Binary and Ternary Cluster Complexes Containing Gold-Selenium, Gold-Indium-Selenium and Gold-Gallium-Tellurium − Synthesis and Structures of $[Au_5Se_2(PPh_3)_4]Cl$, $[(Au_3Se)_2\{Ph_2P(CH_2)_6PPh_2\}_3]Cl_2$, $[Au_{10}Se_4\{Ph_2P(CH_2)_5PPh_2\}_4]InCl_5$, $[Au_4(SeInCl_3)_2\{Ph_2P(CH_2)_5PPh_2\}_2]$, $[Au_2(TeGaCl_3)\{Ph_2P(CH_2)_6PPh_2\}]_2$ and $[Au_8Se_4In\{Ph_2P(CH_2)_2PPh_2\}_4](InCl_4)_3$

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Reactions of gold phosphane complexes $[(AuX)(PR_3)]$ (X = Cl, Br, I; R = organic moiety) with $Se(SiMe_3)_2$ lead to the formation of gold complexes with chalcogenide bridges. The reaction of the complex $[Ph_3PAuCl]$ and *t*BuSe($SiMe_3$) gives the cluster $[Au_5Se_2(PPh_3)_4]Cl$ (**1**). The in situ preparation of the complex $[(AuCl)_2dpph]$ [dpph = $Ph_2P(CH_2)_6PPh_2$] by reaction of dpph with $[Me_2SAuCl]$, and subsequent reaction with $Se(SiMe_3)_2$, leads to the formation of $[(Au_3Se)_2(dpph)_3]Cl_2$ (**2**). Reactions of the gold(I) complex $[(AuCl)_2dpppe]$ [dpppe = $Ph_2P(CH_2)_5PPh_2$] with $Se(SiMe_3)_2$ and $InCl_3$ in different molar ratios lead to the formation of $[Au_{10}Se_4(dpppe)_4]InCl_5$ (**3**) and $[Au_4(SeInCl_3)_2(dpppe)_2]$ (**4**). The reaction of $[(AuCl)_2dpph]$ with $Te(SiMe_3)_2$ and $GaCl_3$ produces the isostructural cluster compound $[Au_4(TeGaCl_3)_2(dpph)_2]$ (**5**). From the reaction of $Se(SiMe_3)_2$ with $[(AuCl)_2dppe]$ [dppe = $Ph_2P(CH_2)_2PPh_2$] and $InCl_3$ $[Au_8Se_4In(dppe)_4](InCl_4)_3$ **6** can be isolated. The structures of **1**–**6** were determined by X-ray diffraction.

Introduction

Due to the important photophysical and photochemical properties of gold(I) complexes, many investigations have been undertaken towards the synthesis and structural analysis of gold complexes and clusters.[1−5] However, only a few examples of gold complexes with selenium or tellurium bridges are known.[2,6]

For the preparation of this kind of cluster complex, a reaction has been developed using metal halides MX_n (M = metal; X = Cl, Br, I) and silylated main group element derivatives, R−E−$SiMe_3$ (R = organic group, $SiMe_3$; E = S, Se, Te), in the presence of a tertiary phosphane PR_3. The driving force of this reaction is the formation of the corresponding trimethylsilyl halide, $XSiMe_3$.[7] The phosphane ligands stabilize the metal cluster complex and avoid theformation of the binary phases.[8] The first results in this kind of preparations, using silylated derivatives of S, Se and Te, were reported by Abel et al. and Schmidbaur et al.[9]

The use of polyphosphanes leads to the formation of large cluster complexes containing copper[10] and silver[11] atoms bridged by chalcogenides. Polyphosphanes were also successfully applied in analogous reactions with gold(I) salts, resulting in the formation of several gold cluster complexes which have been characterized, for example $[Au_{18}Se_8(dppe)_6]Br_2$,[12] $[Au_{10}Se_4(dpppe)_4]Br_2$,[13] $[Au_{34}Se_{14}(tpep)_6(tpep^{Se})_2]Cl_6$ [tpep = $P(PCH_2CH_2PPh_3)_3$ and $tpep^{Se}$ = $Ph_2P(Se)CH_2CH_2P(PCH_2CH_2PPh_3)_2$].[14] Some have been found to have luminescent properties, for example $[Au_{10}Se_4(dpppe)_4]Br_2$,[13] $[Au_{10}(\mu_3\text{-}S)_4(PNP)_4][PF_6]_2$ [PNP = $Ph_2PN(Pr)PPh_2$][15] and $[Au_{12}Se_4(dppm)_6](PF_6)_4$ (dppm = $Ph_2PCH_2PPh_2$).[16]

