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Acylchalcogenourea complexes of silver(I)

Maik Dörner,^[a] Mikko Rautiainen,^[b] Jörg Rust,^[c] Christian W. Lehmann,^[c] and Fabian Mohr*^[a]

Abstract: Acylthio- or acylselenoureas react with silver oxide to form tetranuclear silver(I) complexes containing the deprotonated acylchalcogenourea ligands binding to the silver atoms via the chalcogen and oxygen atoms. These tetrasilver(I) species react with either four or eight equivalents of a phosphine giving either dinuclear silver(I) phosphine complexes or tetrahedral silver diphosphine complexes. In these compounds too, the acylchalcogenourea ligands form six-membered rings coordinating to the metal through the chalcogen and oxygen atoms. In one case we observed a very rare example of an acylthiourea ligand coordinating through the nitrogen and sulfur atoms, resulting in a four-membered ring. A silver(I) complex containing a deprotonated acylselenourea and an *N*-heterocyclic carbene ligands is also reported. This was prepared from the corresponding acetate derivative and the acylselenourea; the acetate in this case acts as the base. All compounds reported were characterised by spectroscopic techniques and many also by X-ray diffraction.

Introduction

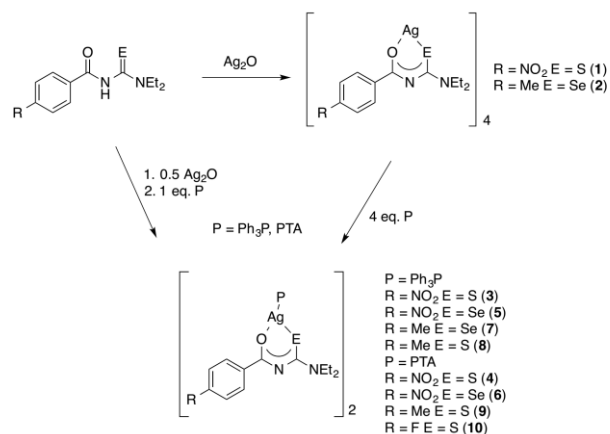
Deprotonated acylthio- or selenoureas of the type $[\text{ArC}(\text{O})\text{NC}(\text{E})\text{NR}_2]^-$ ($\text{E} = \text{S}, \text{Se}$) are monoanionic *O,S*- or *O,Se*-chelating ligands, which readily form complexes with many transition metals and also main-group-metals. Deprotonation of an acylthio/selenourea can either be accomplished using an external base or a basic metal precursor. In some cases, simply heating the acylthio/selenourea with a metal chloride forms the metal chelate complex accompanied by elimination of HCl. A recent review summarizes the structures, chemistry and biological properties of acylthiourea derivatives.^[1] Silver(I) complexes of acylthioureas have to date not been studied systematically. A report from 1985 describes the isolation of colorless crystals from a black tar formed in the reaction of $\text{PhC}(\text{O})\text{NHC}(\text{S})\text{NEt}_2$ with AgNO_3 and sodium acetate in aqueous ethanol.^[2] The crystals were found to consist of a silver(I)hydrosulfide complex containing three, neutral *S*-coordinated acylthioureas bound to the metal. Using slightly different reaction conditions (AgNO_3 in EtOH without base), another group later obtained the same silver(I)hydrosulfide species with $\text{PhC}(\text{O})\text{NHC}(\text{S})\text{N}^i\text{Bu}_2$.^[3] The source of the hydrosulfide ligand in these complexes was never explained, however, it probably originates from decomposition of the

sulfur ligands during the reaction. Richter was the first to report a silver complex containing a deprotonated acylthiourea ligand, formed by the reaction of $\text{PhC}(\text{O})\text{NHC}(\text{S})\text{NEt}_2$ with AgNO_3 and KOH.^[4] In this case, the isolated compound was the tetranuclear silver(I) cluster $[\text{Ag}_4\{\text{PhC}(\text{O})\text{NC}(\text{S})\text{NEt}_2\}_4]$, in which the deprotonated acylthiourea forms *O,S*-chelates with the silver atoms. It was later shown, that an analogous Ag_4 -cluster can also be formed when sodium acetate is used as base.^[5] Yet another structural motif that has been observed in acylthiourea silver(I) chemistry is the dinuclear silver(I) species $[\text{Ag}_2\{\text{RC}(\text{O})\text{NC}(\text{S})\text{NEt}_2\}_2\{\text{RC}(\text{O})\text{NHC}(\text{S})\text{NEt}_2\}_2]$ ($\text{R} = \text{camphanyl}$) containing one deprotonated, chelating acylthiourea ligand and one neutral *S*-coordinating acylthiourea ligand.^[6]

Although the coordination chemistry of acylselenourea ligands has also been studied with a number of transition- and main-group-metals, there are no reports of any silver compounds containing such selenium ligands. Given our interest in the chemistry and applications of metal complexes with acylthio/selenourea ligands,^[7] we report here results of a systematic study of acylselenoureas and their sulfur counterparts with silver(I) ions as well as their reactivity with various phosphines.

Results and Discussion

Given that silver(I)oxide has proven to be such a convenient starting material for the preparation of *N*-heterocyclic carbene complexes of silver,^[8] we thought that Ag_2O could also be a suitable single-component (base and silver-source in one) precursor for silver complexes of acylthio- and selenoureas. Indeed, Ag_2O rapidly dissolves in solutions of the acylthio- and selenoureas $4\text{-RC}_6\text{H}_4\text{C}(\text{O})\text{NHC}(\text{E})\text{NEt}_2$ ($\text{R} = \text{Me}, \text{NO}_2$; $\text{E} = \text{S}, \text{Se}$) leading to pale yellow (*S*) or brownish (*Se*) products **1** and **2**, which can be isolated in good yields (Scheme 1).



Scheme 1.

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The proton NMR spectra of **1** and **2** confirm the absence of the signal due to the NH-proton but provide no further insight into the exact molecular structure of the compounds. Fortunately, we obtained single crystals, which allowed us to determine the solid-state structure of both complexes (Figures 1 and 2). The compounds consist of four deprotonated acylchalcogenourea ligands bound to four silver atoms through the sulfur/selenium and oxygen atoms. In addition, the sulfur/selenium atoms bridge two neighboring silver atoms. The metal cluster core thus consists of four silver atoms arranged in a butterflyshape with Ag-Ag distances of 2.9956(3) Å and 3.0499(5) Å (complex **1**) and 2.9342(5) Å in complex **2**. These silver-silver distances are considerably shorter than the 3.44 Å van der Waals radius of Ag and can therefore be considered argentophilic contacts.^[9]

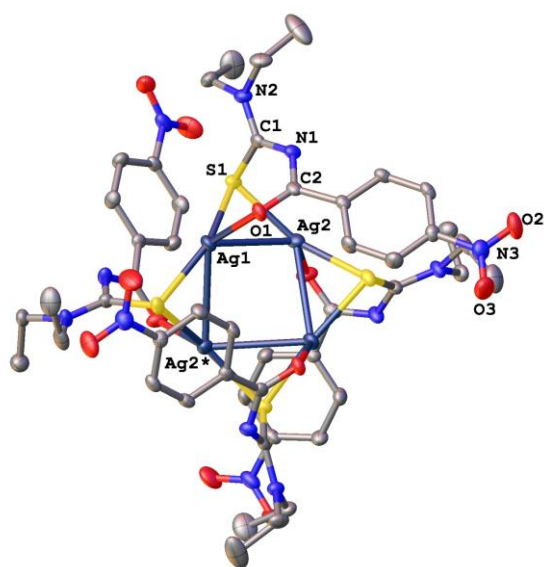


Figure 1. Molecular structure of **1**. Hydrogen atoms as well as the MeOH of solvation have been omitted for clarity. Ellipsoids are drawn at 50% probability levels. Selected bond distances (Å) and angles (°): Ag(1)-Ag(2) 3.0499(5), Ag(1)-Ag(2)* 2.9956(3), Ag(1)-S(1) 2.4366(6), Ag(1)-O(1) 2.4101(15), Ag(1)-S(2) 2.4084(6), Ag(2)-S(2) 2.4668(6), Ag(2)-O(2) 2.4193(6), O(1)-Ag(1)-S(1) 91.33(4), O(2)-Ag(2)-S(2) 92.69(4), Ag(1)-S(1)-Ag(2)* 76.179(19), S(1)-Ag(1)-S(2) 155.24(2).

