

# (Phosphine)silver(I) Sulfonate Complexes

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(Phosphine)silver(I) organosulfonate complexes of the type  $(R_3P)AgOS(O)_2R'$  have been prepared in good yields from the corresponding silver sulfonates and tertiary phosphines in dichloromethane solution [ $R_3 = Ph_3, Ph_2(2-Py), Me_2Ph$ , with  $R' = 4-Me-C_6H_4$ ;  $R = Ph, R' = Et$  and  $2,5-Me_2-C_6H_4$ ]. If ethanol is present in the reaction mixture, the products contain one equivalent of ethanol. The crystal structures of  $(Ph_3P)AgOS(O)_2(C_6H_4-4-Me)(EtOH)$  (**1**), and  $(Me_2PhP)AgOS(O)_2(C_6H_4-4-Me)$  (**5**) have been determined. Complex **1** is present as a dimer in which the monomeric units feature intermolecular Ag-O donor/acceptor bonding in a four-membered ring. The coordination sphere of the silver atoms is further complemented by an ethanol molecule which is also engaged in hydrogen bonding with one of the sulfonate oxygen atoms. The solvent-free complex **5** is associated into helical chains *via* Ag-O coordinative bonds which provide the silver atoms with a distorted planar T-shaped coordination.

*Key words:* Silver Complexes, Sulfonate Complexes, Phosphine Complexes, Ethanol Adduct

## Introduction

(Phosphine)gold(I) alkyl- and arylsulfonate complexes of the type  $(R_3P)Au-OS(O)_2R'$  recently have attracted considerable interest owing to their potential as homogeneous catalysts in alkyne and alkene addition reactions [1]. Extensive studies have suggested that the poorly solvated  $[(R_3P)Au]^+$  units present in solution as components of dissociation equilibria can be regarded as the active species. Structural investigations have shown that in the solid state the complexes are present as monomers with only weak intermolecular aurophilic interactions depending largely on the bulk of the phosphine ligands employed [2].

An extension of the studies of the catalytic activity to include the corresponding silver(I) complexes revealed that these analogues of the type  $(R_3P)AgOS(O)_2R'$  have a strongly reduced efficiency as catalysts for alkyne addition reactions [3]. This observation suggested that under comparable experimental conditions the corresponding dissociation equilibria do not involve significant concentrations of active  $[(R_3P)Ag]^+$  species. In order to investigate the structural chemistry of this type of complexes we have prepared a small series of representative examples and studied their general properties.

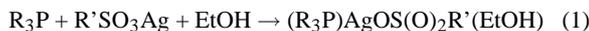
The literature on silver sulfonates and their complexes generally is very limited and gives only scat-

tered information on the composition and structure of these compounds, some of which are commercially available [4–12].

## Preparative Results

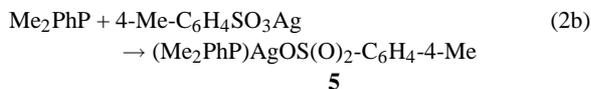
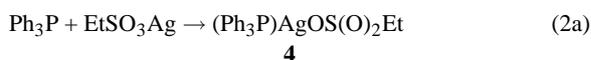
Silver(I) organosulfonates are readily prepared from the corresponding organosulfonic acids and silver oxide in water. The compounds are obtained as colorless precipitates which can be reacted further as a suspension in polar solvents like dichloromethane, chloroform or ethanol, in which they are very sparingly soluble.

The silver organosulfonates dissolve slowly in a dichloromethane/ethanol mixed solvent as a tertiary phosphine is added to the slurry at room temperature. Colorless solutions are obtained from which the products can be precipitated in satisfactory yield upon addition of pentane. The products were found to contain tightly bound ethanol which cannot be removed by washing with excess pentane or diethylether or in a vacuum at room temperature. According to eq. (1) the following products have been isolated and characterized by analytical and spectroscopic data:



**1:**  $R = Ph, R' = 4-MeC_6H_4$ ; **2:**  $R = Ph, R' = 2,5-Me_2C_6H_4$ ;  
**3:**  $R = Ph_2(2-Py), R' = 4-MeC_6H_4$

The same reaction carried out in the absence of ethanol requires longer reaction times and yields an alcohol-free product (eqs. 2a, b).



