Gold Complexes with Selenium Ligands. Part 7.[1] Synthesis and Crystal Structures of Oligonuclear Gold(I)–Selenolate Complexes†

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Cationic and neutral oligonuclear organophosphinegold(I) complexes with organic selenolate ligands $\mathrm{SeR^-}$ [R = Ph, $\mathrm{CH_2Ph}$, $\mathrm{C_6H_4NH_2}$-4, $\mathrm{C_6H_4Cl}$-4 or $\mathrm{C_{10}H_7}$ (naphthyl)] have been prepared and characterized by spectroscopic methods. Additionally, X-ray crystal structure analyses have been performed for $[\mathrm{(AuPPh_3)_2(SeCH_2Ph)}]\mathrm{SbF_6}$, the mixed cationic-neutral complex $[\mathrm{(AuPPh_3)_2(SeC_{10}H_7)}]\mathrm{SbF_6}\cdot[\mathrm{Au(PPh_3)(SeC_{10}H_7)}]$ and for $[\mathrm{(AuSePh)_2(dppe)}]$ [dppe = 1,2-bis(diphenylphosphino)ethane]. The Au–Se bond lengths lie in the range 2.412 Å (neutral complexes) to 2.465 Å (cationic complexes). All crystal structures show distortions of the co-ordination geometry at selenium and reveal short Au ··· Au contacts. The molecular structure of $[\mathrm{(AuPPh_3)_2(SeCH_2Ph)}]\mathrm{SbF_6}$ represents the first example of a cationic alkylselenolate–gold complex. The complex $[\mathrm{(AuPPh_3)_2(SeC_{10}H_7)}]\mathrm{SbF_6}\cdot[\mathrm{Au(PPh_3)(SeC_{10}H_7)}]$ exhibits an unexpected structure: the cationic and the corresponding neutral selenolate complex are linked by intermolecular Au ··· Au interactions, thus forming a trinuclear selenolate complex. The complex $[\mathrm{(AuSePh)_2(dppe)}]$ is the first structurally characterized gold–organoselenolate complex with a bridging diphosphine ligand.

The co-ordination chemistry of gold(I) is of current interest because certain gold(I) complexes, especially thiolates, are found to be potential drugs in the treatment of rheumatoid arthritis.[2,3] In this connection, the monomeric, lipid-soluble gold(I)–thioglucosate derivative Auranofin [2,3,4,6-tetra-acetato-(1-thio-β-D-glucopyranosato-*S*)(triethylphosphine)-gold(I)] plays an important role.[4] However, the toxicity of the thiolates is a serious disadvantage. Recent research has suggested that heavy-metal toxicity can be reduced if selenium derivatives are employed.[5]

Several crystal structures of (phosphine)gold–selenium complexes and selenide/polyselenide complexes have been reported, but, in order to understand the biochemical mechanism of gold–selenium drugs, more information about the nature of the gold–selenium bond is needed.[6–8] Here we report the synthesis and three crystal structures of new gold–selenolate complexes, namely $[\mathrm{(AuPPh_3)_2(SeCH_2Ph)}]\mathrm{SbF_6}$ **1**, $[\mathrm{(AuPPh_3)_2(SeC_{10}H_7)}]\mathrm{SbF_6}\cdot[\mathrm{Au(PPh_3)(SeC_{10}H_7)}]$ **6** ($\mathrm{C_{10}H_7}$ = naphthyl) and $[\mathrm{(AuSePh)_2(dppe)}]$ **7** [dppe = 1,2-bis(diphenylphosphino)-ethane]. We recently reported the synthesis of gold–phenyl-selenolate complexes and the crystal structures of $[\mathrm{Au(PPh_3)(SePh)}]$ and $[\mathrm{(AuPPh_3)_2(SePh)}]\mathrm{SbF_6}$ as a short communication.[6a]

Results and Discussion

Cationic gold(I)–selenolate complexes can be easily prepared according to equation (1).

$$[\mathrm{AuCl(PR^1R^2R^3)}] + \mathrm{Se_2R^4{}_2} + 2\mathrm{AgSbF_6} \longrightarrow \underset{\mathbf{1-6}}{[\mathrm{(AuPR^1R^2R^3)_2(SeR^4)}]\mathrm{SbF_6}} + 2\mathrm{AgCl} + \text{other products} \quad (1)$$

Complex	R^1	R^2	R^3	R^4
1	Ph	Ph	Ph	$\mathrm{CH_2Ph}$
2	Ph	Ph	Ph	$\mathrm{C_6H_4NH_2}$-4
3	Ph	Ph	Ph	$\mathrm{C_6H_4Cl}$-4
4	Me	Ph	Ph	Ph
5	Me	Me	Ph	Ph
6*	Ph	Ph	Ph	$\mathrm{C_{10}H_7}$

* Complex **6** also incorporates $[\mathrm{Au(PPh_3)(SeC_{10}H_7)}]$.

This reaction depends on the organic group bonded to selenium. Aromatic groups give high yields, whereas alkyl groups usually cause decomposition of the reaction mixture. Complex **1**, with a benzyl group bonded at selenium, is the first characterized example of a gold–alkylselenolate complex. With naphthyl as substituent at selenium, a 1 : 1 adduct of the cationic complex $[\mathrm{(AuPPh_3)_2(SeC_{10}H_7)}]\mathrm{SbF_6}$ with the corresponding neutral complex $[\mathrm{Au(PPh_3)(SeC_{10}H_7)}]$ is formed. The complexes **1**–**5** are soluble in $\mathrm{CH_2Cl_2}$, $\mathrm{CHCl_3}$ and acetone, but the solutions are light-sensitive and decompose within hours. Freshly prepared, the adduct **6** is easily soluble in $\mathrm{CH_2Cl_2}$ and $\mathrm{CHCl_3}$ but it denatures even at −20 °C and under exclusion of light and oxygen. The denatured complex is moderately soluble in dimethyl sulfoxide but the solution decomposes rapidly. It was therefore not possible to record $^{77}\mathrm{Se}$ NMR spectra, which require long measuring times and appreciable concentrations.