The overall geometry including bond distances and angles in complex **1** are very similar to those previously reported by Richter and Habtu for $[\text{Ag}_4\{\text{PhC}(\text{O})\text{NC}(\text{S})\text{NEt}_2\}_4]$ and $[\text{Ag}_4\{\text{PhC}(\text{O})\text{NC}(\text{S})\text{N}^i\text{Bu}_2\}_4]$.^[4-5] The Ag-Se bond lengths of 2.5171(5) Å and 2.5341(6) Å in **2** are somewhat shorter than those observed in related tetranuclear silver clusters containing selenium ligands. In the cation $[\text{Ag}_4\{\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2\}_3]^+$ containing an anionic Se₂Se-chelating ligand, the average Ag-Se distance is about 2.6 Å^[10] and, similarly, the same 2.6 Å Ag-Se distance is observed in the silver cluster containing isopropyl selenolato ligands $[\text{Ag}_4(\text{dppe})_2(\text{Se}^i\text{Pr})_4]$.^[11]

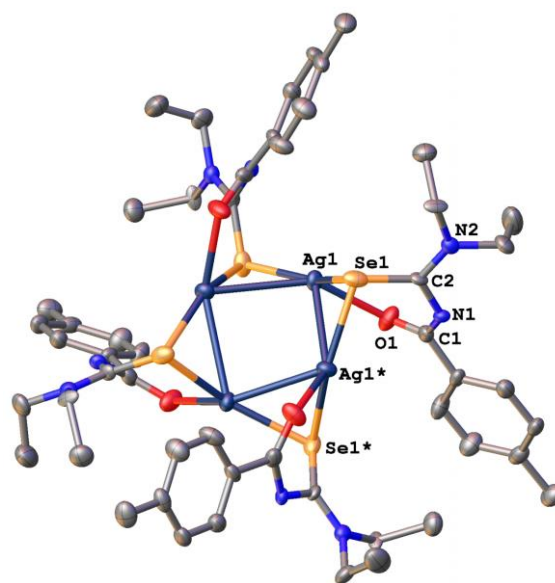


Figure 2. Molecular structure of **2**. Hydrogen atoms as well as the disordered solvent molecules have been omitted for clarity. Ellipsoids are drawn at 50% probability levels. Only one part of the disordered NEt₂-groups is shown. Selected bond distances (Å) and angles (°): Ag(1)-Ag(1)* 2.9351(6), Ag(1)-Se(1) 2.5173(6), Ag(1)-Se(1)* 2.5342(7), Ag(1)-O(1) 2.380(4), Se(1)-Ag(1)-Ag(1)* 127.574(18), Se(1)-Ag(1)-O(1) 114.27(9), Ag(1)-Se(1)-Ag(1)* 71.05(2).

These results thus confirmed our initial idea, that Ag₂O could indeed be used as a precursor for defined silver compounds of acyl-chalcogenoureas. The reaction is fast and clean with water being the only side-product. Our subsequent investigation focused on the reactivity of these tetranuclear silver compounds.

We first examined reactivity of the tetrasilver complexes with phosphines. Addition of one equivalent (per silver atom) of Ph₃P or 1,3,5-triaza-7-phosphaadamantane (PTA) to the *in situ* formed tetranuclear compounds afforded colorless or yellow solids (**3-10**) after work-up (Scheme 1), which were characterized spectroscopically and, in some cases, by X-ray diffraction. The same products can also be obtained from the reaction of the isolated tetranuclear complexes **1** or **2** with four equivalents of the respective phosphine. Apart from the disappearance of the NH-proton resonance, the ¹H NMR spectra of the compounds are of little diagnostic value, since the chemical shifts and multiplicity of the observed resonances remain virtually unchanged. However, the ³¹P NMR spectra confirm that the phosphines are indeed coordinated to the metal center, since the chemical shifts of the singlet resonances are considerably shifted compared to those of the phosphines themselves. The resonances for the Ph₃P complexes are observed at around 10-15 ppm, whilst those of the PTA derivatives appear at around -86 ppm. Unfortunately, we were unable to observe any P-Ag coupling in the ³¹P-NMR spectra. Nevertheless, single crystal X-ray diffraction allowed us to determine the solid-state structures of complexes **3**, **4** and **7**; their molecular structures are shown in Figures 3, 4, and 5, respectively.

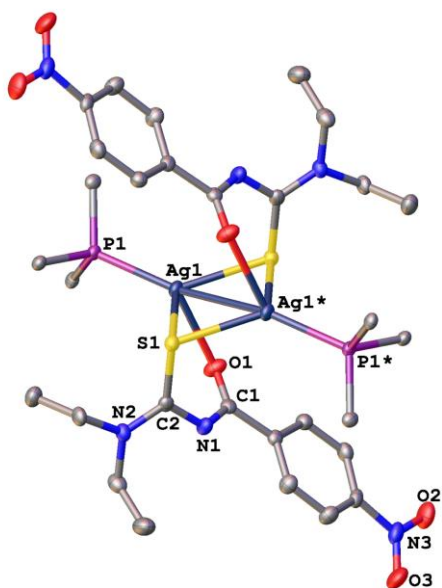


Figure 3. Molecular structure of **3**. Hydrogen atoms have been omitted for clarity. Ellipsoids are drawn at 50% probability levels. Only the *ipso*-carbon atoms of the Ph₃P ligands are shown. Selected bond distances (Å) and angles (°): Ag(1)-Ag(1)* 3.1257(4), Ag(1)-S(1) 2.6893(6), Ag(1)-O(1) 2.4311(17), Ag(1)-P(1) 2.4022(6), S(1)-C(1) 1.742(2), O(1)-C(2) 1.253(3), O(1)-Ag(1)-S(1) 84.55(4), Ag(1)-S(1)-Ag(1)* 73.039(16), P(1)-Ag(1)-O(1) 124.94(5), P(1)-Ag(1)-S(1) 115.050(19).

Because the structural features of these compounds are quite similar, they will be discussed here together. In each case, the molecule consists of a deprotonated acylchalcogenourea chelating a silver(I) center through both oxygen and sulfur or selenium atoms. In addition, the sulfur or selenium atoms bridge two silver atoms forming a planar, four-membered Ag₂S₂ or Ag₂Se₂ rings. The two silver atoms are held together by argentophilic contacts ranging from 3.06 to 3.15 Å. The coordination geometry about each silver atom is completed by the respective phosphine ligand. A similar Ag₂S₂ structural motif is found in a few other dinuclear silver phosphine

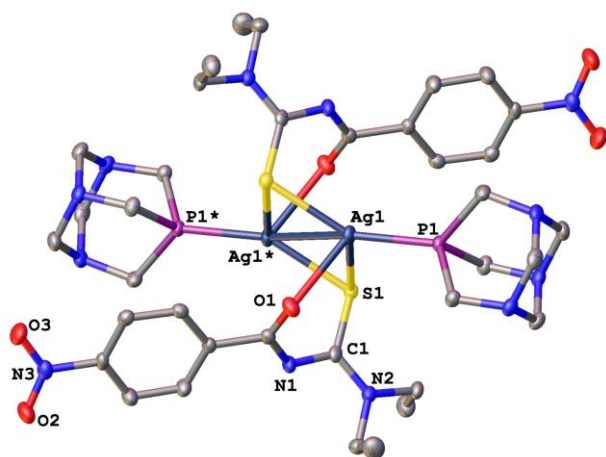


Figure 4. Molecular structure of **4**. Hydrogen atoms have been omitted for clarity. Ellipsoids are drawn at 50% probability levels. Selected bond distances (Å) and angles (°): Ag(1)-Ag(1)* 3.0583(3), Ag(1)-S(1) 2.7762(5), Ag(1)-O(1) 2.4342(13), Ag(1)-P(1) 2.3751(5), O(1)-C(2) 1.251(2), S(1)-C(1) 1.7512(18), O(1)-Ag(1)-S(1) 82.65(3), Ag(1)-S(1)-Ag(1)* 70.559(12), P(1)-Ag(1)-O(1) 114.96(3), P(1)-Ag(1)-S(1) 101.076(15).