In contrast to the well-known binary chalcogenide cluster complexes of group 11 metals,[17,18] ternary chalcogenide compounds containing metals of group 11 and 13 are rare and of special interest due to their promising properties. For example, the ternary compounds $CuInSe_2$ or $CuGaSe_2$ have important potential in thin film technology for solar cells.[19] Recently, some ternary cluster compounds, for example $[Cu_{11}In_{15}Se_{16}(SePh)_{24}(PPh_3)_4]$,[20] $[Cu_6In_8S_{13}Cl_4(PEt_3)_{12}]$[21] and $[Ag_6In_8S_{13}Cl_4(PPh_3)_{12}]$[22] have been synthesized. Ternary In-Au and Ga-Au chalcogenide cluster

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$$[Ph_3PAuCl] + 0.5\ t\text{BuSe}(SiMe_3) \xrightarrow[CH_2Cl_2]{25^\circ C} [Au_5Se_2(PPh_3)_4]Cl\ \mathbf{1}$$

$$Ph_2P(CH_2)_6PPh_2 + 2\ [Me_2SAuCl] + 0.5\ Se(SiMe_3)_2 \xrightarrow[CH_2Cl_2]{25^\circ C} [(Au_3Se)_2(Ph_2P(CH_2)_6PPh_2)_3]Cl_2\ \mathbf{2}$$

$$[(AuCl)_2Ph_2P(CH_2)_5PPh_2] + 2\ Se(SiMe_3)_2 + InCl_3 \xrightarrow[CH_2Cl_2/THF]{25^\circ C} [Au_{10}Se_4(Ph_2P(CH_2)_5PPh_2)_4]InCl_5\ \mathbf{3}$$

$$[(AuCl)_2Ph_2P(CH_2)_5PPh_2] + Se(SiMe_3)_2 + 2\ InCl_3 \xrightarrow[CH_2Cl_2/THF]{25^\circ C} [Au_4(SeInCl_3)_2(Ph2P(CH_2)_5PPh_2)_2]\ \mathbf{4}$$

$$[(AuCl)_2Ph_2P(CH_2)_6PPh_2] + Te(SiMe_3)_2 + GaCl_3 \xrightarrow[CH_2Cl_2/THF]{25^\circ C} [Au_4(TeGaCl_3)_2(Ph2P(CH_2)_6PPh_2)_2]\ \mathbf{5}$$

$$[(AuCl)_2Ph_2P(CH_2)_2PPh_2] + InCl_3 + Se(SiMe_3)_2 \xrightarrow[CH_2Cl_2/THF]{25^\circ C} [Au_8Se_4In(Ph_2P(CH_2)_2PPh_2)_4](InCl_4)_3\ \mathbf{6}$$

Scheme 1. Preparation reactions of compounds **1**−**6**

compounds have, to the best of our knowledge, not yet been prepared.

In this work we report the preparation and X-ray characterization of some Au-chalcogenide, In-Au and Ga-Au chalcogenide cluster compounds.

Results and Discussion

Compounds **1**−**6** were prepared as shown in Scheme 1. From the reaction of $[Ph_3PAuCl]$ with tBuSe($SiMe_3$) in CH_2Cl_2 at room temperature a pale yellow solution was obtained. Layering of the solution with *n*-pentane produced yellow crystals of $[Au_5Se_2(PPh_3)_4]Cl$ (**1**). Crystals of the compound $[(Au_3Se)_2(dpph)_3]Cl_2$ [**2**; dpph = $Ph_2P(CH_2)_6PPh_2$] were obtained from the reaction of the corresponding phosphane ligand with $[Me_2SAuCl]$ and $Se(SiMe_3)_2$ in CH_2Cl_2. The final yellow solution was layered with *n*-pentane and, after a few days, yellow crystals were isolated.

Reaction of the gold(I) complex $[(AuCl)_2dpppe]$ [dpppe = $Ph_2P(CH_2)_5PPh_2$][23] with two equivalents of $Se(SiMe_3)_2$ and one equivalent of $InCl_3$ in CH_2Cl_2/THF gave the formation of small yellow crystals of **3**. If the reaction is carried out using an Se:In molar ratio of 1:2, cubic crystals of **4** are formed. Colorless crystals of the isostructural cluster compound **5** were obtained from the reaction of $[(AuCl)_2dpph]$ with $Te(SiMe_3)_2$ and $GaCl_3$ in CH_2Cl_2/THF, and from the reaction of $Se(SiMe_3)_2$ with $[(AuCl)_2dppe]$ [dppe = $Ph_2P(CH_2)_2PPh_2$] and $InCl_3$ (1:1:1) in CH_2Cl_2/THF colorless needles of **6** could be isolated.

The structures of the six compounds were determined by single-crystal X-ray crystallography.

$[Au_5Se_2(PPh_3)_4]Cl$ (1)

Complex **1** crystallizes in the triclinic space group $P\bar{1}$ with four molecules per unit cell and two molecules per asymmetric unit (Figure 1). These are identical within the standard deviations therefore only one of them will be discussed. Two molecules of dichloromethane are present as lattice-bound solvent in the crystal.

