complexes exhibit one or two resonances, corresponding to the *P*(S)Ph$_2$ moiety and the *P*Ph$_3$ or the PPN groups, respectively, consistent with the presence of only one species in solution. Mass spectra (ESI) suggest a dimeric structure for the gold derivatives **1**–**3** and the silver compounds **10**–**15**. In case of these compounds in the ESI+ mass spectra were observed peaks corresponding to fragments with a greater mass than that corresponding to the monomers, *i.e.* the [(tht)$_2$Au$_2$L]$^+$ ion or ions derived from this (*m*/*z* = 879 in **1**, 1019 in **2** and 1031 in **3**), as well as ions derived from the Ag$_2$L or Ag$_2$L$_2$ moiety (*m*/*z* 626 in **10**, 855 in **11**, and 883 in **12**). For derivatives **13**–**15** the ESI− mass spectra present characteristic ions for the formula [Ag$_2$L$_3$]$^-$, in accordance with the dimeric structure of **14**·2CH$_2$Cl$_2$ determined by single-crystal X-ray diffraction. However, for all compounds in ESI− spectra appear the [ML$_2$]$^-$ (M = Au or Ag) ion accompanied by the [L]$^-$ ion.

For all compounds the IR spectra recorded as KBr discs show no strong absorption around 900 cm^{-1} [ν_{as}[PN(H)S)], typical for the free acids, thus indicating that the ligands moieties are present in the deprotonated form. Medium to very strong bands were

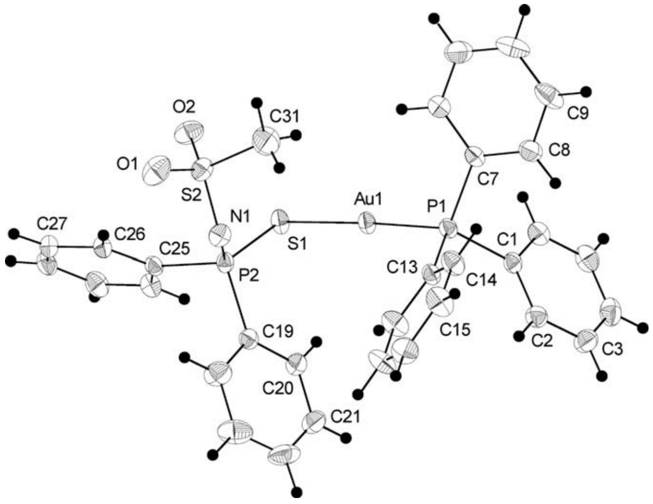

Fig. 1. ORTEP plot of $[Au\{(SPPh_2)(O_2SMe)N\}(PPh_3)]$ (**4**). The atoms are drawn with 30% probability ellipsoids.

assigned to $\nu_{as}(SO_2)$ (1270–1200 cm^{-1}), $\nu_{as}(PNS)$ (1200–1160 cm^{-1}), $\nu_s(SO_2)$ (1160–1040 cm^{-1}) and ν (P–S) (600–530 cm^{-1}) stretching vibrations, consistent with covalent metal–sulfur bonds [47–49]. However, the IR spectra of compounds **10**–**12** contain an additional strong band in the region 660–640 cm^{-1}, typical for a P═S stretching vibration, thus suggesting that ligands attached primarily to silver through oxygen are also present.

*3.2. Crystal and molecular structure of **4** and **6***

The ORTEP-like representations for compounds **4** and **6** are depicted in Figs. 1 and 2, while relevant bond distances and angles are given in Table 2.

The gold(I) complexes **4** and **6** have mononuclear structures, with no intermolecular Au···Au contacts shorter than 3.3 Å [50]. The organophosphorus(V) ligand behaves as a monometallic monoconnective moiety in **4**, being coordinated to the gold centre only through the sulfur atom attached to phosphorus [Au(1)–S(1) 2.3136(10) Å versus Σr_{cov}(Au, S) 2.38 Å] [51], thus resulting in a distorted linear coordination geometry around gold [P(1)–Au(1)–S(1) 175.71(4)°]. The oxygen atoms in the O_2SR moiety are not involved in interactions with the gold center, the Au–O distances being much longer than the sum of the van der Waals radii for gold and oxygen [Au···O 5.697(3) and 4.551(3) Å versus Σr_{vdW}(Au, O) 3.10 Å] [51].