compounds containing sulfur ligands. These include [Ag₂(Ph₃P)₂{ArC=C(S)C(O)OH}₂] (Ar = Ph^[12] or thienyl^[13]), [Ag₂(Ph₃P)₂(2-SC₆H₄NO)₂] ^[14] and [Ag₂(Ph₃P)₂(tu)₂(NO₂)₂] (tu = thiourea).^[15] In these complexes the Ag-Ag distances range from ca. 2.9 to 3.2 Å. The only known selenium derivatives containing an Ag₂Se₂ core are [Ag₂(Ph₃P)₃{SeC(O)Ph}₂] ^[16] and [Ag₂(Ph₃P)₃(SePh)₂].^[17] In these two complexes the Ag-Ag distances range from 2.9 to 3.0 Å. In the molecular structures of complexes **3**, **4** and **7**, the two chalcogen-silver distances are not identical: In each case, one can observe one longer and one shorter Ag-S/Se bond. The difference between these Ag-S/Se distances varies from as little as 0.07 to 0.29 Å

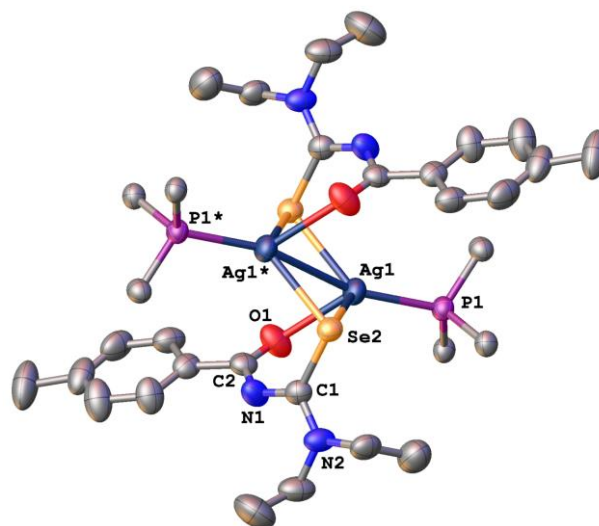
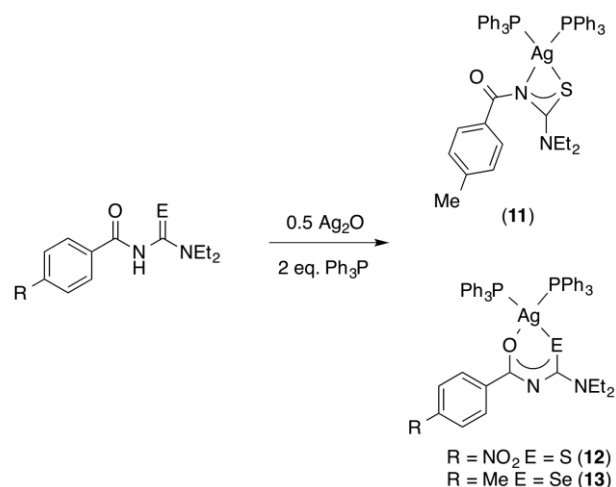


Figure 5. Molecular structure of **7**. Hydrogen atoms have been omitted for clarity. Ellipsoids are drawn at 50% probability levels. Only the *ipso*-carbon atoms of the Ph₃P ligands are shown. Selected bond distances (Å) and angles (°): Ag(1)-Ag(1)* 3.1099(5), Ag(1)-Se(2) 2.7373(4), Ag(1)-O(1) 2.462(2), Ag(1)-P(1) 2.4205(8), O(1)-C(2) 1.246(4), Se(2)-C(1) 1.909(3), O(1)-Ag(1)-Se(2) 85.85(5), Ag(1)-Se(2)-Ag(1)* 70.262(11), P(1)-Ag(1)-O(1) 123.47(7), P(1)-Ag(1)-Se(2) 117.18(2).

The reactions of 4-RC₆H₄C(O)NC(E)NEt₂ (R = Me, NO₂; E = S, Se) with Ag₂O and two equivalents of phosphine per silver atom afford the monomeric silver(I) complexes [Ag{4-RC₆H₄C(O)NC(E)NEt₂-(Ph₃P)₂] [R = Me, E = S (**11**); R = NO₂, E = S (**12**); R = Me, E = Se (**13**)] in high yields (Scheme 2).



Scheme 2.

Whilst the singlet resonances for the dinuclear complexes in the ^{31}P NMR spectra are observed at around 10–15 ppm, those of the monomeric complexes **11–13** appear in the range $\delta = 5$ –8 ppm. The ^1H NMR spectra of these compounds confirm the deprotonation of the NH-group and also indicate 2:1 phosphine/acetylthiourea ratios. The X-ray crystal structure of complex **12** (Figure 6) shows the typical O,S-chelating mode of a deprotonated acylthiourea forming a six-membered ring. The tetrahedral coordination environment about the silver center is completed by the two phosphine ligands.

However, in the case of the *p*-tolyl derivative $[\text{Ag}\{4\text{-MeC}_6\text{H}_4\text{C}(\text{O})\text{NC}(\text{S})\text{NEt}_2\}(\text{PPh}_3)_2]$ (**11**), the coordination mode of the deprotonated acylthiourea ligand is very different (Figure 7). Here, the sulfur- and the nitrogen atoms of the deprotonated acylthiourea are bound to the silver atom forming a four-membered chelate ring. The four-coordinate geometry about the silver is completed by the two phosphine ligands. This N,S- coordination mode is extremely rare for acylthiourea derivatives. The Rhodium(I) complex $[\text{Rh}(\text{CO})\{\text{PhC}(\text{O})\text{-NC}(\text{S})\text{NH}(2\text{-Me-4-HOC}_6\text{H}_3)\}(\text{PPh}_3)_2]$ reported by Warsink is the only other example of a metal complex with this coordination mode.^[18]

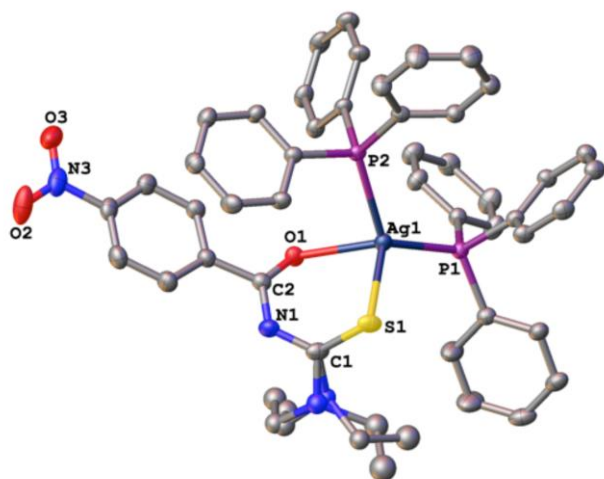


Figure 6. Molecular structure of **12**. Hydrogen atoms have been omitted for clarity. Ellipsoids are drawn at 50% probability levels. Selected bond distances (Å) and angles ($^\circ$): Ag(1)-S(1) 2.5515(5), Ag(1)-O(1) 2.3962(13), Ag(1)-P(1) 2.4631(4), Ag(1)-P(2) 2.5091(5), O(1)-C(2) 1.263(2), S(1)-C(1) 1.7356(19). O(1)-Ag(1)-(S1) 87.41(3), P(1)-Ag(1)-S(1) 113.764(17), P(2)-Ag(1)-O(1) 90.73(3).