The neutral phenylselenolate $[\mathrm{(AuSePh)_2(dppe)}]$ **7** is prepared similarly to the corresponding bis(diphenylphosphino)-methane (dppm) complex [equation (2)].

$$[\mathrm{(AuCl)_2(dppe)}] + 2\mathrm{PhSeSiMe_3} \longrightarrow [\mathrm{(AuSePh)_2(dppe)}] + 2\mathrm{SiMe_3Cl} \quad (2)$$

Complex **7** is soluble in halogenoalkanes and many other polar solvents such as acetone, dimethylformamide (dmf) and

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† *Supplementary data available:* Further details of the structure determinations (complete bond lengths and angles, H atom coordinates, structure factors, thermal parameters) have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany. Any request for this material should quote a full literature citation and the reference numbers CSD-57722 (**1**), CSD-400344 (**6**) and CSD-400345 (**7**).

Table 1 Analytical[a] and physical data for compounds **1**–**7**

Complex	M.p.[b]/°C	Colour	Yield (%)	M^{+c}	Analysis (%) C	H
1 $[(AuPPh_3)_2(SeCH_2Ph)]SbF_6$	110	Pale yellow	43	1088	38.5 (38.9)	2.9 (2.8)
2 $[(AuPPh_3)_2(SeC_6H_4NH_2\text{-}4)]SbF_6$	167	Yellow	78	1089	37.5 (38.1)	2.6 (2.7)[d]
3 $[(AuPPh_3)_2(SeC_6H_4Cl\text{-}4)]SbF_6$	153	Pale yellow	82	1109	37.7 (37.5)	2.5 (2.6)
4 $[(AuPMePh_2)_2(SePh)]SbF_6$	137	Pale yellow	79	950	32.3 (32.4)	2.6 (2.6)
5 $[(AuPMe_2Ph)_2(SePh)]SbF_6$	137	Yellow	86	826	24.7 (24.9)	2.4 (2.6)
6 $[(AuPPh_3)_2(SeC_{10}H_7)]SbF_6\cdot[Au(PPh_3)(SeC_{10}H_7)]$	150	Yellow	43[e]	1125	43.8 (43.9)	2.9 (2.9)[f]
7 $[(AuSePh)_2(dppe)]$	153	White	83	950[g]	41.5 (41.3)	3.2 (3.1)[h]

[a] Required values are given in parentheses. [b] With decomposition. [c] Values for the cations, other fragments also detected. [d] N, 1.4 (1.1)%. [e] Calculated on selenium. [f] P, 4.5 (4.6); Se, 7.6 (7.8)%. [g] Molecular ion peak. [h] P, 5.6 (5.6); Se, 14.4 (14.3)%.

Table 2 NMR data for compounds **1**–**7**

Complex	Solvent	NMR ^1H	$^{31}P\text{-}\{H\}$
1	$CDCl_3$	4.49 (2 H, s, CH_2), 7.27–7.53 (35 H, m, Ph)	35.6 (s)
2	$(CD_3)_2CO$	7.70–7.91 (4 H, m, $C_6H_4NH_2$), 7.98–8.23 (30 H, m, Ph)	31.1 (s)
3	$CDCl_3$	—	45.0 (s)
4	$(CD_3)_2CO$	2.11 [3 H, d, ^2J(PH) 10.6 Hz, CH_3], 7.21–7.65 (25 H, m, Ph)	31.7 (s)[a]
5	CD_3OD	2.15 [6 H, d, ^2J(PH) 11 Hz, CH_3], 7.22–7.78 (15 H, m, Ph)	14.3 (s)
6	CD_2Cl_2	—	36.8 (br s)[b] 34.5 (s), 43.7 (s)[c]
7	$CDCl_3$	—	35.8 (s)[d]

[a] Recorded in $CDCl_3$. [b] $T = 25$ °C. [c] $T = -65$ °C. [d] ^{77}Se NMR: δ −181.5 (br s), 50 mg in $CDCl_3$ (0.6 cm^3), no ^{31}P satellites detected.

MeCN. In contrast to the cationic complexes **1**–**6**, the solutions are stable when exposed to light and oxygen.

For analytical and physical data of the new complexes see Table 1.

Mass spectra show the molecule cation peaks for the new complexes with low intensities. Other gold- and selenium-containing fragments detected were $[(AuPPh_3)_2SeSe(AuPPh_3)]^+$ and $[(AuPPh_3)_2Se]^+$ for complex **1** and $[(AuPPh_3)_2Se]^+$ for complex **6**. The other major ions common to complexes **2**–**5** were $[Au(PPh_3)_2]^+$, $[AuPPh_3]^+$ and $[AuPMePh_2]^+$. For the neutral complex **7**, apart from the molecule ion peak with very low intensity, the major fragments were $[Ph_2PPPh_2]^+$, dppe$^+$, Se(dppe)$^+$ and Se_2(dppe)$^+$.

The NMR data of the new complexes are listed in Table 2. The values for the ^{31}P chemical shifts seem to be typical for cationic gold-selenolates and neutral diphosphine gold–selenolates, whereby substitution of a chlorine by an organic selenolate group has no great influence on the electronic situation at phosphorus. The ^{31}P spectrum of **6** shows a singlet of δ 36.8 at room temperature, which suggests fast exchange reactions of a $AuPPh_3$ group between the cation and the neutral component. Further evidence of fast $AuPPh_3$ group migration is afforded by the splitting of the singlet at 0 °C (δ 34.5 for the neutral part, δ 43.7 for the cationic part). This unusually high temperature for singlet splitting in a dynamic exchange process indicates that the migrating group is sterically demanding.

The molecular structures of $[(AuPPh_3)_2(SeCH_2Ph)]SbF_6$ **1**, $[(AuPPh_3)_2(SeC_{10}H_7)]SbF_6\cdot[Au(PPh_3)(SeC_{10}H_7)]$ **6** and $((AuSe\text{-}Ph)_2(dppe)]$ **7** have been determined and are shown in Figs. 1–4; selected bond lengths and angles are listed in Tables 3–5.