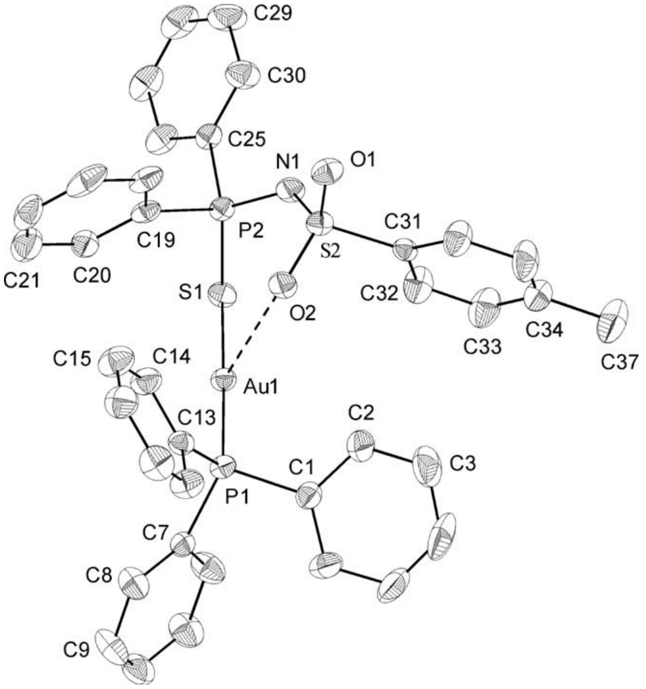

Fig. 2. ORTEP plot of $[Au\{(SPPh_2)(O_2SC_6H_4Me\text{-}4)N\}(PPh_3)]$ (**6**). The atoms are drawn with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

In **6** the organophosphorus ligand is also covalently attached to the metal center through sulfur [Au(1)–S(1) 2.3024(17) Å], but, in contrast to the molecule of **4**, the $SPNSO_2$ skeleton is twisted, probably due to crystal packing, to bring the O_2SR moiety closer to the metal centre. A weak secondary Au(1)···O(2) intramolecular interaction [2.986(5) Å] and thus an *S*,*O*-monometallic biconnective coordination pattern might be considered in **6**, similarly to the situation found in the copper(I) complexes $[Cu\{(SPPh_2)(O_2SR)N\}(PPh_3)_2]$ (R = Me, C_6H_4Me-4) [39]. The result is a distorted T-shaped coordination geometry around the gold center

Table 2
Important interatomic distances (Å) and angles (°) for compounds **4**, **6** and **14**·$2CH_2Cl_2$.

4		**6**		**14**·$2CH_2Cl_2$[a]	
Au(1)–P(1)	2.2545(10)	Au(1)–P(1)	2.2510(16)	Ag(1)–P(2)	2.4025(11)
Au(1)–S(1)	2.3136(10)	Au(1)–S(1)	2.3024(17)	Ag(1)–O(1)	2.491(3)
		Au(1)···O(2)	2.986(5)	Ag(1)–S(1)	2.7008(11)
				Ag(1)–S(1a)	2.5384(11)
N(1)–S(2)	1.577(4)	N(1)–S(2)	1.569(5)	N(1)–S(2)	1.560(3)
N(1)–P(2)	1.601(3)	N(1)–P(2)	1.579(5)	N(1)–P(1)	1.598(3)
P(2)–S(1)	2.0478(14)	P(2)–S(1)	2.038(2)	P(1)–S(1)	2.0025(14)
O(1)–S(2)	1.432(3)	O(1)–S(2)	1.432(4)	O(1)–S(2)	1.450(3)
O(2)–S(2)	1.438(3)	O(2)–S(2)	1.439(4)	O(2)–S(2)	1.427(3)
P(1)–Au(1)–S(1)	175.71(4)	P(1)–Au(1)–S(1)	176.79(6)	P(2)–Ag(1)–O(1)	102.54(7)
P(2)–S(1)–Au(1)	98.26(5)	P(2)–S(1)–Au(1)	99.11(8)	P(2)–Ag(1)–S(1)	122.05(4)
				O(1)–Ag(1)–S(1)	91.17(6)
				P(2)–Ag(1)–S(1a)	141.70(4)
				O(1)–Ag(1)–S(1a)	98.85(7)
				S(1)–Ag(1)–S(1a)	88.56(3)
				Ag(1)–S(1)–Ag(1a)	91.44(3)
N(1)–P(2)–S(1)	119.34(14)	N(1)–P(2)–S(1)	118.7(2)	N(1)–P(1)–S(1)	118.29(13)
O(1)–S(2)–O(2)	115.1(2)	O(1)–S(2)–O(2)	115.2(3)	O(1)–S(2)–O(2)	115.86(18)
S(2)–N(1)–P(2)	126.2(2)	S(2)–N(1)–P(2)	129.1(3)	S(2)–N(1)–P(1)	129.0(2)