To try and explain why this unusual coordination mode is observed, we carried out some computational studies. Energy differences between the four- and six-membered ring silver complexes for both the nitro- and methyl-substituted ligands were calculated. The results indicate that the energy differences (ΔG_{298}) between the six- and four-membered ring

isomers are +7.6 kJ/mol for the nitro-derivative and +6.8 kJ/mol for the methyl congener. Given the similarity of the stabilities of the six- and four-membered ring isomers, we conclude that the observed crystallization of the four-membered ring complex is most probably due to solubility and not a consequence of any systematic energy difference.

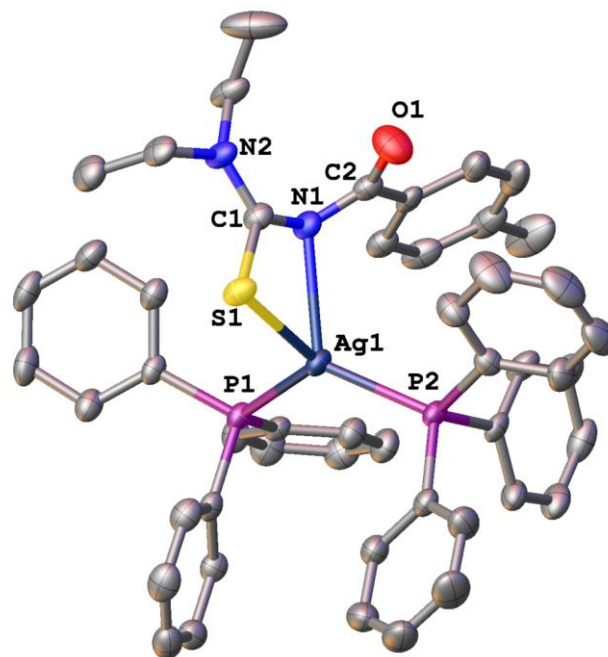
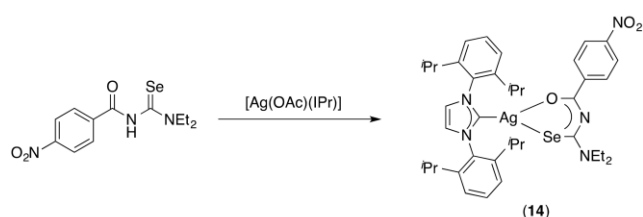


Figure 7. Molecular structure of **11**. Hydrogen atoms have been omitted for clarity. Ellipsoids are drawn at 50% probability levels. Selected bond distances (Å) and angles ($^\circ$): Ag(1)-S(1) 2.5861(6), Ag(1)-N(1) 2.5687(18), Ag(1)-P(1) 2.4685(6), Ag(1)-P(2) 2.4380(5), C(1)-N(1) 1.368(3), C(1)-S(1) 1.718(2). S(1)-Ag(1)-N(1) 61.50(4), N(1)-C(1)-S(1) 116.86(16), P(1)-Ag(1)-S(1) 108.72(2), P(2)-Ag(1)-N(1) 119.00(4).

Silver(I) complexes containing NHCs as C-donor ligands are nowadays common synthons for transmetalation reactions in organometallic chemistry. In addition, they have been shown to be biologically active molecules and also useful in homogeneous catalysis.^[19] Most known silver NHC-complexes are either halide derivatives $[\text{AgX}(\text{NHC})]$ or bis(carbene) salts $[\text{Ag}(\text{NHC})_2]^+$. There are very few examples where the halide ligand has been exchanged for a different monoanionic ligand. Given the similarity between phosphines and carbenes as donor ligands, we wished to prepare silver NHC complexes containing a deprotonated acylselenourea ligand. The reaction of $4\text{-O}_2\text{NC}_6\text{H}_4\text{C}(\text{O})\text{NC}(\text{Se})\text{NEt}_2$ with $[\text{Ag}(\text{OAc})(\text{IPr})]$ [$\text{IPr} = 1,3\text{-bis}(2,6\text{-diisopropylphenyl})\text{imidazolyli-dene}$] afforded the desired product (**14**) as yellow solid in good yield (Scheme 3).



Scheme 3.

The compound was spectroscopically and also structurally characterized. The ^1H NMR data is consistent with a 1:1 ratio of IPr and deprotonated acylselenourea. Due to poor solubility of the compound and inherent low intensity of the signal, we were unable to directly observe the ^{13}C resonance of the Ag-carbene carbon atom. However, through a 2D HMBC experiment, we could identify this resonance at 188 ppm, a typical value for a silver-bound carbene carbon atom. We were able to obtain X-ray quality crystals, which allowed us to unambiguously determine the solid-state structure of the compound (Figure 8). The molecule consists of a tricoordinate silver atom bound to the IPr ligand *via* the carbon atom and the deprotonated acylselenourea ligand *via* the O and Se atoms. The coordination geometry at the silver center is distorted trigonal planar, with an O–Ag–Se angle of *ca.* 88°, the other two angles (C–Ag–O and C–Ag–Se) being 117° and 155°, respectively. Such a distorted trigonal planar coordination at a silver center is found in a few other mononuclear compounds. Examples include the diketonato-derivatives $[\text{Ag}(\text{L})\{\text{RC}(\text{O})\text{CHC}(\text{O})\text{R}\}]$ (L = Ph_3P , Me_3P , MeNC ; R = CF_3 , *t*Bu)^[20] and silver carbene complexes containing O,O-chelating acetate ligands $[\text{Ag}(\text{OAc})(\text{NHC})]$.^[21] In the diketonato-compounds the O–Ag–O angles are considerably smaller (80–82.5°) than the corresponding O–Ag–Se angle in (14). The other bond distances and angles in (14) are as expected for this class of compounds. Whilst the Ag–O bond lengths in (14) are very similar to those in the dimeric complex (7), the Ag–Se bond length in (14) (*ca.* 2.49 Å) is significantly shorter than that in (7). Uniquely, the six-membered ring formed by the coordinating acylselenourea is significantly distorted from planarity. In the phosphine complexes described above, the ring is virtually planar, whereas in (14) it adopts almost a saddle-shaped conformation. The silver, oxygen, selenium and nitrogen atoms lie in a plane whilst the two carbon atoms are found above and below this plane, respectively.

Conclusions

Overall, we have shown that silver(I)oxide is suitable starting material for silver complexes of thio- and selenourea ligands. The initially formed tetrameric compounds react with phosphines resulting in different products depending on the stoichiometry. For a 1:1 ratio of silver/phosphine, sulfur- or selenium-bridged dinuclear species form in which the acylchalcogenourea ligands act as monoanionic O,S⁻ or O,Se-

chelates. With two equivalents of phosphine per silver atom, mononuclear compounds result in which the acylchalcogenourea ligands adopt either the rare monoanionic N,S⁻ or the monoanionic O,S⁻ coordination mode. With the carbene precursor $[\text{Ag}(\text{OAc})(\text{IPr})]$, a tricoordinate silver carbene complex was obtained containing a monoanionic O,Se-coordinated acylselenourea ligand. Further studies with this class of compounds and their applications are currently ongoing in our group.