The complexes are colorless, crystalline solids which melt with decomposition at temperatures most of well above 100 °C. Decomposition of both the solids and their solutions is observed upon exposure to incandescent light. All compounds gave satisfactory elemental analysis data, and their NMR spectra have confirmed the proposed composition. In solution ( $\text{CD}_2\text{Cl}_2$ ) there appears to be rapid ligand exchange on the NMR time scale. As demonstrated for compound **2**, the  $^{31}\text{P}$ - $^{107/109}\text{Ag}$  coupling is absent at 25 °C but appears as the samples are cooled to -63 °C. The coupling constants determined at the low-temperature limit [ $J = 466/536$  Hz] are in agreement with literature data for low-coordinate silver atoms.

The mass spectra (FAB) show dinuclear cations of the general formula  $[(\text{LAg})_2\text{Y}]^+$  as the cations of highest mass which indicate association of the complexes in the solid state (L = tertiary phosphine, Y =  $\text{R}'\text{SO}_3$ ). Ligand-bridged dinuclear cations are among the most common fragments in the mass spectra of  $\text{LAuY}$  and  $\text{LAgY}$  complexes, the halogen-bridged examples being particularly prominent [13]. As expected, the cations  $[\text{L}_2\text{Ag}]^+$  and  $[\text{LAg}]^+$  are the most abundant species.

### Structural Studies

Two representative examples were selected from the above series of complexes **1**–**5** for structure investigation.

Compound **1** crystallizes in the triclinic space group  $P\bar{1}$  with  $Z = 2$  formula units in the unit cell. The molecules have been found to be associated into centrosymmetrical dimers as shown in Figure 1. The core unit is a parallelogram  $(\text{AgO1})_2$  – planar by symmetry – with edges  $\text{Ag-O1}$  2.5568(17) /  $\text{Ag-O1}'$  2.3085(17) Å and angles  $\text{O1-Ag-O1}'$  78.83(6)° /  $\text{Ag-O1-Ag}'$  111.7(6)°. The silver atoms are further coordinated by the phosphine [ $\text{Ag-P}$  2.3483(6) Å] and by the ethanol molecule [ $\text{Ag-O4}$  2.405(2) Å]. It should be noted that this  $\text{Ag-O4}$  distance is intermediate in its length between the  $\text{Ag-O1}$  /  $\text{Ag-O1}'$  distances (above)

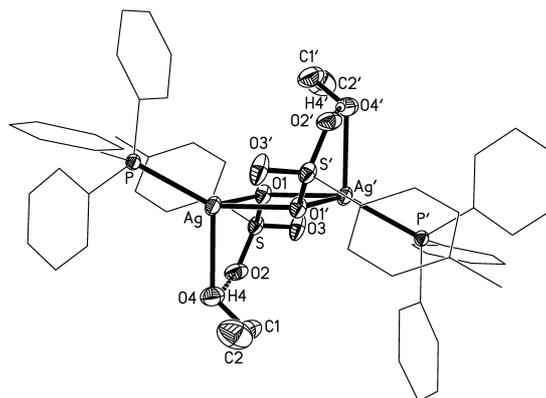


Fig. 1. Molecular structure of  $[(\text{Ph}_3\text{P})\text{AgOS}(\text{O})_2\text{-}p\text{-Tol}(\text{EtOH})_2]$ , (**1**). The two monomers are related by a center of inversion. Selected bond lengths [Å] and angles [°]:  $\text{Ag-O1}$  2.5568(17),  $\text{Ag-O1A}$  2.3085(17),  $\text{Ag-P}$  2.3483(6),  $\text{S-O1}$  1.4804(17),  $\text{S-O2}$  1.449(2),  $\text{S-O3}$  1.437(2);  $\text{P-Ag-O1}$  112.83(4),  $\text{P-Ag-O1}'$  146.48(4),  $\text{O1-Ag-O1}'$  78.83(6),  $\text{Ag-O1-Ag}'$  101.17(6),  $\text{S-O1-Ag}$  122.90(10),  $\text{S-O1-Ag}'$  112.73(9). Hydrogen bond:  $\text{O4-H4}$  0.776,  $\text{O2-H4}$  1.949,  $\text{O4-O2}$  2.716,  $\text{O2-H4-O4}$  169.18.