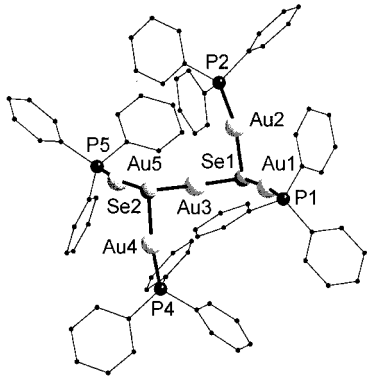

Figure 1. Crystal structure of the cation in **1**; selected distances (pm) and angles (°): Au1−Au2 305.94(9), Au2−Au3 299.56(10), Au3−Au4 304.87(10), Au3−Au5 327.04(11), Au1−Se1 245.17(12), Au2−Se1 245.58(14), Au3−Se1 246.43(12), Au3−Se2 245.75(12), Au4−Se2 243.48(14), Au5−Se2 243.83(12), Au1−P1 227.4(2), Au2−P2 226.6(3), Au4−P4 226.4(3), Au5−P5 226.6(3); Au1−Se1−Au2 77.13(4), Au1−Se1−Au3 78.64(4), Au2−Se1−Au3 75.01(4), Au4−Se2−Au5 79.89(4), Au4−Se2−Au3 77.09(4), Au5−Se2−Au3 83.82(4), Se2−Au3−Se1 177.87(4), P1−Au1−Se1 171.15(7), P2−Au2−Se1 167.65(7), P4−Au4−Se2 170.93(7), P5−Au5−Se2 170.27(7)

The Au_5Se_2 units in **1** are composed of two Au_3Se tetrahedra which share a corner; there are no bonds between the gold atoms inside the Au_5Se_2 unit (see Figure 1). The observed Au−Au distances are within the range 299.56(10)−327.04(11) pm. All selenium atoms act as μ_3-bridges above and below the plane defined by the gold atoms Au1 to Au5, with Au−Se−Au angles between 75.01(4)° and 83.82(4)°. Au−Se distances range from 243.48(14) to 246.43(12) pm, and are within the range of commonly observed distances in other Au−Se cluster complexes.[12−16]

The central gold atom has an almost linear coordination to two selenium atoms (Se1, Se2) with an angle of 177.87(4)°. The peripheral gold atoms also show a linear

coordination geometry. The Se−Au−P angles are between 167.65(7) and 171.15(7)°, and the Au−P distances range from 226.4(3) to 227.4(2) pm. An isostructural compound $[Au\{S(AuPPh_3)_2\}_2][(CH_3)_3SnCl_2]$, prepared using a different procedure, has already been reported by Jones et al.[24]

Au_5Se_2 units are known building blocks in other Au−Se cluster cations. Some examples are $[Au_{10}Se_4(dppm)_4]^{2+}$, $[Au_{10}Se_4(dpppe)_4]^{2+}$ and $[Au_{10}Se_4(depe)_4]^{2+}$ [depe = $Et_2P(CH_2)_2PEt_2$].[13,14] In these cases, the complex cations are formed by two Au_5Se_2 units bridged by the phosphane ligands. In the complexes containing dppm and depe, the phosphane carbon chains are shorter, resulting in the formation of more-distorted Au_3Se tetrahedra. In the case of dpppe, the phosphane bridge is longer, resulting in an almost regular Au_3Se tetrahedron. In **1**, however, where a monodentate phosphane ligand was used for the preparation, almost regular Au_3Se tetrahedra are observed as there is no distortion due to the formation of bridges (see above).

$[(Au_3Se)_2(dpph)_3]Cl_2$ (2)

Complex **2** crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell. One molecule of *n*-pentane and one of dichloromethane are present as lattice-bound solvent in the crystal. The bond lengths and angles are within the expected range.[12−16] The cation $[(Au_3Se)_2(dpph)_3]^{2+}$ is composed of two Au_3Se tetrahedra bridged by dpph ligands (see Figure 2).