[a] Symmetry equivalent positions (1−*x*, 1−*y*, −*z*) are given by “a”.

[P(1)–Au(1)–S(1) 176.79(6)°, P(1)–Au(1)···O(2) 89.38(8)°, S(1)–Au(1)···O(2) 93.82(8)°]. In addition, the same O(2) atom is involved in a weak intramolecular C(2)–H(2)···O(2) contact [2.541(4) Å versus Σr_{cov}(O, H) 2.60 Å] [51]. The second oxygen atom is placed far away from the coordination sphere of gold [Au(1)···O(1) 5.220(5) Å] and is not involved in any interaction. The weakness of the intramolecular Au···O interaction in **6** is consistent with the fact that no significant difference can be observed between the two sulfur–oxygen distances of the ligand unit, a behavior also noted for the complex **4** in which the ligand acts as monodentate moiety.

In the crystal there should be noted intramolecular C–H···π contacts [3.15 Å in **4** and 3.06 Å in **6**] [52], between the hydrogen of a C–H bond from a phenyl ring of the $\mathrm{PPh_3}$ ligand and one of the aromatic ring from the $\mathrm{Ph_2PS}$ moiety of the anionic ligand.

The six membered AuSPNSO ring in **6** has a twisted boat conformation, with P(2) and O(2) in apices, at 0.964 and 0.35 Å, respectively, from the Au(1)S(1)N(1)S(2) best plane. The P(2)–S(1) bond distances [2.0478(14) Å in **4** and 2.038(2) Å in **6**] are longer, while the N(1)–P(2) [1.601(3) Å in **4** and 1.579(5) Å in **6**] and N(1)–S(2) [1.577(4) Å in **4** and 1.569(5) Å in **6**] bond distances are shorter than in the corresponding protonated ligands [cf. P–S, N–P and N–S in $\mathrm{(SPPh_2)(O_2SMe)NH}$: 1.9284(7)/1.708(2)/1.634(2) Å; $\mathrm{(SPPh_2)(O_2SC_6H_4Me\text{-}4)NH}$: 1.9326(8)/1.703(1)/1.641(1) Å] [38]. Their magnitude is intermediate between double and single phosphorus–sulfur, phosphorus–nitrogen or sulfur–nitrogen bonds, respectively. Surprisingly, the sulfur–oxygen bonds in the $\mathrm{N{-}SO_2R}$ moiety of the complexes [S(2)–O(1)/S(2)–O(2) 1.432(3)/1.438(3) Å in **4** and 1.432(4)/1.439(4) Å in **6**] are of the same magnitude to the double S═O bonds observed in the protonated ligands [*i.e.* $\mathrm{(SPPh_2)(O_2SMe)NH}$: 1.427(1)/1.428(1) Å; $\mathrm{(SPPh_2)(O_2SC_6H_4Me\text{-}4)NH}$: 1.429(1)/1.446(1) Å] [38]. The lengths of the Au(1)–P(1) bond [2.2545(10) Å in **4** and 2.2510(16) Å in **6**] are of the same magnitude as in the gold precursor $\mathrm{[AuCl(PPh_3)]}$ [P–Au 2.235(3) Å] [53] and other complexes containing the $\mathrm{Au(PR_3)}$ fragment [20,21,24,54,55].