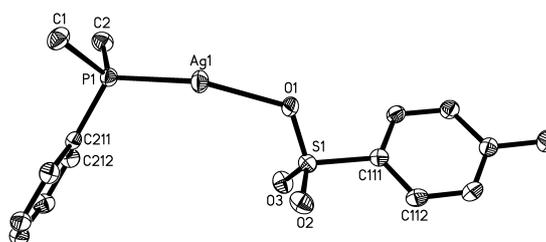


Fig. 2. Monomeric unit  $(\text{Me}_2\text{PhP})\text{AgOS}(\text{O})_2\text{-}p\text{-Tol}$ , (**5**), with atomic numbering. Selected bond lengths [Å] and angles [°]:  $\text{Ag1-O1}$  2.2333(16),  $\text{Ag1-P1}$  2.3590(6),  $\text{S1-O1}$  1.4719(17),  $\text{S1-O2}$  1.4604(17),  $\text{S1-O3}$  1.4450(17);  $\text{P1-Ag1-O1}$  157.59(5),  $\text{Ag1-O1-S1}$  122.54(9).

and should therefore not be rated as only a weak solvation. The silver atoms are tetracoordinated with largely equidistant oxygen and phosphorus donor atoms, but with strongly distorted X-Ag-Y angles when referred to a standard tetrahedral geometry. Two of these are constrained by the chelate rings. The bridgehead oxygen atoms (O1 and O4) are in a pyramidal configuration.

The ethanol molecule is engaged in hydrogen bonding with one of the two terminal sulfonate oxygen atoms [ $\text{O4-H4}$  0.776 Å,  $\text{O4-O2}$  2.716 Å,  $\text{O4-H4-O2}$  169.18°] and are thus supporting the solvation of the dimer. As expected, the remaining of the three sulfonate oxygen atoms O3 is most tightly bound to the sulfur atom:  $\text{S-O3}$  1.437(2) vs.  $\text{S-O2}$  (hydro-

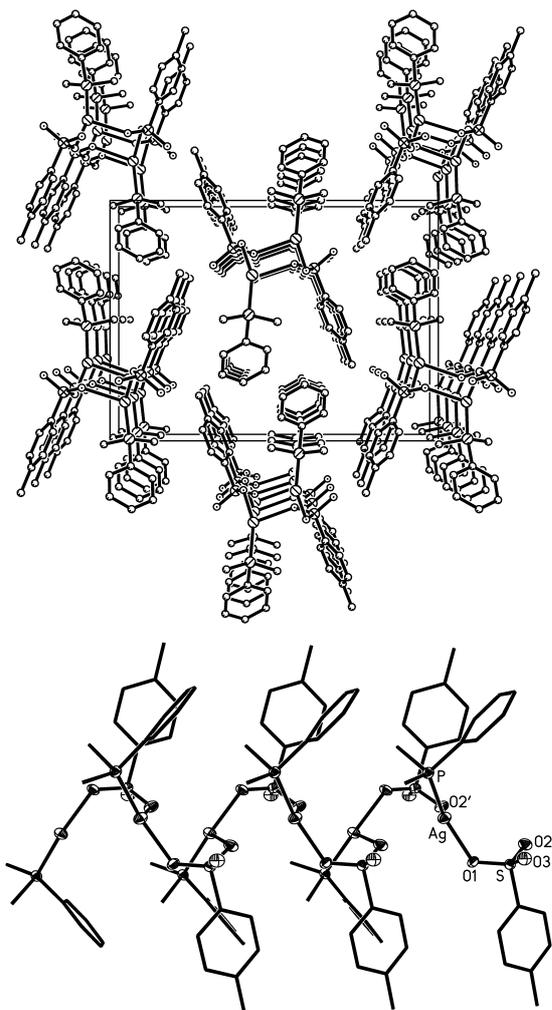


Fig. 3. Projections parallel (top, along *a*-axis) and perpendicular to (bottom, along *c*-axis) a helical chain of molecules  $(\text{Me}_2\text{PhP})\text{AgOS}(\text{O})_2\text{-}p\text{-Tol}$ , **5**, in the crystal associated via Ag-O2' contacts. Ag-O2' 2.5283(17) Å; O1-Ag-O2' 82.32(6), P-Ag-O2' 116.48(4)°.

gen bonded) 1.449(2) and S-O1(silver coordinated) 1.4804(17) Å.