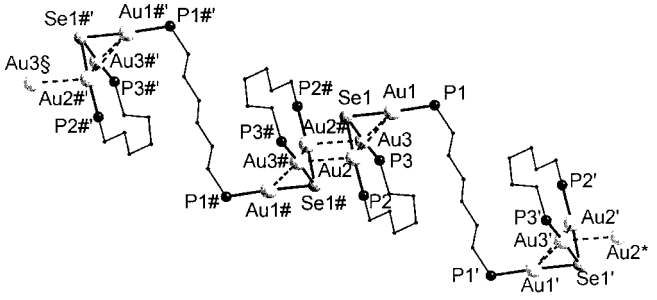

Figure 2. Crystal structure showing two cations in **2**; phenyl rings are omitted for clarity; symmetry transformations for the generation of equivalent atoms: $-x + 1, -y + 1, -z + 1$; selected distances (pm) and angles (°): Au1−Au2 326.19(10), Au1−Au3 301.66(8) Au2−Au3# 304.27(7), Au3−Au2# 304.27(7), Au1−Se1 242.47(10), Au2−Se1 245.38(11), Au3−Se1 247.35(11), Au1−P1 226.2(2), Au2−P2 227.6(3), Au3−P3 227.3(2); P1−Au1−Se1 175.10(7), P2−Au2−Se1 176.10(9), P3−Au3−Se1 177.58(7), Au1−Se1−Au3 76.02(3), Au2−Se1−Au3 82.58(3), Au3−Au2−Au1 55.18(2), Au3−Au1−Au2 62.23(2), Au3#−Au2−Au3 84.98(2), Au3#−Au2−Au1 124.55(1), Au1−Au3−Au2# 135.04(2), Au2#−Au3−Au2 95.02(2)

Selenium atoms act as μ_3-bridges to three gold atoms, building slightly distorted Au_3Se tetrahedra. The Se−Au distances are between 242.47(10) and 247.35(11) pm, and the Au−Se−Au angles range from 76.02(3) to 82.58(3)°.

All gold atoms exhibit an almost linear coordination geometry and are coordinated by a phosphorus and a selenium atom. The P−Au−Se angles are within the range 175.10(7)−177.58(7)° and the Au−P distances are between 226.2(2) and 227.6(3) pm.

Within the Au_3Se tetrahedra, the non-bonding Au−Au distances range from 301.66(8) to 326.19(10) pm. The intermolecular Au−Au distances between two Au_3Se units are relatively short, with a value of 304.27(7) pm. This shows that the short interactions, probably due to the "aurophilic attraction", lead to the formation of a polymeric chain of cations in the solid state.[25] Other examples of gold cluster complexes with secondary Au−Au bonding and solid-state polymers can be found in the literature.[14,26,27]

$[Au_{10}Se_4(dpppe)_4]InCl_5$ (3)

Complex **3** crystallizes in the monoclinic space group $C2/c$ with four molecules per unit cell. The Au_5Se_2 units within the cation of **3** are bridged by dpppe ligands (see Figure 3). The Au−Au distances between the Au_5Se_2 units are 312.3(2) and 333.2(2) pm. The Au_5Se_2 units consist of two Au_3Se tetrahedra sharing a corner (see above). In these tetrahedra, the selenium atoms are acting as μ_3-bridges to three gold atoms, being placed above and below the plane formed by the gold atoms (Au1−Au5 and symmetry equivalents) with Au−Se−Au angles of 74.02(9)° and 82.61(8)°. The Au−Se distances range between 245.2(3) and 247.4(3) pm (Figure 3).

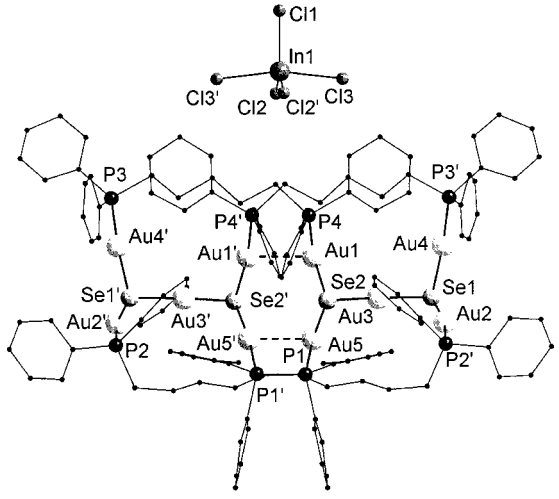

Figure 3. Crystal structure of **3**; symmetry transformations for the generation of equivalent atoms: $-x + 1, y, -z + 1/2$; selected distances (pm) and angles (°): Au1−Se2 244.9(3), Au1−Au3 302.32(16), Au1−Au1′ 312.3(2), Au1−Au5 323.47(19), Au2−Se1 247.4(3), Au2−Au3 294.72(14), Au3−Se1 242.2(3), Au3−Se2 242.7(3), Au3−Au5 306.18(15), Au3−Au4 328.29(16), Au4−P3′ 225.6(8), Au4−Se1 244.5(3), Au4−Au2′ 314.27(18), Au5−P1 226.4(7), Au5−Se2 245.2(3), Au5−Au5′ 333.2(2); P4−Au1−Se2 171.9(2), P4−Au1−Au1′ 108.9(2), Se2−Au1−Au1′ 78.70(7), Au3−Au1−Au1′ 130.03(4), P4−Au1−Au5 132.0(2), Se2−Au1−Au5 48.73(7), Au3−Au1−Au5 58.47(4), Au3−Au2−Au4 64.92(4), Se1−Au3−Se2 175.17(9), Au2−Au3−Au1 160.88(5), P1−Au5−Au1 131.6(2), Se2−Au5−Au1 48.66(8), Au3−Au5−Au1 57.31(4), Au3−Se1−Au2 74.02(9), Au1−Se2−Au5 82.61(8)