Attempts to obtain single-crystals suitable for X-ray diffraction studies for compounds of the type $\mathrm{[Au\{(SPPh_2)(O_2SR)N\}(tht)]}$ [R = Me (**1**), Ph (**2**), $\mathrm{C_6H_4Me}$-4 (**3**)], and $\mathrm{PPN[Au\{(SPPh_2)(O_2SR)N\}_2]}$ [R = Me (**7**), Ph (**8**), $\mathrm{C_6H_4Me}$-4 (**9**)] failed. Taking into account the ESI MS data for derivatives **1**–**3**, as well as the existence of Au···Au interactions in complexes of type [AuX(tht)] (X = Cl, Br) [56], a dimeric structure could be assumed for these derivatives, while for compounds **7**–**9** monomeric structures with a linear S–Au–S core can be assigned.

3.3. Crystal and molecular structure of 14·$\mathrm{2CH_2Cl_2}$

The ORTEP-like representation for compound **14**·$\mathrm{2CH_2Cl_2}$ is depicted in Fig. 3, while relevant bond distances and angles are given in Table 2.

The crystal of the complex **14** consists of centrosymmetric dinuclear units in which the organophosphorus(V) ligands act as *S*,*O*-bridges between two silver(I) atoms [Ag(1a)–S(1) 2.5384(11) Å, Ag(1)–O(1) 2.491(3) Å; cf. Σr_{cov}(Ag, S) 2.38 Å/Σr_{vdW}(Ag, S) 3.55 Å, and Σr_{cov}(Ag, O) 2.00 Å/Σr_{vdW}(Ag, O) 3.10 Å] [51], resulting in a twelve-membered cycle. In addition, transannular Ag···S interactions are also present [Ag(1)–S(1) 2.7008(11) Å], the overall coordination pattern of the ligand being *S*,*S*,*O*-bimetallic triconnective. The resulting tricyclic system exhibits two six-membered AgSPNSO rings on opposite sides of the central planar $\mathrm{Ag_2S_2}$ core [Ag(1)···Ag(1a) 3.753(1) Å]. The AgSPNSO ring has twisted boat conformation, with O(1) and P(1) in apices, at 0.71 and 0.53 Å, respectively out of the best Ag(1)S(2)N(1)S(1) plane. The coordination geometry achieved around silver is distorted tetrahedral, with the S(1a) atom in the apex and Ag(1) atom 2.246 Å out of the O(1)/S(1)/P(2) basal plane. The bond angles at the metal centre range between 88.56(3) and 141.70(4)° (see Table 2). The whole tricyclic system in **14** is similar to the central part of the tetranuclear derivative $\mathrm{[Ag\{(OPPh_2)_2N\}]_4{\cdot}2EtOH}$, which contain a central planar $\mathrm{Ag_2O_2}$ ring and tetrahedral $\mathrm{AgO_4}$ cores [33].

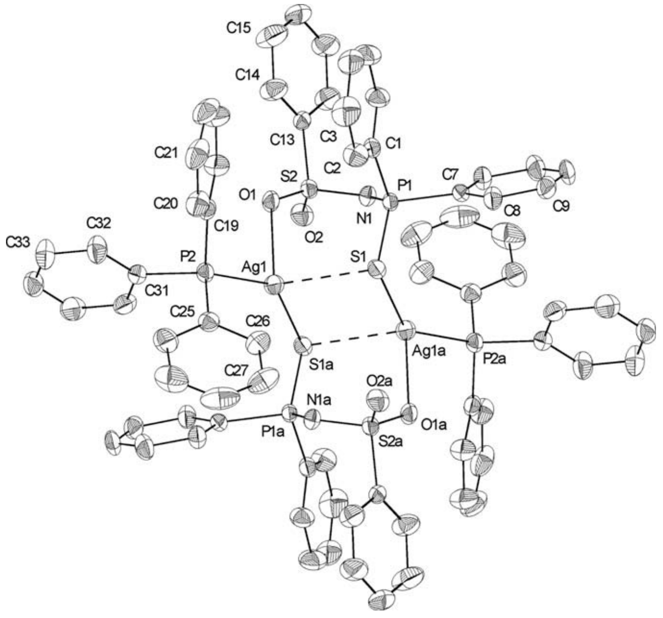

Fig. 3. ORTEP plot of the dimeric unit of $\mathrm{[Ag\{(SPPh_2)(O_2SPh)N\}(PPh_3)]_2}$ (**14**·$\mathrm{2CH_2Cl_2}$). The atoms are drawn with 30% probability ellipsoids. Hydrogen atoms and $\mathrm{CH_2Cl_2}$ are omitted for clarity.