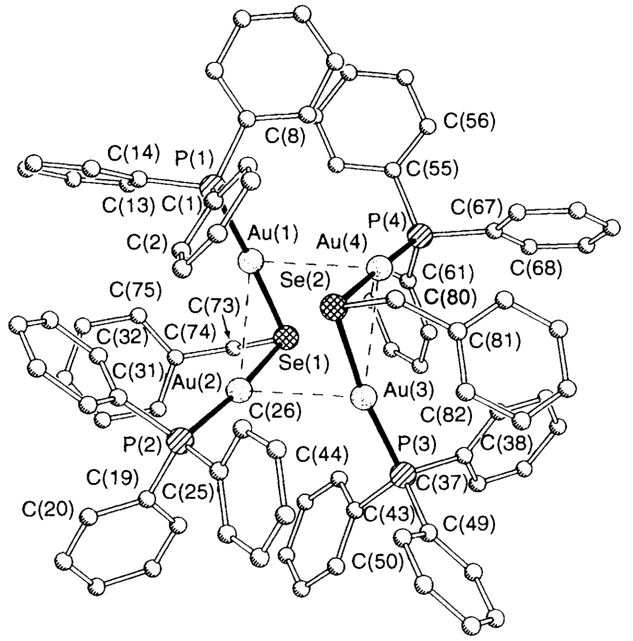

Fig. 1 The dimeric cation of compound **1** in the crystal. Radii are arbitrary; H atoms are omitted for clarity

The benzylselenolate complex **1** crystallizes with two independent formula units and five $CDCl_3$ molecules in the asymmetric unit (Fig. 1). The molecular structure is closely related to those of the corresponding phenylselenolate complex and the benzylthiolate complex $[(AuPPh_3)_2(SCH_2Ph)]NO_3$, which were reported recently.[6a,9] The Au–Se bond lengths are 2.440(3) and 2.443(3) Å respectively and therefore similar to those observed in the phenylselenolate and in the $[(AuPPh_3)_3Se]^+$ cation (average of six bonds 2.444 Å), but 0.02 Å shorter than in the $[(AuPPh_3)_2(SeC_6F_4Cl\text{-}4)]^+$ cation.[6b,d] There are short intramolecular Au···Au contacts of 3.149(2) and 3.203(2) Å, with corresponding Au···Se···Au angles of 80.3(1) and 82.1(1)° {in $[(AuPPh_3)_2(SeC_6F_4Cl\text{-}4)]^+$ 76.0(1)°}, respectively. Two cations are linked by short intermolecular Au···Au interactions of Au(1)···Au(4) 3.071(2) Å and Au(2)···Au(3) 3.083(2) Å. These intermolecular contacts are shorter than those in the phenylselenolate (3.112 Å) and in the (*p*-chlorotetrafluorophenyl)selenolate (3.746 Å). Such Au···Au contacts are often observed in gold(I) complexes and they have a significant influence on the molecular structures.[10–13] In the case of **1**, a loose cation dimer is formed. The Au···Au···Au angles of the resulting Au_4-squares (average deviation from plane: 0.13 Å) are close to 90°. Two of the four gold atoms [Au(1), Au(4)] show slight deviations from linear co-ordination [171.6, 172.0(2)°]. The Au–P bond lengths are in the range 2.267(8)–2.290(8) Å. These values are typical of (phosphine)gold(I) complexes.[10]

Table 3 Selected bond lengths (Å) and angles (°) for compound **1**

Au(1)–Au(2)	3.149(2)	Au(1)–Au(4)	3.071(2)
Au(1)–Se(1)	2.444(3)	Au(1)–P(1)	2.283(7)
Au(2)–Au(3)	3.083(2)	Au(2)–Se(1)	2.443(3)
Au(2)–P(2)	2.268(7)	Au(3)–Au(4)	3.203(2)
Au(3)–Se(2)	2.440(3)	Au(3)–P(3)	2.267(8)
Au(4)–Se(2)	2.439(3)	Au(4)–P(4)	2.290(7)
Se(1)–C(73)	2.002(25)	Se(2)–C(80)	1.968(27)
P(1)–C(1)	1.815(17)	P(1)–C(7)	1.817(17)
P(1)–C(13)	1.783(15)	P(2)–C(19)	1.765(21)
P(2)–C(25)	1.841(20)	P(2)–C(31)	1.790(17)
P(3)–C(37)	1.792(16)	P(3)–C(43)	1.825(21)
P(3)–C(49)	1.817(21)	P(4)–C(55)	1.847(19)
P(4)–C(61)	1.828(21)	P(4)–C(67)	1.777(15)
C(73)–C(74)	1.504(29)	C(80)–C(81)	1.529(29)
Au(2)–Au(1)–Au(4)	89.3(1)	Au(2)–Au(1)–Se(1)	49.9(1)
Au(4)–Au(1)–Se(1)	76.0(1)	Au(2)–Au(1)–P(1)	128.3(2)
Au(4)–Au(1)–P(1)	105.7(2)	Se(1)–Au(1)–P(1)	177.7(2)
Au(1)–Au(2)–Au(3)	91.0(1)	Au(1)–Au(2)–Se(1)	49.9(1)
Au(3)–Au(2)–Se(1)	84.5(1)	Au(1)–Au(2)–P(2)	128.3(2)
Au(3)–Au(2)–P(2)	104.0(2)	Se(1)–Au(2)–P(2)	171.6(2)
Au(2)–Au(3)–Au(4)	88.0(1)	Au(2)–Au(3)–Se(2)	82.8(1)
Au(4)–Au(3)–Se(2)	49.0(1)	Au(2)–Au(3)–P(3)	105.0(2)
Au(4)–Au(3)–P(3)	128.4(2)	Se(2)–Au(3)–P(3)	172.0(2)
Au(1)–Au(4)–Au(3)	90.2(1)	Au(1)–Au(4)–Se(2)	77.1(1)
Au(3)–Au(4)–Se(2)	49.0(1)	Au(1)–Au(4)–P(4)	103.5(2)
Au(3)–Au(4)–P(4)	129.9(2)	Se(2)–Au(4)–P(4)	178.8(2)
Au(1)–Se(1)–Au(2)	80.3(1)	Au(1)–Se(1)–C(73)	107.8(8)
Au(2)–Se(1)–C(73)	100.8(8)	Au(3)–Se(2)–Au(4)	82.1(1)
Au(3)–Se(2)–C(80)	102.1(9)	Au(4)–Se(2)–C(80)	106.3(8)
Au(1)–P(1)–C(1)	111.4(6)	Au(1)–P(1)–C(7)	116.7(6)
C(1)–P(1)–C(7)	106.2(8)	Au(1)–P(1)–C(13)	108.9(6)
C(1)–P(1)–C(13)	107.1(7)	C(7)–P(1)–C(13)	105.9(8)
Au(2)–P(2)–C(19)	111.5(6)	Au(2)–P(2)–C(25)	114.1(5)
C(19)–P(2)–C(25)	108.2(9)	Au(2)–P(2)–C(31)	111.1(7)
C(19)–P(2)–C(31)	104.5(8)	C(25)–P(2)–C(31)	106.9(9)
Au(3)–P(3)–C(37)	111.1(7)	Au(3)–P(3)–C(43)	115.0(6)
C(37)–P(3)–C(43)	105.8(9)	Au(3)–P(3)–C(49)	113.6(7)
C(37)–P(3)–C(49)	105.6(8)	C(43)–P(3)–C(49)	105.0(9)
Au(4)–P(4)–C(55)	112.8(5)	Au(4)–P(4)–C(61)	111.8(6)
C(55)–P(4)–C(61)	106.9(8)	Au(4)–P(4)–C(67)	109.8(7)
C(55)–P(4)–C(67)	108.9(8)	C(61)–P(4)–C(67)	106.3(8)
Se(1)–C(73)–C(74)	113.9(16)	Se(2)–C(80)–C(81)	115.9(18)