A distorted linear coordination geometry is found for the central gold atom (Au3 and symmetry equivalents), bonded to two selenium atoms with an Se−Au−Se angle of

175.17(9)° and Au−Se distances of 242.2(3) and 242.7(3) pm. All non-central gold atoms also display a linear geometry and are coordinated to a selenium and a phosphorus atom, with Au−P bond lengths between 225.6(8) and 227.7(7) pm and P−Au−Se angles ranging from 169.06(8)° to 175.28(19)°.

An isostructural cation was found in the complex $[Au_{10}Se_4(dpppe)_4]Br_2$.[13,14] However, the Au−Au distances between the Au_5Se_2 units in **3** [312.3(2) and 333.2(2) pm] are longer than those in $[Au_{10}Se_4(dpppe)_4]Br_2$ [300.2(3) and 326.0(4) pm]. The Au−Au distances within the Au_5Se_2 units are shorter in **3** [range from 294.7(30) to 328.3(8) pm] than the ones found in the isostructural cluster $[Au_{10}Se_4(dpppe)_4]Br_2$ [298.0(3) to 334.1(3) pm].

$[Au_2(SeInCl_3)dpppe]_2$ (4)

Cluster **4** crystallizes in the triclinic space group $P\bar{1}$ with two molecules per unit cell. In **4** two gold atoms (Au1, Au2′) are coordinated to a selenium atom (Se1) and two phosphorous atoms (P1′, P2) of the bidentate phosphane ligand (see Figure 4), leading to a distorted linear coordination at gold (P−Au−Se from 173.59(4)° to 178.39(4)°]. The μ_3-Se^{2-} ligand is also coordinated to an In atom (In1) of an $InCl_3$ molecule. In the crystal lattice, two $[Au_2(SeInCl_3)dpppe]$ units form a dimer by inversion symmetry, with a planar square of gold atoms (Au1′−Au2−Au1 83.94(3) and Au2′−Au1−Au2 96.06(3)°]. The Au−Au distances within the Au_2Se units [Au1−Au2′ 320.88(9) pm] are slightly longer than the ones found between both Au_2Se-units [(Au1−Au2 311.67(10) pm]. Related Au_4 arrangements have been observed before in the ionic complex $[(PPh_3Au)_2(SCH_2Ph)](NO_3)$, with values of 307.7 and 319.4 pm for the non-bridged Au−Au distances and distances of 307.7 and 314.2 pm for the bridged ones,[28] and also in $[(PPh_3Au)_2(SC_6H_4CH_3)_2](PF_6)$, which has Au−Au distances of 317.3 pm for the free edges and 315.2 pm for the sulfur-bridged ones.[28] In analogy to these sulfur-bridged complexes, the selenium atoms in **4** are placed above and below the plane of the four-membered ring of gold atoms (Au1−Au2−Au1′−Au2′) with an Au1′−Se1′−Au2 angle of 78.83(3)°. With the $InCl_3$ directly bonded to the selenium atom, compound **4** represents the first step in the build-up of ternary gold indium chalcogenide complexes.

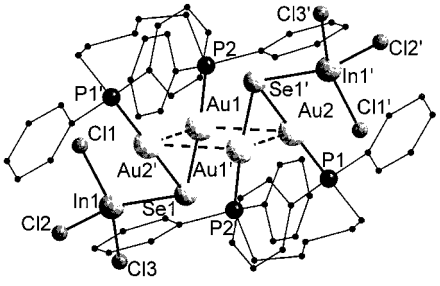

Figure 4. Crystal structure of **4**; symmetry transformations for the generation of equivalent atoms: $-x + 2, -y + 1, -z$; selected distances (pm) and angles (°): In1−Se1 254.74(11), Se1−Au1 244.60(8), Se1−Au2′ 244.95(8), Au1−P2 226.07(16), Au1−Au2 311.67(10), Au1−Au2′ 320.88(9), Au2−Se1′ 244.95(8); Au1−Se1−Au2′ 81.91(3), Au1−Se1−In1 93.95(4), P2−Au1−Se1 173.59(4), P2−Au1−Au2 100.64(5), Se1−Au1−Au2 85.61(4), Se1−Au1−Au2′ 49.09(2), Au2−Au1−Au2′ 96.06(3), P1−Au2−Se1′ 178.39(4), P1−Au2−Au1′ 130.20(4), Au1−Au2−Au1′ 83.94(3)

$[Au_2(TeGaCl_3)dpph]_2$ (5)