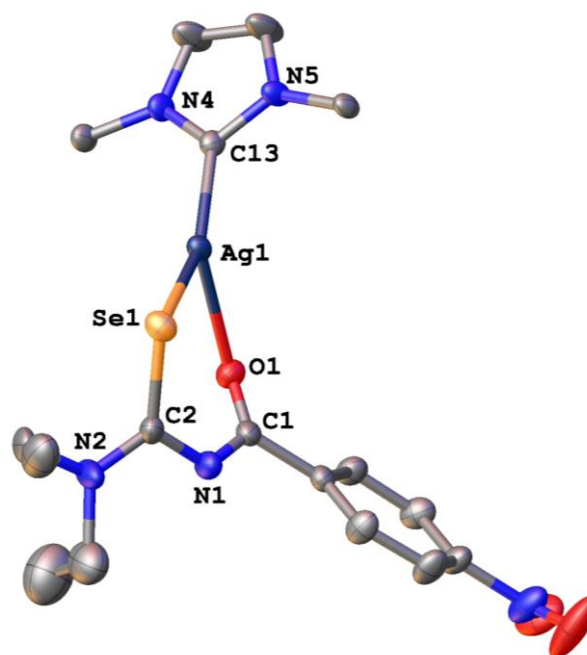


Figure 8. Molecular structure of 14. Hydrogen atoms have been omitted for clarity. Ellipsoids are drawn at 50% probability levels. Only the *ipso*-carbon atoms of the aryl rings are shown. Selected bond distances (Å) and angles (°): Ag(1)–C(13) 2.102(3), Ag(1)–Se(1) 2.4920(4), Ag(1)–O(1) 2.465(2), C(1)–O(1) 1.253(3), C(2)–Se(1) 1.902(3). Se(1)–Ag(1)–O(1) 88.82(5), C(13)–Ag(1)–Se(1) 154.53(8), C(13)–Ag(1)–O(1) 116.55(9).

Experimental Section

General

Reactions were carried out under ambient conditions in reaction vessels shielded from light. Solvents (HPLC quality) and reagents were sourced commercially and were used as received. The acylthio/selenoureas,^[22] $[\text{Ag}(\text{OAc})(\text{IPr})]$ ^[23] as well as PTA^[24] were prepared following literature procedures. NMR spectra were recorded on Bruker Avance 400 or Bruker Avance III 600 instruments. Elemental analyses were carried out in-house using an Elementar Vario EL instrument. Samples for elemental analysis were dried in vacuum at 60 °C overnight.

Preparation of the silver(I) tetramers

To a solution of the acylthio- or selenourea (0.36 mmol) in CH_2Cl_2 (10 mL) was added solid Ag_2O (0.55 equivalents, 0.19 mmol). After 30–40 minutes most of the silver oxide had dissolved. The mixture was filtered and left to stand in the dark. Within a few days X-ray quality crystals deposited, which were isolated by filtration and dried. To isolate the bulk material, the filtrate was evaporated to dryness in vacuum and the resulting solid was washed with Et_2O and dried in air.

$[Ag_4\{4-O_2NC_6H_4C(O)NC(S)NEt_3\}_2] (1)$

Compound (1) was isolated as pale yellow solid in 75% yield. 1H -NMR ($CDCl_3$) $\delta = 1.10$ (t, $J = 7.1$ Hz, 12 H NCH_2CH_3), 1.20 (t, $J = 7.1$ Hz, 12 H NCH_2CH_3), 3.48 (q, $J = 7.1$ Hz, 8 H NCH_2CH_3), 3.59 (q, $J = 7.1$ Hz, 8 H NCH_2CH_3), 8.24 (d, $J = 8.8$ Hz, 8 H, C_6H_4), 8.48 (d, $J = 8.8$ Hz, 8 H, C_6H_4). ^{13}C -NMR ($CDCl_3$) $\delta = 12.88$ (NCH_2CH_3), 13.15 (NCH_2CH_3), 46.15 (NCH_2CH_3), 46.31 (NCH_2CH_3), 122.96, 130.66, 144.40, 149.30 (C_6H_4), 168.13 (CS), 170.61 (CO). $C_{48}H_{56}N_{12}O_{12}S_4Ag_4$ (1552.76): calcd. C 37.13, H 3.64, N 10.82; found C 37.29, H 3.52, N 11.06 %.

 $[Ag_4\{4-MeC_6H_4C(O)NC(Se)NEt_3\}_2] (2)$

Compound (2) was isolated as a brownish solid in 60% yield. 1H -NMR ($CDCl_3$) $\delta = 1.25$ (m, 24 H, NCH_2CH_3), 2.38 (s, 12 H, Me), 3.69 (m, 16 H, NCH_2CH_3), 7.15 (d, $J = 7.9$ Hz, 8 H, C_6H_4), 7.91 (d, $J = 7.8$ Hz, 8 H, C_6H_4). ^{13}C -NMR ($CDCl_3$) $\delta = 13.44$ (NCH_2CH_3), 21.53 (Me), 46.57 (NCH_2CH_3), 127.73, 129.56, 134.23, 141.52 (C_6H_4), 170.93 (CO), CSe was not observed. $C_{52}H_{68}N_8O_4Se_4Ag_4$ (1616.48): calcd. C 38.64, H 4.24, N 6.93; found C 38.70, H 4.34, N 7.03 %.

Preparation of the dinuclear silver(I) phosphine complex

To a solution of the acylthio- or selenourea (0.36 mmol) in a mixture of MeOH and CH_2Cl_2 (5 mL each) was added solid Ag_2O (0.55 equivalents, 0.19 mmol). After 30-40 minutes the mixture was filtered and subsequently one equivalent (0.36 mmol) of the appropriate phosphine was added to the filtrate. After a further 30 minutes at room temperature, the product was isolated by evaporation of the solvent and washing the residue with Et_2O . X-ray quality crystals were obtained by slow evaporation of CH_2Cl_2 solutions of the compounds.

 $[Ag_2\{4-O_2NC_6H_4C(O)NC(S)NEt_3\}_2(PPh_3)_2] (3)$

Compound (3) was isolated as bright yellow solid in 77% yield. $^3P\{^1H\}$ -NMR ($CDCl_3$) $\delta = 14.0$ (s). 1H -NMR ($CDCl_3$) $\delta = 1.21$ (t, $J = 7.1$ Hz, 6 H NCH_2CH_3), 1.32 (t, $J = 7.1$ Hz, 6 H NCH_2CH_3), 3.72 (q, $J = 7.1$ Hz, 4 H, NCH_2CH_3), 3.95 (q, $J = 7.1$ Hz, 4 H, NCH_2CH_3), 7.37-7.55 (m, 30 H, Ph_3P), 8.08 (d, $J = 8.8$ Hz, 4 H, C_6H_4), 8.17 (d, $J = 8.8$ Hz, 4 H, C_6H_4). ^{13}C -NMR ($CDCl_3$) $\delta = 12.98$ (NCH_2CH_3), 13.21 (NCH_2CH_3), 45.39 (NCH_2CH_3), 46.02 (NCH_2CH_3), 122.68 (C_6H_4), 128.95 (d, $J = 10$ Hz, m - Ph_3P), 129.70 (C_6H_4), 130.65 (d, $J = 2$ Hz, p - Ph_3P), 131.27 (d, $J = 32$ Hz, $ipso$ - Ph_3P), 134.02 (d, $J = 17$ Hz, o - Ph_3P), 145.65 (C_6H_4), 148.68 (C_6H_4), 166.74 (CO), 179.11 (CS). $C_{60}H_{58}N_6O_6P_2S_2Ag_2$ (1300.96): calcd. C 55.39, H 4.49, N 6.46; found C 55.23, H 4.64, N 6.12 %.