Table 4 Selected bond lengths (Å) and angles (°) for compound **6**

Au(1)–P(1)	2.273(6)	Au(1)–Se(1)	2.456(2)
Au(2)–P(2)	2.272(6)	Au(2)–Se(1)	2.430(2)
Au(3)–P(3)	2.264(6)	Au(3)–Se(2)	2.465(2)
Au(4)–P(4)	2.267(6)	Au(4)–Se(2)	2.442(2)
Au(5)–P(5)	2.261(6)	Au(5)–Se(3)	2.413(2)
Au(6)–P(6)	2.269(6)	Au(6)–Se(4)	2.415(2)
Se(1)–C(191)	1.949(9)	Se(2)–C(211)	1.961(9)
Se(3)–C(201)	2.001(11)	Se(4)–C(221)	1.965(9)
P(1)–C(11)	1.786(13)	P(1)–C(21)	1.790(11)
P(1)–C(31)	1.820(11)	P(2)–C(51)	1.796(13)
P(2)–C(61)	1.806(11)	P(2)–C(41)	1.817(13)
P(3)–C(91)	1.807(11)	P(3)–C(71)	1.826(12)
P(3)–C(81)	1.826(11)	P(4)–C(101)	1.817(11)
P(4)–C(121)	1.819(14)	P(4)–C(111)	1.820(12)
P(5)–C(151)	1.802(11)	P(5)–C(131)	1.809(12)
P(5)–C(141)	1.832(11)	P(6)–C(161)	1.801(13)
P(6)–C(181)	1.807(12)	P(6)–C(171)	1.826(11)
P(1)–Au(1)–Se(1)	167.5(2)	P(2)–Au(2)–Se(1)	171.4(2)
P(3)–Au(3)–Se(2)	159.3(2)	P(4)–Au(4)–Se(2)	171.2(2)
P(5)–Au(5)–Se(3)	174.8(2)	P(6)–Au(6)–Se(4)	175.0(2)
C(191)–Se(1)–Au(2)	101.7(3)	C(191)–Se(1)–Au(1)	106.3(4)
Au(2)–Se(1)–Au(1)	89.15(8)	C(211)–Se(2)–Au(4)	101.0(3)
C(211)–Se(2)–Au(3)	100.4(4)	Au(4)–Se(2)–Au(3)	84.64(7)
C(201)–Se(3)–Au(5)	96.5(4)	C(221)–Se(4)–Au(6)	99.3(3)
C(11)–P(1)–C(21)	105.8(8)	C(11)–P(1)–C(31)	105.3(7)
C(21)–P(1)–C(31)	106.1(7)	C(11)–P(1)–Au(1)	112.2(6)
C(21)–P(1)–Au(1)	118.4(5)	C(31)–P(1)–Au(1)	108.1(5)
C(51)–P(2)–C(61)	107.6(7)	C(51)–P(2)–C(41)	106.3(8)
C(61)–P(2)–C(41)	106.2(7)	C(51)–P(2)–Au(2)	112.7(6)
C(61)–P(2)–Au(2)	106.4(5)	C(41)–P(2)–Au(2)	117.1(6)
C(91)–P(3)–C(71)	103.8(7)	C(91)–P(3)–C(81)	107.2(7)
C(71)–P(3)–C(81)	106.0(7)	C(91)–P(3)–Au(3)	118.6(5)
C(71)–P(3)–Au(3)	110.5(6)	C(81)–P(3)–Au(3)	109.9(6)
C(101)–P(4)–C(121)	104.6(7)	C(101)–P(4)–C(111)	106.8(7)
C(121)–P(4)–C(111)	105.4(8)	C(101)–P(4)–Au(4)	106.4(5)
C(121)–P(4)–Au(4)	119.1(6)	C(111)–P(4)–Au(4)	113.7(5)
C(151)–P(5)–C(131)	105.5(7)	C(151)–P(5)–C(141)	105.2(7)
C(131)–P(5)–C(141)	106.6(7)	C(151)–P(5)–Au(5)	115.4(5)
C(131)–P(5)–Au(5)	115.8(5)	C(141)–P(5)–Au(5)	107.4(5)
C(161)–P(6)–C(181)	106.0(7)	C(161)–P(6)–C(171)	106.9(7)
C(181)–P(6)–C(171)	105.0(7)	C(161)–P(6)–Au(6)	113.3(6)
C(181)–P(6)–Au(6)	115.7(5)	C(171)–P(6)–Au(6)	109.4(5)

Table 5 Selected bond lengths (Å) and angles (°) for compound **7**

Au(1)–P(1)	2.262(2)	Au(1)–Se(1)	2.4170(14)
Au(1)–Au(2)	3.0442(9)	Au(2)–P(2)	2.274(2)
Au(2)–Se(2)	2.4117(11)	P(1)–C(11′)	1.750(8)
P(1)–C(121)	1.815(4)	P(1)–C(1)	1.818(8)
P(1)–C(111)	1.897(9)	C(1)–C(1$^{\mathrm{I}}$)	1.54(2)
C(2)–C(2$^{\mathrm{II}}$)	1.52(2)	C(2)–P(2)	1.819(8)
P(2)–C(211)	1.813(5)	P(2)–C(221)	1.819(4)
Se(1)–C(11)	1.910(5)	Se(2)–C(21)	2.017(9)
Se(2)–C(21′)	1.884(9)		
P(1)–Au(1)–Se(1)	171.05(6)	P(1)–Au(1)–Au(2)	107.45(6)
Se(1)–Au(1)–Au(2)	78.75(4)	P(2)–Au(2)–Se(2)	172.74(6)
P(2)–Au(2)–Au(1)	105.79(5)	Se(2)–Au(2)–Au(1)	78.80(3)
C(11′)–P(1)–C(121)	106.3(4)	C(11′)–P(1)–C(1)	107.9(5)
C(121)–P(1)–C(1)	107.4(3)	C(11′)–P(1)–Au(1)	111.7(4)
C(121)–P(1)–Au(1)	114.0(2)	C(1)–P(1)–Au(1)	109.2(3)
C(111)–P(1)–Au(1)	123.4(4)	C(1$^{\mathrm{I}}$)–C(1)–P(1)	111.0(7)
C(2$^{\mathrm{II}}$)–C(2)–P(2)	111.9(7)	C(211)–P(2)–C(221)	104.0(3)
C(211)–P(2)–C(2)	103.7(3)	C(221)–P(2)–C(2)	107.0(3)
C(211)–P(2)–Au(2)	117.0(2)	C(221)–P(2)–Au(2)	115.9(2)
C(2)–P(2)–Au(2)	108.2(3)	C(11)–Se(1)–Au(1)	97.1(2)
C(21)–Se(2)–Au(2)	94.9(3)	C(21′)–Se(2)–Au(2)	109.2(3)