Compound **5** crystallizes in the monoclinic space group $P2_1/c$ with two molecules per unit cell. This cluster shows the same structural motif as **4**, with a central arrangement of four gold atoms, bridged by tellurium atoms, which are also coordinated to a $GaCl_3$ molecule (see Figure 5). A distorted linear geometry at each of the gold atoms is observed, with P−Au−Te angles ranging from 171.45(4)° to 176.42(4)°. The μ_3-Te^{2-} ligands are also coordinated to a Ga atom (Ga1, Ga1′) of a $GaCl_3$ molecule. The Au−Au distances are Au1−Au2 305.03(9) and Au2−Au1′ 340.8(1) pm with Au1−Au2−Au1′ and Au2′−Au1′−Au2 angles of 92.10(1)° and 87.90(1)°, respectively.

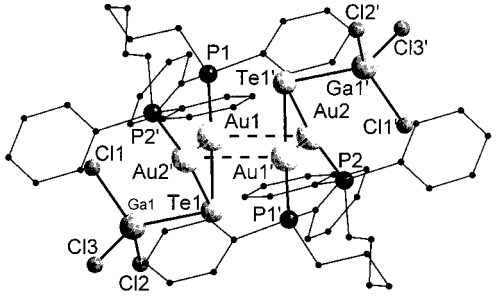

Figure 5. Molecular structure **5**; symmetry transformations for the generation of equivalent atoms: $-x + 1, -y + 1, -z$; selected distances (pm) and angles (°): Ga1−Te1 258.92(12), Te1−Au1 259.43(6), Te1−Au2′ 260.69(6), Au1−Au2 305.03(9), Au2−P2 228.66(14), Au2−Te1′ 260.69(6); Ga1−Te1−Au1 93.96(3), Ga1−Te1−Au2′ 88.89(2), Au1−Te1−Au2′ 81.87(2), P1−Au1−Te1 171.45(4), P1−Au1−Au2 107.21(4), Te1−Au1−Au2 81.34(2), P2−Au2−Te1′ 176.42(4), P2−Au2−Au1 98.32(4), Te1′−Au2−Au1 84.145(19)

$[Au_8Se_4In(dppe)_4](InCl_4)_3$ (6)

Compound **6** crystallizes in the monoclinic space group $C2/c$ (Figure 6). The hydrogen atoms were not calculated for this crystal structure. One molecule of dichloromethane is present as lattice-bound solvent in the crystal. The cation consists of a central indium atom (In1) enclosed within a distorted tetrahedron of four selenium atoms (Se1, Se2, Se1′, Se2′). The In−Se distances range from 258.5(3) to 259.5(3) pm with Se−In−Se angles ranging between 107.10(14)° and 110.85(8)°. Each of these μ_3-Se atoms coordinates to two Au atoms (Au1−Au4 and symmetry equivalent atoms) forming four Au_2Se units with Au−Se bond lengths ranging from 244.7(3) to 244.8(3) pm and Au−Se−Au angles within the range 77.12(7)−78.29(8)°. All the bidentate phosphane ligands (P1−P4 and symmetry equivalent atoms) bridge two Au atoms belonging to two different Au_2Se units, resulting in a distorted linear coordination environment for all Au atoms. Each gold atom is

coordinated by one Se and one P atom [Se−Au−P: 167.52(9)−177.75(18)°; Au−P: 226.7(6)−228.2(7) pm]. A distorted eight-membered ring in the boat conformation is formed by the Au atoms, with Au−Au distances ranging from 301.41(15) (Au3−Au4) to 309.04(17) pm (Au4−Au1′). A similar Au−Au distance of 305.1(1) pm is found in $[(PPh_3Au)_2Se]$.[29] The structure of the cation in **3** can be rationalized as an In atom tetrahedrally coordinated by four $dppeAu_2Se$ units, where phosphane ligands connect neighbouring Au_2Se units. Similar Au_2Se units have been stabilized and crystallized before by the use of either monodentate phosphane ligands like PPh_3 in monomeric $[(PPh_3Au)_2Se]$[21] or bidentate phosphanes, such as $Ph_2PC_6H_4PPh_2$ (dppbe), in the polymeric $[Au_2Se(dppbe)]_\infty$.[14]