 $[Ag_2\{4-O_2NC_6H_4C(O)NC(S)NEt_3\}_2(PTA)_2] (4)$

Compound (4) was isolated as a dark yellow solid in 92% yield. $^3P\{^1H\}$ -NMR ($CDCl_3$) $\delta = -87.5$ (s). 1H -NMR ($CDCl_3$) $\delta = 1.23$ (t, $J = 7.1$ Hz, 6 H NCH_2CH_3), 1.35 (t, $J = 7.1$ Hz, 6 H NCH_2CH_3), 3.70 (q, $J = 7.2$ Hz, 4 H, NCH_2CH_3), 3.93 (q, $J = 7.2$ Hz, 4 H, NCH_2CH_3), 4.18 (m, 12 H, PTA), 4.58 (s, 12 H, PTA), 7.72-7.83 (m, 8 H, C_6H_4). ^{13}C -NMR ($CDCl_3$) $\delta = 13.24$ (NCH_2CH_3), 44.43 (NCH_2CH_3), 51.29 (PTA), 73.43 (d, $J = 4.0$ Hz, PTA), 122.93 (C_6H_4), 129.66 (C_6H_4), 130.85 (C_6H_4), 148.90 (C_6H_4), 163.20 (CO), 171.27 (CS). $C_{36}H_{52}N_{12}O_6P_2S_2Ag_2$ (1090.69): calcd. C 39.64, H 4.81, N 15.41; found C 39.91, H 4.55, N 15.83 %.

 $[Ag_2\{4-O_2NC_6H_4C(O)NC(Se)NEt_3\}_2(PPh_3)_2] (5)$

Compound (5) was isolated as dark orange solid in 49% yield. $^3P\{^1H\}$ -NMR ($CDCl_3$) $\delta = 10.03$ (s). 1H -NMR ($CDCl_3$) $\delta = 1.15$ (t, $J = 7.1$ Hz, 6 H NCH_2CH_3), 1.24 (t, $J = 7.1$ Hz, 6 H NCH_2CH_3), 3.64 (q, $J = 7.3$ Hz, 4 H, NCH_2CH_3), 3.89 (q, $J = 7.3$ Hz, 4 H, NCH_2CH_3), 7.33-7.51 (m, 30 H, Ph_3P), 7.99 (d, $J = 8.9$ Hz, 4 H, C_6H_4), 8.05 (d, $J = 8.9$ Hz, 4 H, C_6H_4). ^{13}C -NMR ($CDCl_3$) $\delta = 13.08$ (NCH_2CH_3), 13.36 (NCH_2CH_3), 45.45 (NCH_2CH_3), 47.97 (NCH_2CH_3), 122.66 (C_6H_4), 128.76 (d, $J = 10$ Hz, m -

Ph_3P), 129.84 (C_6H_4), 130.28 (d, $J = 2$ Hz, p - Ph_3P), 132.09 (d, $J = 29$ Hz, $ipso$ - Ph_3P), 134.04 (d, $J = 17$ Hz, o - Ph_3P), 145.06 (C_6H_4), 148.68 (C_6H_4), 166.66 (CO), 170.66 (CSe). $C_{60}H_{58}N_6O_6P_2Se_2Ag_2$ (1394.76): calcd. C 51.67, H 4.19, N 6.03; found C 52.03, H 4.11, N 6.25 %.

 $[Ag_2\{4-O_2NC_6H_4C(O)NC(Se)NEt_3\}_2(PTA)_2] (6)$

Compound (6) was isolated as an orange solid in 48% yield. $^3P\{^1H\}$ -NMR ($CDCl_3$) $\delta = -88.6$ (s). 1H -NMR ($CDCl_3$) $\delta = 1.23$ (t, $J = 7.1$ Hz, 6 H NCH_2CH_3), 1.36 (t, $J = 7.1$ Hz, 6 H NCH_2CH_3), 3.69 (q, $J = 7.3$ Hz, 4 H, NCH_2CH_3), 3.95 (q, $J = 7.3$ Hz, 4 H, NCH_2CH_3), 4.11 (s, 6 H, PTA), 4.52 (m, 6 H, PTA), 8.17-8.25 (m, 8 H, C_6H_4). ^{13}C -NMR ($CDCl_3$) $\delta = 12.49$ (NCH_2CH_3), 44.69 (NCH_2CH_3), 47.20 (NCH_2CH_3), 50.46 (PTA), 72.59 (d, $J = 4.1$ Hz, PTA), 122.19 (C_6H_4), 129.23 (C_6H_4), 130.85 (C_6H_4), 148.28 (C_6H_4), 166.30 (CO), 170.46 (CSe). $C_{36}H_{52}N_{12}O_6P_2Se_2Ag_2$ (1184.49): calcd. C 36.50, H 4.43, N 14.19; found C 36.57, H 4.52, N 14.39 %.

 $[Ag_2\{4-MeC_6H_4C(O)NC(Se)NEt_3\}_2(PPh_3)_2] (7)$

Compound (7) was isolated as a brownish solid in 60% yield. $^3P\{^1H\}$ -NMR ($CDCl_3$) $\delta = 15.42$ (s). 1H -NMR ($CDCl_3$) $\delta = 1.28$ (m, 12 H NCH_2CH_3), 2.36 (s, 6 H, Me), 3.71 (m, 4 H, NCH_2CH_3), 3.95 (m, 4 H, NCH_2CH_3), 7.08 (d, $J = 7.9$ Hz, 4 H, C_6H_4), 7.35-7.57 (m, 30 H, Ph_3P), 7.93 (d, $J = 7.9$ Hz, 4 H, C_6H_4). ^{13}C -NMR ($CDCl_3$) $\delta = 12.68$ (NCH_2CH_3), 20.83 (Me), 44.68 (NCH_2CH_3), 127.68 (C_6H_4), 128.21 (d, $J = 10$ Hz, m - Ph_3P), 128.59 (C_6H_4), 129.71 (p - Ph_3P), 131.48 (d, $J = 29$ Hz, $ipso$ - Ph_3P), 133.37 (d, $J = 17$ Hz, o - Ph_3P), 135.36 (C_6H_4), 139.89 (C_6H_4), 166.28 (CO), 170.08 (CSe). $C_{62}H_{64}N_4O_2P_2Se_2Ag_2$ (1332.82): calcd. C 55.87, H 4.84, N 4.20; found C 56.01, H 5.00, N 4.34 %.

 $[Ag_2\{4-MeC_6H_4C(O)NC(S)NEt_3\}_2(PPh_3)_2] (8)$

Compound (8) was isolated as a colourless solid in 65% yield. $^3P\{^1H\}$ -NMR ($CDCl_3$) $\delta = 15.66$ (s). 1H -NMR ($CDCl_3$) $\delta = 1.27$ (m, 6 H NCH_2CH_3), 1.34 (m, 6 H NCH_2CH_3), 2.38 (s, 6 H, Me), 3.76 (m, 4 H, NCH_2CH_3), 3.98 (m, 4 H, NCH_2CH_3), 7.13 (d, $J = 7.8$ Hz, 4 H, C_6H_4), 7.39-7.62 (m, 30 H, Ph_3P), 8.04 (d, $J = 8.1$ Hz, 4 H, C_6H_4). ^{13}C -NMR ($CDCl_3$) $\delta = 13.26$ (NCH_2CH_3), 21.45 (Me), 45.22 (NCH_2CH_3), 128.23 (C_6H_4), 128.96 (d, $J = 10$ Hz, m - Ph_3P), 129.13 (C_6H_4), 130.63 (d, $J = 2$ Hz, p - Ph_3P), 131.30 (d, $J = 35$ Hz, $ipso$ - Ph_3P), 134.13 (d, $J = 17$ Hz, o - Ph_3P), 136.82 (C_6H_4), 140.13 (C_6H_4), 166.73 (CO), 170.19 (CS). $C_{62}H_{64}N_4O_2P_2S_2Ag_2$ (1239.82): calcd. C 60.10, H 5.21, N 4.52; found C 60.29, H 5.55, N 4.48 %.