The P(1)–S(1) [2.0025(14) Å], N(1)–P(1) [1.598(3) Å] and N(1)–S(2) [1.560(3) Å] bond distances in **14** are similar to those found in the gold(I) derivatives described above (see Table 2) and for the $\mathrm{[Cu\{(SPPh_2)(O_2SR)N\}(PPh_3)_2]}$ derivatives [P–S 1.9886(14), P–N 1.602(3) for R = Me; P–S 1.995(2) Å, P–N 1.605(6) for R = $\mathrm{C_6H_4Me}$-4] [39], which contain *S*,*O*-monometallic biconnective ligand moieties, indicating an intermediate magnitude between double and single bonds. Although only O(1) atom is involved in a strong interaction with a silver atom in **14**, this is only slightly reflected in the lengths of the two sulfur–oxygen bonds of the $\mathrm{N{-}SO_2Ph}$ moiety [O(1)–S(2)/O(2)–S(2) 1.450(3)/1.427(3) Å], indicating a considerable double bond character for the O(1)–S(2) bond [cf. $\mathrm{(SPPh_2)(O_2SPh)NH}$: O(1)–S(2)/O(2)–S(2) 1.422(2)/1.429(2) Å].

All attempts to obtain single crystals suitable for X-ray diffraction studies for the related compounds **13** and **15** or for those of the type $\mathrm{[Ag\{(SPPh_2)(O_2SR)N\}]}$ [R = Me (**10**), Ph (**11**), $\mathrm{C_6H_4Me}$-4 (**12**)] failed. Complexes **13** and **15** are very likely to exhibit in solid state a dimeric structure similar to that established for compound **14**. Taking into account the analogy between ligands of type **A**, **B** and **C**, it is plausible to assume that solid state clusters or polymeric associations based on silver–oxygen, silver–sulfur and/or even silver–nitrogen interactions are expected for compounds **10**–**12**, as found for example in the related $\mathrm{[Ag\{(O_2SR)_2N\}]_n}$ (R = Me [57], $\mathrm{C_6H_4I}$-4 [58]), $\mathrm{[Ag\{(OPPh_2)_2N\}]_4{\cdot}2EtOH}$ [33], $\mathrm{[Ag\{(X\text{-}P^{i}Pr_2)_2N\}]_3}$ (X = Se [59], S [60]), X $\mathrm{[Ag\{(SePPh_2)_2N\}]_4}$ [31].

4. Conclusions

Our studies demonstrate that anionic ligands of type $\mathrm{[(SPPh_2)(O_2SR)N]^-}$ build easily gold(I) and silver(I) complexes. Single-crystal X-ray diffraction studies revealed a different behavior of the ligands substituted at sulfur with Me and $\mathrm{C_6H_4Me}$-4 groups, respectively, towards the gold centre. Due to the weak Au···O secondary interaction, the coordination number increased from 2 in $[Au\{(SPPh_2)(O_2SMe)N\}(PPh_3)]$ to 3 in $[Au\{(SPPh_2)(O_2SC_6H_4Me\text{-}4)N\}(PPh_3)]$. A dimeric structure with bridging ligand units was found for the silver(I) compound $[Ag\{(SPPh_2)(O_2SPh)N\}(PPh_3)]_2$. According to ESI MS data dimeric associations are probable for the gold(I) derivatives **1**–**3** and for the silver(I) compounds **10**–**15**.

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Appendix A. Supplementary material

CCDC 711789, 711790 and 711791 contain the supplementary crystallographic data for **4**, **6** and **14**·$2CH_2Cl_2$. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2009.10.022.

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