The structure of complex **1** is remarkable for two reasons. The mode of dimerization reflects the high acceptor character of the silver atoms in these sulfonate complexes which leads not only to strong binding of an extra oxygen atom of a neighbouring molecule but also to a fixation of an ethanol molecule. For the corresponding gold complexes no such acceptor properties regarding oxygen donors are discernible. In crystals of  $(\text{Ph}_3\text{P})\text{Au-OS}(\text{O})_2\text{-C}_6\text{H}_4\text{-4-Me}$  the monomers are only weakly associated via aurophilic contacts (Au–Au) and

no solvent is accepted in the coordination sphere of the metal atoms [2b].

For compounds **2** and **3** a similar structure as that found for **1** is to be proposed.

Crystals of the ethanol-free compound **5** are orthorhombic, space group  $P2_12_12_1$ , with  $Z = 2$  formula units in the unit cell. The monomers are aggregated into a unidimensional polymer through intermolecular Ag–O coordination. The silver atom of a monomeric unit (Fig. 2) accepts a dative bond from one of the two terminal oxygen atoms (O2) of a neighbouring molecule to become three-coordinate in a distorted T-shaped geometry. The distance to the incoming atom O2 is much larger [Ag1-O2' 2.5283(7) Å] than the internal distance of the monomer [Ag1-O1 2.2333(16) Å], making this difference larger than observed for complex **1** above (Figs 3a,b).

The large angle of the P1-Ag1-O1 unit [157.59(5)°] (the horizontal bar of the T) shows that the bending away from linearity induced by the incoming O2 is not very pronounced. With the remaining angles O1-Ag1-O2' at 82.32(6)° and P1-Ag1-O2' at 116.48(4)° the sum of the angles of 356.4° indicates only a small deviation of the T from planarity.

In the absence of ethanol the silver atom in complex **5** thus clearly adopts the standard trigonal planar configuration while in the ethanol adduct **1** the silver atoms become tetrahedrally tetracoordinate.

The chain of molecules present in the crystals of compound **5** is helical. Fig. 3a shows a projection parallel to the helical axis. As judged from the distances and orientations of the substituents there is no significant  $\pi$ -stacking or phenyl / tolyl embracing in the structure which could influence the packing of the molecules.

## Conclusions

The results of the present study show very clearly the fundamental differences in the coordination chemistry of silver and gold. The structural chemistry of the organosulfonate complexes is an example where these variations become immediately obvious.

The *gold* compounds appear as monomers or loosely aggregated oligomers in which weak, but significant aurophilic bonding is determining the association of the molecules. The linear two-coordination of the metal atoms is largely retained.

By contrast, the *silver* compounds feature standard intermolecular donor-acceptor interactions which lead

to an increase in the coordination number beyond two. In the absence of additional, external donor ligands the silver atoms are found three-coordinate, but there is still acceptor capacity to accommodate other ligands. Ethanol was found to be a suitable component which is not only accepted as an oxygen donor, but also as a partner for chelating hydrogen bonding. The observations made with the gold and silver sulfonate complexes have parallels in the chemistry of phosphate/phosphonate [14] as well as of carboxylate compounds [15], where oxygen donor and hydrogen bonding capacities are also available.