Symmetry transformations used to generate equivalent atoms: I $1 - x, -y + 1, -z$; II $2 - x, -y + 1, -z + 1$.

The naphthylselenolate complex **6** crystallizes with two independent cation–neutral complex units and two molecules of CH_2Cl_2 per asymmetric unit (Fig. 2). Two Sb atoms lie on the two-fold axes 0.5, *y*, 0.25 and 0.5, *y*, 0.75, respectively.

The molecular structure is remarkable: in each independent unit an intermolecular Au ··· Au contact links the cationic with the neutral moiety. Additionally, intracationic Au ··· Au contacts and intermolecular formally non-bonding Au ··· Se contacts are observed.

The intermolecular Au ··· Au and Au ··· Se contacts cause unusually large distortions of the linear co-ordination at gold. The corresponding angles are P(1)–Au(1)–Se(1) 167.5(2)° and P(3)–Au(3)–Se(2) 159.3(2)°. The cation gold atoms that are not linked by short contacts to the neutral complex show less pronounced deviations from linearity [171.2(2)° at Au(4), 171.4(2)° at Au(2)].

The intracationic Au ··· Au contacts are different in the independent units and significantly longer [3.304(1), 3.429(1) Å] than the 3.240(1) Å in the phenylselenolate and 3.031(1) Å in $[(AuPPh_3)_2(SeC_6F_4Cl\text{-}4)]^+$. The corresponding Au–Se–Au angles are 89.2(1)° for Se(1) and 84.6(1)° for Se(2) {*cf.* 76.0(1)° in $[(AuPPh_3)_2(SeC_6F_4Cl\text{-}4)]^+$ and 83.0(1)° in the phenylselenolate}.[6a,b] Recently, a correlation based on Cambridge Structural Database (CSD) data between the lengths of Au ··· Au interactions and the corresponding Au–Z–Au angles in Au_2Z fragments (Z = B, C, S, Se and other elements) was published.[13] The authors suggest that weak Au ··· Au interactions in $Au_2Se(Te)$ units are perhaps due to a weak Au–Z bond, which is polarized $Au^{\delta-}$–$Z^{\delta+}$.

Table 6 Crystal data for compounds **1**, **6** and **7**

Compound	$[(AuPPh_3)_2(SeCH_2Ph)]SbF_6$-·2.5 $CDCl_3$ **1**·2.5 $CDCl_3$	$[(AuPPh_3)_2(SeC_{10}H_7)]SbF_6$·$[Au(PPh_3)$-$(SeC_{10}H_7)]$·$CH_2Cl_2$ **6**·CH_2Cl_2	$[(AuSePh)_2(dppe)]$ **7**
Formula	$C_{45.5}H_{37}D_{2.5}Au_2Cl_{7.5}F_6P_2SbSe$	$C_{75}H_{61}AuCl_2F_6P_3SbSe_2$	$C_{38}H_{34}Au_2P_2Se_2$
Crystal size/mm	0.5 × 0.3 × 0.25	0.76 × 0.32 × 0.2	0.4 × 0.2 × 0.2
M	1625.3	2110.62	1104.44
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$C2/c$	$P\bar{1}$
a/Å	11.847(5)	36.665(8)	10.613(3)
b/Å	42.768(15)	27.773(6)	11.568(3)
c/Å	20.970(6)	28.780(5)	16.409(4)
α/°			70.40(2)
β/°	99.67(3)	103.72(2)	86.69(2)
γ/°			68.81(2)
U/Å^3	10 474(4)	28 470(10)	1764.9(8)
Z	8	16	2
D_c/g cm^{-3}	2.061	1.97	2.078
μ/mm^{-1}	7.293	7.763	10.482
Max., min. transmissions	0.99, 0.46	0.77, 0.45	0.99, 0.54
F(000)	6136	16 000	1036
No. data measured	15 701	26 809	9681
$2\theta_{max}$/°	45	50	50
No. unique data	13 470	25 175	6240
No. observed data	6823		
$R(F)$, $F > 4\sigma(F)$	0.070	0.062	0.037
Weighting parameters:			
g	0.000 3		
a		0.0878	0.0215
b		998.53	17.83
$wR(F)$	0.066		
$wR(F^2)$ (all reflections)		0.2453	0.0876
Goodness of fit	1.7	1.03	1.04
Max. $\Delta\rho$/e Å^{-3}	2.2	2.2	2.1

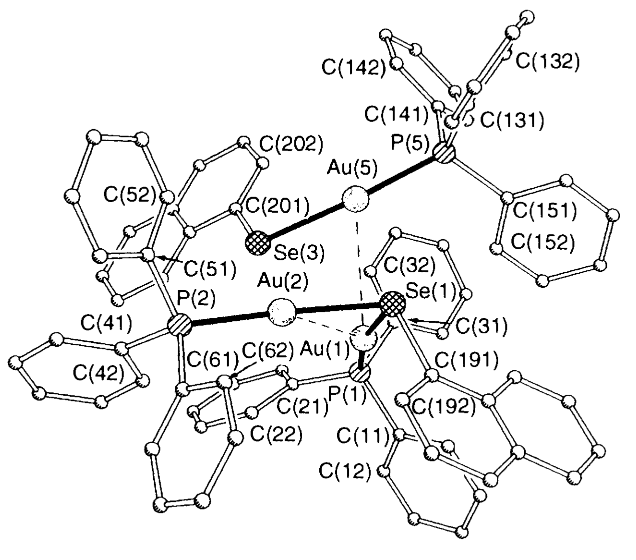

Fig. 2 One of the two independent cation–neutral adducts of compound **6** in the crystal. Radii are arbitrary; H atoms are omitted for clarity