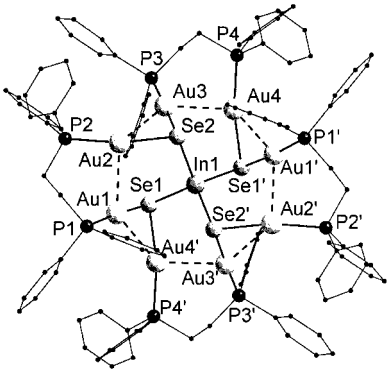

Figure 6. Molecular structure of the cation in **6**; symmetry transformations for the generation of equivalent atoms: $-x + 1$, y, $-z + 0.5$; selected distances (pm) and angles (°): Au1−P1 228.2(7), Au1−Se1 244.8(3), Au1−Au4′ 309.04(17), Au2−P2 226.7(6), Au2−Se2 244.7(3), Au2−Au3 305.06(15), Au3−P3 227.9(7), Au3−Se2 244.7(3), Au3−Au4 301.41(15), Au4−P4 227.4(8), In1−Se1 258.5(3), In1−Se2 259.5(3); P1−Au1−Se1 175.7(2), P1−Au1−Au2 92.62(19), Se1−Au1−Au2 91.61(7), P1−Au1−Au4′ 125.01(19), Se1−Au1−Au4′ 50.85(7) Au2−Au1−Au4′ 137.92(5), P2−Au2−Se2 167.52(19), P2−Au2−Au1 92.49(18), Se1−In1−Se2 110.85(8), Se2−In1−Se2′ 107.10(14), Au4′−Se1−Au1 78.29(8), Au4′−Se1−In1 97.73(9)

Experimental Section

All experiments with chalcogenide ligands were carried out under a dry nitrogen atmosphere. THF was dried over sodium-benzophenone, and CH_2Cl_2 over P_2O_5 followed by distillation of the solvents under nitrogen. Anhydrous $InCl_3$ was obtained from Aldrich.

Preparation of $[Ph_3PAuCl]$: A solution of [Au(thiodiglycol)Cl][30] (0.51 g Au, 2.59 mmol) in MeOH (5 mL) was added to a solution of PPh_3 (0.68 g, 2.59 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred for 2 hours. The volume was reduced to a few milliliters and water (50 mL) was added to produce a white solid. The solid was filtered off, washed with water and dried in vacuo. Yield 85% (1.09 g).

Preparation of $[(AuCl)_2(phosphane)]$:[23,26] A solution of [Au(thiodiglycol)Cl][30] (0.40 g Au, 2.04 mmol) in MeOH (5 mL) was added to a solution of phosphane (phosphane = dppe, dpppe, dppph; 1.02 mmol) in CH_2Cl_2 (10 mL). The final mixture was stirred for 24 hours. The solvents were removed in vacuo and water (50 mL) added. The white precipitate was filtered off, washed with water and Et_2O, and dried in vacuo. Yield 70−85% (dppe 0.62 g, dpppe 0.74 g, dpph 0.80 g).

Preparation of $[Au_5Se_2(PPh_3)_4]Cl$ (1): tBuSe($SiMe_3$) (0.02 mL, 0.022 g, 0.107 mmol) was added at room temperature to a solution of $[Ph_3PAuCl]$ (0.10 g, 0.21 mmol) in CH_2Cl_2 (10 mL),. The final mixture was stirred for 14 hours to give a light yellow solution. This solution was layered with n-pentane and, after a few days, light yellow crystals of **1** had formed (see Table 1). Yield 60% (0.06 g). $C_{74}H_{48}Au_5Cl_5P_4Se_2$ (2396.6): calcd. C 37.05, H 2.67; found C 37.17, H 2.71.

Preparation of $[(Au_3Se)_2(dpph)_3]Cl_2$ (2): A solution of $[Me_2SAuCl]$ (19) (0.1 g, 0.35 mmol) in CH_2Cl_2 (5 mL) was added to a solution of dpph (0.08 g, 0.18 mmol) in CH_2Cl_2 (5 mL). The solutions were stirred for 30 minutes and $Se(SiMe_3)_2$ (0.04 mL, 0.039 g, 0.18 mmol) was added to give a yellow solution. This solution was layered with n-pentane and, a few days later, crystals of **2** had formed (see Table 1). Yield 40% (0.07 g). $C_{102}H_{96}Au_6Cl_2P_6Se_2$ (2916.9): calcd. C 41.96, H 3.29; found C 41.82, H 3.25.

Preparation of $[Au_{10}Se_4(dpppe)_4]InCl_5$ (3): $Se(SiMe_3)_2$ (0.10 mL, 0.44 mmol) was added to a solution of $[(AuCl)_2dpppe]$ (0.20 g, 0.22 mmol) in CH_2Cl_2 (25 mL) to give a yellow solution. A solution of $InCl_3$ (0.05 g, 0.22 mmol) in THF (2 mL) was added and a yellow precipitate was formed. The solid was filtered off and a few days later small yellow crystals of **3** were isolated (see Table 1). Yield 10% (0.02 g). $C_{116}H_{120}Au_{10}Cl_5InP_8Se_4$ (4339.6): calcd. C 32.11, H 2.79; found C 29.96, H 2.78.