The low catalytic reactivity of LAgX as compared to LAuX complexes, *e.g.* in the addition of alcohols or water to alkynes, is readily explained by the much stronger ligand binding at the silver atoms. The proposed active [LAg]<sup>+</sup> species are therefore much less abundant in the corresponding dissociation equilibria than the [LAu]<sup>+</sup> species [1,2]. High [LAg]<sup>+</sup> activity is to be expected only in cases with counterions X<sup>-</sup> devoid of any donor capacity and in the complete absence of donor solvent molecules. The corresponding gold systems are much less sensitive to the nature of X<sup>-</sup> and of the solvent owing to the strongly reduced acceptor properties of the metal atom.

## Experimental Section

The silver(I) organosulfonates were prepared following literature procedures [16]. All other reagents were commercially available. The reactions were routinely carried out in an atmosphere of dry and pure nitrogen in standard equipment. Solvents were purified, dried and saturated with nitrogen. Glassware was oven-dried and filled with nitrogen. Reaction vessels were protected against incandescent light.

### *(Triphenylphosphine)silver(I) p-toluenesulfonate (ethanol) (1)*

4-MeC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>Ag (290 mg, 1.04 mmol) was suspended in a mixture of dichloromethane and ethanol (10 ml each) at room temperature and treated with Ph<sub>3</sub>P (270 mg, 1.04 mmol) for 2 h with stirring to give an almost clear colorless solution. Small amounts of residue were filtered off and the volume of the filtrate was reduced to a few ml. The product was precipitated by addition of *n*-pentane, filtered, washed with *n*-pentane and diethylether, and dried in a vacuum (430 mg, 76% yield, m.p. 124 °C with decomposition). Single crystals can be grown from *n*-pentane/ethanol at -30 °C. NMR (CDCl<sub>3</sub>, 20 °C), <sup>31</sup>P{<sup>1</sup>H}: 14.2, s. <sup>1</sup>H: 6.87-7.96, m, 19 H, Ph and C<sub>6</sub>H<sub>4</sub>; 3.55, q, 2 H, *J* = 7.4 Hz, CH<sub>2</sub>; 2.14, s, 3 H, 4-Me; 1.16, t, 3H, Me. MS(FAB):

*m/z* 910 (5.4%), [(Ph<sub>3</sub>P)<sub>2</sub>Ag<sub>2</sub>SO<sub>3</sub>C<sub>6</sub>H<sub>4</sub>Me]<sup>+</sup>; 631 (16.3) [(Ph<sub>3</sub>P)<sub>2</sub>Ag]<sup>+</sup>; 369 (100) [Ph<sub>3</sub>PAG]<sup>+</sup>; 262 (26.4) [Ph<sub>3</sub>P]<sup>+</sup>. C<sub>27</sub>H<sub>28</sub>AgO<sub>4</sub>PS (587.40): calcd. C 55.2, H 4.8, S 5.5; found C 55.4, H 4.6, S 5.7.

### *(Triphenylphosphine)silver(I) 2,5-dimethylphenylsulfonate (ethanol) (2)*

As described for **1**, 2,5-Me<sub>2</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>Ag (200 mg, 0.61 mmol) was treated with Ph<sub>3</sub>P (160 mg, 0.61 mmol) to give 330 mg of colorless, microcrystalline product (92% yield), m.p. 131 °C with decomposition. NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C), <sup>31</sup>P{<sup>1</sup>H}: 11.3, s; 9.45, d [*J*(Ag/P) 466 and 536 Hz] at -63 °C; <sup>1</sup>H: 7.00-7.77, m, 18 H, Ph and C<sub>6</sub>H<sub>3</sub>; 3.59, q, 2 H, *J* = 7.3 Hz, CH<sub>2</sub>; 2.50 and 2.12, s, 3 H each, Me(xylene); 1.11, t, 3 H, Me. <sup>13</sup>C{<sup>1</sup>H}: 135.1, 133.6, 131.5, 130.7 for xylene; 134.3 (d, *J* = 10.4), 131.1 (d, *J* = 84.0), 129.4 (d, *J* = 5.2 Hz), 128.3 (s) for Ph; 54.3 and 18.7 for EtOH; 20.95 and 20.3 for Me(xylene). MS(FAB): 631 (100) [(Ph<sub>3</sub>P)<sub>2</sub>Ag]<sup>+</sup>; 369 (91.5) [Ph<sub>3</sub>PAG]<sup>+</sup>; 262 (20.2) [Ph<sub>3</sub>P]<sup>+</sup>. C<sub>28</sub>H<sub>29</sub>AgO<sub>4</sub>PS (600.42): calcd. C 56.0, H 4.9, S 5.3; found C 56.1, H 4.7, S 5.4.