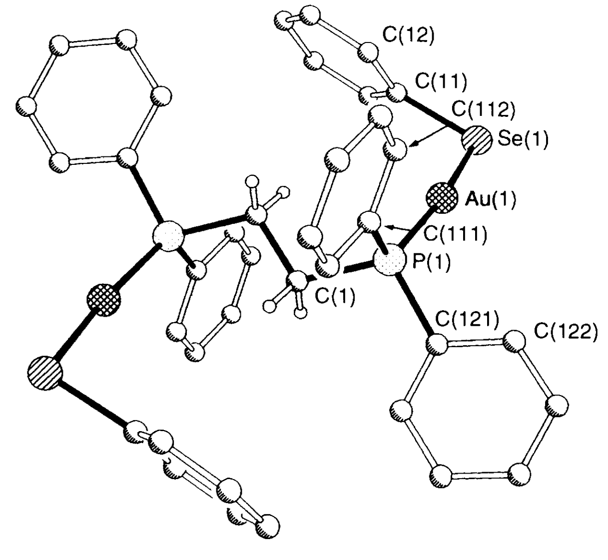

Fig. 3 One of the two independent molecules of compound **7** in the crystal. Only one position of the disordered rings is shown. Only the asymmetric unit is numbered. Radii are arbitrary; H atoms are omitted for clarity

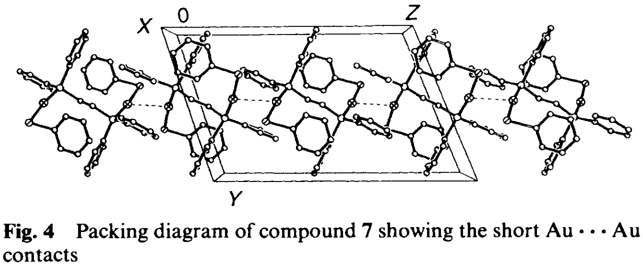

Fig. 4 Packing diagram of compound **7** showing the short Au ··· Au contacts

The observed non-bonding Au ··· Se contacts lie in the range 3.226(3) to 3.357(2) Å and may be considered as weak interactions. Comparable Au ··· Se contacts are observed in $[Au(PPh_3)(SePh)]$ (3.381, 3.460 Å),[6a] $[Au(PPh_3)(SePMe_2$-$Ph)]^+$ (3.353 Å)[6c] and [AuCl{Se(dppm)}] (3.277 Å).[8]

The Au ··· Se bond lengths are slightly different in the cationic and in the neutral moieties [neutral: 2.413, 2.415(2) Å; cationic: 2.430–2.465(2) Å] but similar to those observed in $[Au(PPh_3)(SePh)]$ [2.422(1), 2.415(1) Å, two independent molecules] and cationic gold selenolates {2.445(2) Å in