 $[Ag_2\{4-MeC_6H_4C(O)NC(S)NEt_3\}_2(PTA)_2] (9)$

Compound (9) was isolated as a colourless solid in 66% yield. $^3P\{^1H\}$ -NMR ($CDCl_3$) $\delta = -85.69$ (s). 1H -NMR ($CDCl_3$) $\delta = 1.24$ (m, 12 H NCH_2CH_3), 2.38 (s, 6 H, Me), 3.75 (m, 8 H, NCH_2CH_3), 4.01 (s, 6 H, PTA), 4.40 (AB quart., $J = 13.7$ Hz, 6 H, PTA), 7.17 (d, $J = 7.8$ Hz, 4 H, C_6H_4), 8.00 (d, $J = 8.1$ Hz, 4 H, C_6H_4). ^{13}C -NMR ($CDCl_3$) $\delta = 13.23$ (NCH_2CH_3), 21.47 (Me), 45.65 (NCH_2CH_3), 51.07 (d, $J = 3.6$ Hz, PTA), 73.12 (d, $J = 5.9$ Hz, PTA), 128.42 (C_6H_4), 129.39 (C_6H_4), 136.32 (C_6H_4), 140.59 (C_6H_4), 163.01 (CO), 170.50 (CS). $C_{38}H_{58}N_{10}O_2P_2S_2Ag_2$ (1028.75): calcd. C 44.37, H 5.68, N 13.62; found C 44.19, H 5.73, N 13.97 %.

 $[Ag_2\{4-FC_6H_4C(O)NC(S)NEt_3\}_2(PTA)_2] (10)$

Compound (10) was isolated as a dark yellow solid in 92% yield. $^3P\{^1H\}$ -NMR ($CDCl_3$) $\delta = -87.51$ (s). 1H -NMR ($CDCl_3$) $\delta = 1.21$ (t, $J = 7.1$ Hz, 6 H NCH_2CH_3), 1.32 (t, $J = 7.1$ Hz, 6 H NCH_2CH_3), 3.69 (q, $J = 7.1$ Hz, 4 H, NCH_2CH_3), 3.89 (q, $J = 7.1$ Hz, 4 H, NCH_2CH_3), 4.24 (d, $J = 3.8$ Hz, 6 H, PTA), 4.57 (AB quart., $J = 13.3$ Hz, 6 H, PTA), 8.20-8.28 (m, 8 H, C_6H_4). ^{13}C -NMR ($CDCl_3$) $\delta = 12.44$ (NCH_2CH_3), 12.63 (NCH_2CH_3), 44.70 (NCH_2CH_3), 44.93 (NCH_2CH_3), 50.57 (d, $J = 5.5$ Hz, PTA), 72.53 (d, $J = 6.5$ Hz, PTA), 122.20 (C_6H_4), 129.13 (C_6H_4), 140.63 (C_6H_4), 148.15

(C₆H₄), 165.62 (CO), 170.13 (CS). C₃₆H₅₂F₂N₁₀O₂P₂S₂Ag₂ (1036.68): calcd. C 41.71, H 5.06, N 13.51; found C 42.01, H 5.11, N 13.79 %.

Preparation of the mononuclear silver(I) phosphine complexes

These were prepared as described above except that after filtration two equivalents (0.72 mmol) of the appropriate phosphine were added to the filtrate. After 30 minutes at room temperature, the products were subsequently isolated by evaporation of the solvent and washing the residue with Et₂O. X-ray quality crystals were obtained by slow evaporation of CH₂Cl₂ solutions of the compounds.

[Ag{4-MeC₆H₄C(O)NC(S)NEt₂}(PPh₃)₂] (11)

Compound (11) was isolated as yellowish solid in 60 % yield. ³¹P{¹H}-NMR (CDCl₃) δ = 6.4 (s). ¹H-NMR (CDCl₃) δ = 1.28 (m, 6 H NCH₂CH₃), 2.37 (s, 3 H, Me), 3.71 (m, 4 H, NCH₂CH₃), 3.85 (m, 4 H, NCH₂CH₃), 7.09 (d, J = 8.0 Hz, 2 H, C₆H₄), 7.31–7.49 (m, 30 H, Ph₃P), 7.98 (d, J = 8.0 Hz, 2 H, C₆H₄). ¹³C-NMR (CDCl₃) δ = 13.23 (NCH₂CH₃), 21.42 (Me), 45.32 (NCH₂CH₃), 128.15 (C₆H₄), 128.69 (d, J = 10 Hz, *m*-Ph₃P), 129.09 (C₆H₄), 129.74 (*p*-Ph₃P), 133.69 (d, J = 30 Hz, *ipso*-Ph₃P), 133.97 (d, J = 17 Hz, *o*-Ph₃P), 136.88 (C₆H₄), 139.90 (C₆H₄), 169.95 (CO), 177.13 (CS). C₄₉H₄₇N₂OP₂SAg (881.80): calcd. C 66.74, H 5.37, N 3.18; found C 66.23, H 5.12, N 3.34 %.

[Ag{4-O₂NC₆H₄C(O)NC(S)NEt₂}(PPh₃)₂] (12)

Compound (12) was isolated as bright yellow solid in 68% yield. ³¹P{¹H}-NMR (CDCl₃) δ = 5.25 (s). ¹H-NMR (CDCl₃) δ = 1.23 (t, J = 7.2 Hz, 6 H, NCH₂CH₃), 3.71 (q, J = 7.2 Hz, 2 H, NCH₂CH₃), 3.90 (q, J = 7.2 Hz, 2 H, NCH₂CH₃), 7.28–7.42 (m, 30 H, Ph₃P), 7.98 (d, J = 8.9 Hz, 2 H, C₆H₄), 8.04 (d, J = 8.9 Hz, 2 H, C₆H₄). ¹³C-NMR (CDCl₃) δ = 12.86 (NCH₂CH₃), 13.33 (NCH₂CH₃), 45.17 (NCH₂CH₃), 45.99 (NCH₂CH₃), 122.49 (C₆H₄), 128.64 (d, J = 9 Hz, *m*-Ph₃P), 129.53 (C₆H₄), 129.69 (d, J = 1 Hz, *p*-Ph₃P), 133.61 (d, J = 28 Hz, *ipso*-Ph₃P), 133.91 (d, J = 17 Hz, *o*-Ph₃P), 145.94 (C₆H₄), 148.35 (C₆H₄), 166.10 (CO), 181.24 (CS). C₄₈H₄₄N₃O₃P₂SAg (912.77): calcd. C 63.16, H 4.86, N 4.60; found C 63.18, H 4.93, N 4.93 %.

[Ag{4-MeC₆H₄C(O)NC(Se)NEt₂}(PPh₃)₂] (13)

Compound (13) was isolated as dark yellow solid in 71% yield. ³¹P{¹H}-NMR (CDCl₃) δ = 7.85 (s). ¹H-NMR (CDCl₃) δ = 1.28 (br. m, 6 H, NCH₂CH₃), 2.37 (s, 3 H, Me), 3.72 (br. m, 2 H, NCH₂CH₃), 3.97 (br. m, 2 H, NCH₂CH₃), 7.10 (d, J = 7.9 Hz, 2 H, C₆H₄), 7.37–7.57 (m, 30 H, Ph₃P), 7.95 (d, J = 8.1 Hz, 2 H, C₆H₄). ¹³C-NMR (CDCl₃) δ = 21.45 (Me), 50.83 (NCH₂CH₃), 128.28 (C₆H₄), 128.86 (d, J = 10 Hz, *m*-Ph₃P), 129.31 (C₆H₄), 130.31 (d, J = 2 Hz, *p*-Ph₃P), 133.08 (d, J = 30 Hz, *ipso*-Ph₃P), 134.11 (d, J = 17 Hz, *o*-Ph₃P), 140.47 (C₆H₄), 153.39 (C₆H₄), 167.04 (CO). The CSe signal was not observed. C₄₉H₄₇N₂OP₂SeAg (928.70): calcd. C 63.37, H 5.10, N 3.02; found C 63.53, H 5.08, N 3.26 %.