Preparation of $[Au_4(SeInCl_3)_2(dpppe)_2]$ (4): $Se(SiMe_3)_2$ (0.05 mL, 0.22 mmol) was added to a solution of $[(AuCl)_2dpppe]$ (0.20 g, 0.22 mmol) in CH_2Cl_2 (25 mL). The solution became yellow. After five days $InCl_3$ (0.10 g, 0.44 mmol) in THF (2 mL) was added to the former solution, to produce colourless cubic crystals of **4** (see Table 1). Yield 65% (0.16 g). $C_{58}H_{60}Au_4Cl_6In_2P_4Se_2$ (2269.2): calcd. C 30.70, H 2.67; found C 29.56, H 2.48.

Preparation of $[Au_4(TeGaCl_3)_2(dpph)_2]$ (5): $Te(SiMe_3)_2$ (0.05 mL, 0.21 mmol) was added to a solution of $[(AuCl)_2dpph]$ (0.19 g, 0.21 mmol) in CH_2Cl_2 (25 mL). A solution of $GaCl_3$ (0.04 g, 0.22 mmol) in THF (2 mL) was then added to the resultant dark brown mixture After a few days colourless crystals of **5** had formed (see Table 1). Yield 40% (0.10 g). $C_{60}H_{64}Au_4Cl_6Ga_2P_4Te_2$ (2304.3): calcd. C 31.27, H 2.80; found C 30.48, H 2.75.

Preparation of $[Au_8Se_4In(dppe)_4](InCl_4)_3$ (6): A solution of $InCl_3$ (0.03 g, 0.12 mmol) in THF (2 mL) was added to a suspension of $[(AuCl)_2dppe]$ (0.10 g, 0.12 mmol) in CH_2Cl_2 (25 mL). $Se(SiMe_3)_2$ (0.03 mL, 0.12 mmol) was added. The mixture was stirred for 2 hours. After 2 days colourless needles of **6** started to grow in the flask (see Table 1). Complete crystallization was achieved by reducing the volume in vacuo. Yield 85% (0.09 g). $C_{104}H_{96}Au_8Cl_{12}In_4P_8Se_4$ (4370.0): calcd. C 28.58, H 2.21; found C 28.15, H 2.21.

X-ray Analyses: STOE-IPDS II (Mo-K_α); data collection and refinement (SHELXTL-97).[31] CCDC-214542 to -214547 (for **1**−**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystallographic data for compounds **1**−**6**

	1·2CH_2Cl_2	**2**·CH_2Cl_2·C_5H_{12}	**3**	**4**	**5**	**6**·CH_2Cl_2
Formula	$C_{148}H_{128}Au_{10}Cl_{10}P_8Se_4$	$C_{204}H_{192}Au_{12}Cl_4P_{12}Se_4$	$C_{116}H_{120}Au_{10}Cl_5InP_8Se_4$	$C_{29}H_{30}Au_2Cl_3InP_2Se$	$C_{60}H_{64}Au_4Cl_6Ga_2P_4Te_2$	$C_{105}H_{98}Au_8Cl_{16}In_4P_8Se_4$
Space group	$P\bar{1}$	$P2_1/c$	$C2/c$	$P\bar{1}$	$P2_1/c$	$C2/c$
Z	2	4	4	2	2	4
Temperature (K)	203(2)	203(2)	150(2)	190(2)	180(2)	180(2)
a (pm)	1750.4(4)	1446.8(3)	1870.3(4)	1020.4(2)	1298.7(3)	3660.2(7)
b (pm)	2014.7(4)	1475.9(3)	2169.5(4)	1224.9(2)	1463.6(3)	1102.8(2)
c (pm)	2027.5(4)	2322.9(5)	3112.5(6)	1350.5(3)	1856.9(4)	3733.0(8)
α (°)	89.99(3)	90	90	73.29(3)	90	90
β (°)	89.98(3)	94.76(3)	97.87(3)	84.94(3)	105.39(3)	116.01(3)
γ (°)	86.57(3)	90	90	78.19(3)	90	90
Volume (10^6 pm^3)	7140(1)	4943.1(17)	12510(4)	1581.7(5)	3403.2(12)	13542(5)
Density (calcd.) (g/cm^3)	2.231	1.961	2.304	2.380	2.249	2.185
Theta range for data collection $2\theta_{max}$ (°)	1.54 to 28.33	1.97 to 28.29	1.53 to 27.16	3.63 to 31.69	1.63 to 24.92	1.24 to 23.97
Refl. collected	53765	30257	15551	11852	16894	26799
Ind. reflections	32153	12146	9086	6823	5895	10370
R_{int}	0.0979	0.1409	0.1085	0.0519	0.0635	0.0621
Refl. with $F_o > 4\sigma(F_o)$	14113	10698	5226	6627	4993	8336
Refined parameters	981	490	650	343	352	473
R_1	0.0595	0.0848	0.0755	0.0495	0.0305	0.0841
wR_2	0.1750	0.2172	0.1806	0.1456	0.0791	0.1939
Goodness of fit	1.040	1.042	1.026	1.298	0.655	1.230

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