Table 7 Atom coordinates (× 10^4) for compound **1**

Atom	*x*	*y*	*z*
Au(1)	4 117.7(9)	3 169.5(3)	8 081.1(4)
Au(2)	4 210.3(10)	3 905.4(3)	8 088.8(5)
Au(3)	1 832.7(10)	3 939.6(3)	7 227.7(5)
Au(4)	1 973.6(9)	3 198.7(3)	7 032.2(4)
Se(1)	4 646(2)	3 532.7(8)	7 281.2(11)
Se(2)	1 420(2)	3 506.1(7)	7 909.7(12)
Sb(1)	1 933(2)	7 510.5(5)	7 414.8(10)
Sb(2)	3 593(3)	4 149.9(6)	2 946.4(12)
P(1)	3 659(6)	2 843(2)	8 860(3)
P(2)	4 069(6)	4 236(2)	8 917(3)
P(3)	1 983(7)	4 325(2)	6 504(3)
P(4)	2 485(6)	2 919(2)	6 195(3)
F(1)	2 665(19)	7 219(5)	7 998(8)
F(2)	938(20)	7 206(5)	7 080(8)
F(3)	3 010(28)	7 801(6)	7 752(14)
F(4)	1 282(22)	7 782(6)	6 808(13)
F(5)	2 855(22)	7 386(6)	6 832(10)
F(6)	1 020(29)	7 638(7)	7 931(14)
F(7)	3 550(19)	4 472(5)	3 540(11)
F(8)	3 266(22)	4 426(6)	2 301(10)
F(9)	3 846(21)	3 872(5)	3 635(9)
F(10)	5 187(19)	4 222(6)	3 019(13)
F(11)	2 052(19)	4 087(6)	2 903(11)
F(12)	3 607(31)	3 831(6)	2 354(11)
C(2)	2 728(11)	3 293(4)	9 543(7)
C(3)	1 867	3 441	9 810
C(4)	797	3 300	9 774
C(5)	588	3 010	9 470
C(6)	1 449	2 862	9 203
C(1)	2 519	3 004	9 240
C(8)	2 305(14)	2 417(4)	8 094(7)
C(9)	1 912	2 120	7 891
C(10)	2 428	1 855	8 201
C(11)	3 337	1 887	8 713
C(12)	3 731	2 184	8 916
C(7)	3 215	2 449	8 607
C(14)	4 810(12)	2 809(4)	10 136(7)
C(15)	5 800	2 779	10 598
C(16)	6 859	2 738	10 402
C(17)	6 928	2 727	9 744
C(18)	5 938	2 758	9 283
C(13)	4 879	2 799	9 479
C(20)	5 595(16)	4 658(5)	9 566(6)
C(21)	6 417	4 894	9 600
C(22)	6 732	5 011	9 034
C(23)	6 224	4 893	8 434
C(24)	5 402	4 657	8 400
C(19)	5 088	4 540	8 966
C(26)	1 739(16)	4 212(3)	8 936(7)
C(27)	632	4 331	8 900
C(28)	430	4 650	8 806
C(29)	1 334	4 851	8 748
C(30)	2 441	4 733	8 784
C(25)	2 643	4 414	8 878
C(32)	5 187(15)	3 796(4)	9 730(7)
C(33)	5 478	3 635	10 313
C(34)	4 975	3 717	10 845
C(35)	4 181	3 961	10 794
C(36)	3 891	4 122	10 212
C(31)	4 393	4 040	9 680
C(38)	895(15)	3 938(4)	5 557(7)
C(39)	601	3 826	4 926
C(40)	1 103	3 954	4 430
C(41)	1 899	4 196	4 565
C(42)	2 193	4 308	5 195
C(37)	1 691	4 179	5 691
C(44)	4 297(17)	4 320(3)	6 481(8)
C(45)	5 396	4 446	6 532
C(46)	5 587	4 760	6 691
C(47)	4 679	4 949	6 800
C(48)	3 580	4 824	6 749
C(43)	3 389	4 510	6 590
C(50)	565(17)	4 694(4)	7 106(7)
C(51)	−237	4 929	7 142
C(52)	−621	5 116	6 603
C(53)	−202	5 066	6 027
C(54)	600	4 831	5 992
C(49)	984	4 645	6 531
C(56)	2 531(12)	2 257(4)	6 144(6)
C(57)	2 949	1 962	6 352
C(58)	3 875	1 937	6 857
C(59)	4 383	2 206	7 154
C(60)	3 965	2 500	6 947
C(55)	3 038	2 525	6 442
C(62)	4 680(17)	2 987(3)	5 845(8)
C(63)	5 507	3 153	5 583
C(64)	5 252	3 449	5 316
C(65)	4 170	3 578	5 311
C(66)	3 343	3 412	5 573
C(61)	3 598	3 117	5 840
C(68)	1 376(12)	2 913(4)	4 912(8)
C(69)	395	2 900	4 441
C(70)	−674	2 853	4 621
C(71)	−761	2 820	5 272
C(72)	220	2 833	5 744
C(67)	1 288	2 880	5 564
C(73)	6 356(21)	3 559(7)	7 421(11)
C(75)	7 236(17)	3 425(4)	8 571(9)
C(76)	7 758	3 516	9 189
C(77)	7 929	3 833	9 334
C(78)	7 580	4 058	8 861
C(79)	7 058	3 967	8 243
C(74)	6 886	3 650	8 098
C(80)	−265(23)	3 506(8)	7 769(12)
C(82)	−1 064(15)	3 961(4)	7 061(7)
C(83)	−1 564	4 085	6 465
C(84)	−1 860	3 889	5 932
C(85)	−1 655	3 568	5 995
C(86)	−1 155	3 444	6 591
C(81)	−859	3 640	7 124
C(101)	3 212(44)	5 698(12)	8 188(22)
C(102)	850(32)	6 695(9)	8 227(15)
C(103)	−162(57)	4 255(17)	979(30)
C(104)	3 758(42)	5 385(12)	5 400(21)
C(105)	3 685(73)	6 454(21)	6 612(39)
Cl(1)	2 064(18)	5 552(5)	7 627(9)
Cl(2)	4 223(15)	5 407(4)	8 264(7)
Cl(3)	2 742(14)	5 668(4)	8 987(7)
Cl(4)	−157(13)	6 406(4)	7 865(7)
Cl(5)	178(10)	6 930(3)	8 711(5)
Cl(6)	1 902(11)	6 456(3)	8 783(6)
Cl(7)	898(19)	4 029(5)	704(9)
Cl(8)	−254(17)	4 544(5)	357(9)
Cl(9)	798(14)	4 492(4)	1 621(7)
Cl(10)	2 473(18)	5 516(5)	5 641(9)
Cl(11)	3 367(17)	5 108(5)	4 835(9)
Cl(12)	4 428(10)	5 697(3)	5 099(5)
Cl(13)	3 347(14)	6 501(4)	7 337(8)
Cl(14)	3 498(21)	6 733(6)	6 099(11)
Cl(15)	1 985(28)	6 315(7)	6 291(13)

$[(AuPPh_3)_2(SePh)]^+$; 2.458(2), 2.467(1) Å in $[(AuPPh_3)_2(SeC_6F_4Cl\text{-}4)]^+$}.[6a,b]

The molecular dppe complex **7** possesses crystallographic inversion symmetry. The crystal structure consists of two half molecules, each with an inversion centre at the midpoint of the ethylene bridge (Fig. 3). As a result of the observed intermolecular gold–gold interactions [Au(1) ··· Au(2) 3.044(9) Å] {*cf.* 3.118(1) Å in $[Au(PPh_3)(SePh)]$} the molecules are linked to form loose polymeric chains in the unit cell (Fig. 4). In contrast to this observation, weak intermolecular Au ··· Au