### *[Diphenyl(2-pyridyl)phosphine]silver(I) p-toluenesulfonate (ethanol) (3)*

As described for **1**, 4-MeC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>Ag (200 mg, 0.72 mmol) was reacted with Ph<sub>2</sub>(2-Py)P (190 mg, 0.72 mmol) to give 360 mg of colorless microcrystalline product (92% yield), m.p. 126 °C with decomposition. NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C), <sup>31</sup>P{<sup>1</sup>H}: 16.5, s; <sup>1</sup>H: 9.26 and 7.98, m, 1 H each, 6.89-7.65, m, 16 H, aryl; 2.24, s, Me; 3.52, q, 2 H, and 1.04, t, 3 H, *J* = 7.7 Hz for EtOH. MS (FAB): 913 (5.6) [Ph<sub>2</sub>(2-Py)PAG]<sub>2</sub>SO<sub>3</sub>C<sub>6</sub>H<sub>4</sub>Me<sup>+</sup>; 633 (23.3) [L<sub>2</sub>Ag]<sup>+</sup>, 370 (100) [LAg]<sup>+</sup>, 263 (3.4) [L]<sup>+</sup>. C<sub>26</sub>H<sub>27</sub>AgNO<sub>4</sub>PS (588.39): calcd. C 53.1, H 4.6, N 2.4, S 5.4; found C 53.7, H 4.4, N 2.3, S 5.4.

### *(Triphenylphosphine)silver(I) ethylsulfonate (4)*

As described for **1**, EtSO<sub>3</sub>Ag (220 mg, 1.01 mmol) was treated with Ph<sub>3</sub>P (265 mg, 1.01 mmol) in dichloromethane (10 ml) to give 440 mg of colorless, microcrystalline product (90% yield), m.p. 109 °C with decomposition. NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C), <sup>31</sup>P{<sup>1</sup>H}: 16.0, s. <sup>1</sup>H: 6.96-7.89, m, 15 H, Ph; 2.96, q, 2 H, and 1.21, t, 3 H, *J* = 7.9 Hz, Et. MS (FAB): 848 (8.7) [(Ph<sub>3</sub>P)<sub>2</sub>Ag<sub>2</sub>SO<sub>3</sub>Et]<sup>+</sup>; 631 (3.4) [(Ph<sub>3</sub>P)<sub>2</sub>Ag]<sup>+</sup>; 369 (100) [(Ph<sub>3</sub>P)Ag]<sup>+</sup>; 262 (12.3) [Ph<sub>3</sub>P]<sup>+</sup>. C<sub>20</sub>H<sub>20</sub>AgO<sub>3</sub>PS (479.29): calcd. C 50.1, H 4.2, S 6.7; found C 49.7, H 4.3, S 6.6.

### *(Dimethylphenylphosphine)silver(I) p-toluenesulfonate (5)*

As described for **1**, 4-MeC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>Ag (160 mg, 0.57 mmol) was reacted with Me<sub>2</sub>PhP (80 mg, 0.57 mmol)