[Ag(IPr){4-O₂NC₆H₄C(O)NC(Se)NEt₂}] (14)

To a solution of 4-O₂NC₆H₄C(O)NHC(Se)NEt₂ (0.050 g, 0.152 mmol) in CH₂Cl₂ (5 mL) was added [Ag(OAc)(IPr)] (0.084 g, 0.151 mmol). After stirring for ca. 2 h, the mixture was concentrated in vacuum to ca. 2 mL. Addition of hexanes precipitated a solid, which was isolated by filtration and dried in air. 0.097 g (78%) of a yellow product was obtained. ¹H-NMR (CDCl₃) δ = 1.12 (br. m, 6 H, NCH₂CH₃), 1.22 (d, J = 6.9 Hz, 12 H, Me-*i*Pr), 1.26 (d, J = 6.9 Hz, 12 H Me-*i*Pr), 2.64 (sept., J = 6.9 Hz, 4 H, CH-*i*Pr), 3.66 (br. m, 4 H, NCH₂CH₃), 7.20 (s, 2 H, imidazole H), 7.29 (d, J = 8.8 Hz, 2 H, C₆H₄), 7.49 (t, J = 7.8 Hz, 4 H, IPr), 7.86 (d, J = 8.3 Hz, 2 H, IPr), 8.08 (d, J = 8.8 Hz, 2 H, C₆H₄). ¹³C-NMR (CDCl₃) δ = 13.21 (NCH₂CH₃), 24.09 (Me-*i*Pr), 24.46 (Me-*i*Pr), 28.66 (CH-*i*Pr), 122.43 (C₆H₄), 123.22 (imidazole C), 123.28 (imidazole C), 124.01 (C₆H₄), 129.82 (IPr), 130.19 (IPr), 135.22 (C₆H₄), 145.77 (IPr), 148.47 (C₆H₄), 167.86 (CO). The CSe and CAg signals could not be detected. C₃₉H₅₀N₅O₃SeAg (823.69): calcd. C 56.87, H 6.12, N 8.50; found C 57.01, H 6.10, N 8.72 %.

X-ray crystallography

Data were collected at 150 K on a Rigaku Oxford Diffraction Gemini Ultra diffractometer or at 100 K on a Bruker AXS Apex II with an Incoatec μS micro focus source (Mo-K_α radiation λ = 0.71073 Å). Calculations were carried out using Olex2 incorporating the SHELXL programs.^[25] Important crystallographic and refinement details are collected in Table 1. In the structure of complex (2) the NEt₂ group is disordered over two positions. In addition, the asymmetric unit

Table 1. Crystallographic and refinement details of complexes 1–4, 7, 11, 12 and 14.

	1	2	3	4	7	12	11	14
Empirical formula	C ₅₀ H ₆₄ Ag ₄ N ₁₂ O ₁₄ S ₄	C ₁₀₈ H ₁₄₆ Ag ₈ Cl ₂ N ₁₆ O ₉ Se ₈	C ₆₀ H ₅₈ Ag ₂ N ₆ O ₆ P ₂ S ₂	C ₃₆ H ₅₂ Ag ₂ N ₁₂ O ₆ P ₂ S ₂	C ₆₁ H ₆₄ Ag ₂ N ₄ O ₂ P ₂ Se ₂	C ₄₈ H ₄₄ AgN ₃ O ₃ P ₂ S	C ₄₆ H ₄₇ AgN ₂ O ₃ P ₂ S	C ₃₉ H ₅₀ AgN ₅ O ₃ S
Formula weight	1616.85	3377.94	1300.92	1090.70	1332.77	912.73	881.76	823.67
Crystal system	Monoclinic	Tetragonal	Triclinic	Orthorhombic	Triclinic	Triclinic	Triclinic	Orthorhombic
Space group	C2/c	P-4 ₂ c	P-1	Pbca	P-1	P-1	P-1	Pbcn
a/Å	30.9086(16)	15.1806(4)	11.1445(5)	11.46875(18)	11.2549(6)	12.4006(6)	12.7264(4)	16.8313(3)
b/Å	10.7720(3)		11.7112(4)	18.7320(3)	11.9594(5)	13.3291(15)	13.1751(4)	19.7431(4)
c/Å	24.5346(13)	13.1866(6)	12.1238(3)	20.3173(3)	12.2256(6)	15.463(2)	15.4150(4)	23.4509(4)
α/°	90	90	98.096(2)	90	97.090(4)	69.192(11)	81.454(3)	90
β/°	130.586(9)	90	97.826(3)	90	99.417(4)	73.276(8)	73.055(3)	90
γ/°	90	90	113.812(9)	90	114.243(5)	64.699(6)	63.782(3)	90
Volume/Å ³	6203.6(5)	3038.9(2)	1400.29(9)	4364.81(11)	1446.63(12)	2131.9(4)	2217.49(11)	7792.8(2)
Z	4	1	1	4	1	2	2	8
ρ _{calc} mg/mm ³	1.731	1.847	1.543	1.660	1.530	1.422	1.321	1.404
μ/mm ⁻¹	1.449	3.760	0.889	1.125	2.036	0.642	0.611	1.493
F(000)	3248.0	1660.0	664.0	2224.0	672.0	940.0	912.0	3392.0
Crystal size/mm ³	0.04×0.06×0.08	0.05×0.08×0.11	0.03×0.07×0.09	0.05×0.06×0.08	0.04×0.06×0.13	0.02×0.07×0.21	0.04×0.08×0.13	0.06×0.07×0.09

2 θ range [°]	4.14–58.8	4.09–58.96	3.9–59.12	4.34–58.84	3.82–58.84	6.436–71.93	3.84–59.04	4.234–59.09
Reflections collected	16670	8408	13028	15736	13191	205487	21841	28508
Independent reflections	7261[R(int) = 0.0240]	3470[R(int) = 0.0218]	6546[R(int) = 0.0301]	5260[R(int) = 0.0205]	6655[R(int) = 0.0235]	20095[R(int) = 0.0350]	10337[R(int) = 0.0253]	9533[R(int) = 0.0336]
Data/restraints/parameter S	7261/0/385	3470/78/244	6546/0/354	5260/0/273	6655/0/337	20095/0/522	10337/0/508	9433/0/452
Goodness-of-fit on F^2	1.032	1.058	1.057	1.027	1.046	1.073	1.039	1.039
Final R, [$I > 2\sigma(I)$]	0.0272	0.0268	0.0330	0.0235	0.0360	0.0550	0.0355	0.0403
Final R, [all data]	0.0360	0.0317	0.0409	0.0341	0.0533	0.0644	0.0496	0.0695
Largest diff. peak/hole / $e\text{\AA}^{-3}$	0.49/–0.49	0.69/–0.51	0.82/–0.70	0.34/–0.43	0.53/–0.42	2.75/–3.78	0.58/–0.46	1.15/–0.82

contains one quarter each of methanol and dichloromethane. The oxygen atom of the MeOH and the carbon atom of CH_2Cl_2 have identical coordinates. In the structure model of complex (**11**) there remained a solvent accessible void of 110 \AA^3 , containing 32 electrons. No satisfactory model could be found to account for this electron density, the data was therefore treated using the Squeeze procedure implemented in Platon.^[26] CCDC 1513650 (for **1**), 1513651 (for **2**), 1513652 (for **3**), 1513653 (for **4**), 1513654 (for **7**), 1406811 (for **11**), 1513655 (for **12**), and 1513654 (for **14**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Computational details

Structures were optimized with a revPBE GGA^[27] functional and def2-TZVPP^[28] basis sets as implemented in the ORCA^[29] program; resolution of identity (RI) approximation^[30] was employed to speed the calculations and Grimme's empirical corrections^[31] to treat the dispersion forces. The fundamental frequencies were calculated to assess the nature of stationary points and to estimate the zero-point energy (ZPE) corrections and Gibbs energies.

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Keywords: Silver • Selenium • Sulfur • Cluster compounds • X-ray structure

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