in dichloromethane (20 ml). Evaporation of the solvent from the filtrate left a colorless resinous residue which could be crystallized from dichloromethane/pentane [1:1] at  $-30\text{ }^{\circ}\text{C}$  to give 190 mg of product (79% yield), m.p.  $87\text{ }^{\circ}\text{C}$  with decomposition. NMR ( $\text{CD}_2\text{Cl}_2$ ,  $20\text{ }^{\circ}\text{C}$ ),  $^{31}\text{P}\{^1\text{H}\}$ :  $-20.2$ , s,  $^1\text{H}$ : 7.16-7.73, m, 9 H, Ph and  $\text{C}_6\text{H}_4$ ; 2.35, s, 3 H, Me; 1.66, d, 6 H,  $J = 8.9\text{ Hz}$ ,  $\text{Me}_2$ .  $^{13}\text{C}\{^1\text{H}\}$ : 140.7, 131.6, 128.9, 126.1 (all for *p*-tolyl). 134.1, d,  $J = 51$ ; 131.4, d,  $J = 14.1$ ; 130.6, d,  $J = 4.1\text{ Hz}$ ; 128.5, s; (all for Ph). 21.2, s, 3 H, Me; 14.3, d,  $J = 21\text{ Hz}$ ,  $\text{Me}_2$ . MS (FAB): 663 (2.9) [ $\text{L}_2\text{Ag}_2\text{SO}_3\text{C}_6\text{H}_4\text{Me}\text{H}^+$ ]; 417 (2.0) [ $\text{M}]^+$ ; 383 (26.1) [ $\text{L}_2\text{Ag}\text{H}^+$ ]; 245 (100) [ $\text{LAg}\text{H}^+$ ]; 138 (8.8) [ $\text{L}]^+$ .  $\text{C}_{15}\text{H}_{18}\text{AgO}_3\text{PS}$  (417.19): calcd. C 43.2, H 4.4; found C 42.9, H 4.4.

#### Crystal structure determination

The crystalline samples were placed in inert oil, mounted on a glass pin, and transferred to the cold gas stream of the diffractometer. Crystal data were collected and integrated using a Nonius DIP2020 system with monochromated  $\text{Mo-K}\alpha$  ( $\lambda = 0.71073\text{ \AA}$ ) radiation at  $-130\text{ }^{\circ}\text{C}$ . The structure was solved by direct methods using SHELXS-97 and refined by full matrix least-squares calculations on  $F^2$  (SHELXL-97). Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms, except for the O-H atom of the solvent ethanol in compound **1** which was located and refined isotropically, were placed in idealized positions and refined using a riding model with fixed isotropic contributions.

Crystal data for  $\text{C}_{27}\text{H}_{28}\text{AgO}_4\text{PS}$  (**1**):  $M = 587.39$ , triclinic,  $a = 10.8837(2)$ ,  $b = 11.0192(2)$ ,  $c = 11.7906(3)\text{ \AA}$ ,  $\alpha = 94.890(1)$ ,  $\beta = 109.465(1)$ ,  $\gamma = 90.329(1)^\circ$ , space group  $P\bar{1}$ ,  $Z = 2$ ,  $V = 1327.49(5)\text{ \AA}^3$ ,  $\mu(\text{Mo-K}\alpha) = 9.28\text{ cm}^{-1}$ , 42437 measured and 5534 unique reflections [ $R_{\text{int}} = 0.043$ ],  $wR2 = 0.0742$ ,  $R = 0.0322$  for 5534 reflections [ $I \geq 2\sigma(I)$ ] and 311 parameters.

Crystal data for  $\text{C}_{15}\text{H}_{18}\text{AgO}_3\text{PS}$  (**5**):  $M = 417.19$ , orthorhombic,  $a = 6.0429(1)$ ,  $b = 13.9308(3)$ ,  $c = 18.8836(3)\text{ \AA}$ , space group  $P2_12_12_1$ ,  $Z = 4$ ,  $V = 1589.67(5)\text{ \AA}^3$ ,  $\mu(\text{Mo-K}\alpha) = 15.06\text{ cm}^{-1}$ , 30910 measured and 3692 unique reflections [ $R_{\text{int}} = 0.031$ ],  $wR2 = 0.0590$ ,  $R = 0.0225$  for 3692 reflections [ $I \geq 2\sigma(I)$ ] and 190 parameters; absolute structure parameter: 0.007(18). – The function minimized was  $wR2 = \Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]^{1/2}$ ;  $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$ ;  $p = (F_o^2 + 2F_c^2)/3$ ;  $a = 0.0221$  (**1**), 0.0289 (**5**);  $b = 1.34$  (**1**), 0.54 (**5**).

Displacement parameters and complete tables of interatomic distances and angles have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. The data are available on request on quoting CCDC-199148 (**1**), 199149 (**5**).

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