Table 8 Atom coordinates (× 10^4) for compound **6**

Atom	*x*	*y*	*z*
Au(1)	6 045.9(2)	6 310.1(3)	4 786.1(3)
Au(2)	5 963.3(2)	5 424.2(3)	5 584.6(3)
Au(3)	8 534.5(3)	3 806.2(3)	5 035.8(3)
Au(4)	8 405.9(2)	4 793.2(4)	5 617.6(3)
Au(5)	6 526.4(2)	5 422.5(3)	4 510.6(3)
Au(6)	9 019.9(2)	4 613.1(3)	4 598.6(3)
Se(1)	5 689.2(6)	5 556.0(8)	4 739.2(7)
Se(2)	8 156.2(6)	4 537.3(8)	4 791.7(7)
Se(3)	6 770.8(6)	5 693.3(10)	5 321.5(8)
Se(4)	9 250.6(6)	4 487.5(9)	5 448.1(8)
P(1)	6 281(2)	7 049(2)	4 681(2)
P(2)	6 134(2)	5 255(2)	6 379(2)
P(3)	8 671(2)	3 026(2)	5 232(2)
P(4)	8 558(2)	4 977(2)	6 408(2)
P(5)	6 351.1(15)	5 171(2)	3 743(2)
P(6)	8 855(2)	4 747(2)	3 798(2)
C(11)	5 921(4)	7 495(5)	4 528(6)
C(12)	5 999(4)	7 975(6)	4 648(5)
C(13)	5 719(5)	8 320(5)	4 519(6)
C(14)	5 361(4)	8 186(6)	4 269(6)
C(15)	5 283(4)	7 706(7)	4 149(6)
C(16)	5 563(5)	7 360(5)	4 278(6)
C(21)	6 632(3)	7 301(5)	5 160(4)
C(22)	6 570(3)	7 274(5)	5 617(5)
C(23)	6 819(4)	7 493(6)	5 999(4)
C(24)	7 130(4)	7 739(5)	5 923(4)
C(25)	7 192(3)	7 766(5)	5 465(5)
C(26)	6 943(4)	7 547(5)	5 084(4)
C(31)	6 492(4)	7 017(5)	4 169(4)
C(32)	6 790(4)	6 699(5)	4 206(4)
C(33)	6 949(3)	6 629(5)	3 818(5)
C(34)	6 809(4)	6 876(6)	3 393(4)
C(35)	6 510(4)	7 194(5)	3 356(4)
C(36)	6 352(3)	7 264(5)	3 745(5)
C(41)	6 473(4)	5 655(5)	6 752(5)
C(42)	6 494(4)	6 129(6)	6 605(5)
C(43)	6 725(5)	6 456(5)	6 903(6)
C(44)	6 935(4)	6 309(5)	7 348(6)
C(45)	6 915(4)	5 835(6)	7 495(4)
C(46)	6 684(4)	5 508(4)	7 197(5)
C(51)	6 318(4)	4 656(4)	6 499(5)
C(52)	6 526(4)	4 470(6)	6 195(5)
C(53)	6 688(4)	4 016(6)	6 282(5)
C(54)	6 641(4)	3 748(5)	6 672(6)
C(55)	6 432(4)	3 935(5)	6 975(5)
C(56)	6 270(4)	4 389(6)	6 888(5)
C(61)	5 712(3)	5 295(5)	6 597(5)
C(62)	5 412(4)	4 996(4)	6 396(5)
C(63)	5 069(3)	5 054(5)	6 515(5)
C(64)	5 026(3)	5 411(5)	6 836(5)
C(65)	5 326(4)	5 710(5)	7 038(5)
C(66)	5 669(3)	5 652(5)	6 918(5)
C(71)	8 334(4)	2 628(5)	4 848(5)
C(72)	8 352(4)	2 604(5)	4 372(5)
C(73)	8 089(4)	2 336(6)	4 047(5)
C(74)	7 807(4)	2 092(5)	4 198(5)
C(75)	7 789(4)	2 115(5)	4 674(5)
C(76)	8 052(4)	2 384(6)	4 999(4)
C(81)	8 628(4)	2 913(5)	5 842(4)
C(82)	8 884(3)	2 636(5)	6 166(5)
C(83)	8 836(4)	2 565(5)	6 626(5)
C(84)	8 531(4)	2 772(6)	6 761(4)
C(85)	8 275(3)	3 049(5)	6 436(5)
C(86)	8 323(4)	3 120(5)	5 977(4)
C(91)	9 122(3)	2 792(5)	5 188(5)
C(92)	9 399(4)	3 118(4)	5 143(5)
C(93)	9 751(3)	2 954(5)	5 116(5)
C(94)	9 826(3)	2 463(5)	5 133(5)
C(95)	9 549(4)	2 136(4)	5 177(6)
C(96)	9 197(4)	2 301(5)	5 205(5)
C(101)	8 137(3)	4 881(5)	6 623(5)
C(102)	7 823(4)	5 159(5)	6 424(4)
C(103)	7 490(3)	5 090(5)	6 568(5)
C(104)	7 472(3)	4 743(6)	6 909(5)
C(105)	7 785(4)	4 465(5)	7 108(5)
C(106)	8 118(3)	4 534(5)	6 965(5)
C(111)	8 921(4)	4 591(5)	6 761(5)
C(112)	9 186(4)	4 773(4)	7 149(5)
C(113)	9 444(4)	4 466(5)	7 436(4)
C(114)	9 436(4)	3 976(5)	7 334(5)
C(115)	9 171(4)	3 794(4)	6 947(5)
C(116)	8 913(4)	4 101(5)	6 660(4)
C(121)	8 703(4)	5 589(5)	6 590(6)
C(122)	8 972(5)	5 815(6)	6 399(5)
C(123)	9 106(4)	6 268(6)	6 563(6)
C(124)	8 970(5)	6 494(5)	6 919(6)
C(125)	8 701(5)	6 267(6)	7 110(5)
C(126)	8 567(4)	5 815(6)	6 946(6)
C(131)	6 174(4)	4 562(4)	3 654(5)
C(132)	6 208(4)	4 284(5)	3 265(4)
C(133)	6 037(4)	3 835(5)	3 190(5)
C(134)	5 832(4)	3 663(4)	3 504(5)
C(135)	5 798(4)	3 941(5)	3 894(5)
C(136)	5 969(4)	4 390(5)	3 969(4)
C(141)	6 767(3)	5 197(5)	3 494(5)
C(142)	7 071(4)	4 907(5)	3 700(5)
C(143)	7 410(3)	4 960(5)	3 568(5)
C(144)	7 444(3)	5 304(5)	3 229(5)
C(145)	7 139(4)	5 594(5)	3 023(5)
C(146)	6 801(3)	5 540(5)	3 156(5)
C(151)	6 005(3)	5 540(4)	3 352(4)
C(152)	5 991(3)	6 026(5)	3 460(4)
C(153)	5 747(4)	6 331(4)	3 151(5)
C(154)	5 517(3)	6 149(5)	2 733(4)
C(155)	5 530(4)	5 663(5)	2 625(4)
C(156)	5 775(4)	5 358(4)	2 934(5)
C(161)	8 698(4)	5 353(4)	3 644(5)
C(162)	8 772(4)	5 585(5)	3 248(5)
C(163)	8 630(4)	6 044(5)	3 125(5)
C(164)	8 415(5)	6 271(5)	3 398(6)
C(165)	8 341(4)	6 039(6)	3 794(6)
C(166)	8 483(4)	5 580(6)	3 917(5)
C(171)	9 262(3)	4 646(5)	3 547(5)
C(172)	9 257(3)	4 324(5)	3 176(5)
C(173)	9 582(4)	4 240(5)	3 020(4)
C(174)	9 913(3)	4 479(5)	3 235(5)
C(175)	9 917(3)	4 801(5)	3 606(5)
C(176)	9 592(4)	4 885(5)	3 762(4)
C(181)	8 493(3)	4 358(5)	3 460(5)
C(182)	8 487(4)	3 880(5)	3 603(4)
C(183)	8 229(4)	3 561(4)	3 334(5)
C(184)	7 978(4)	3 719(5)	2 922(5)
C(185)	7 984(4)	4 197(6)	2 779(4)
C(186)	8 242(4)	4 516(4)	3 048(5)
C(191)	5 176(2)	5 737(4)	4 744(4)
C(192)	5 034(3)	5 580(4)	5 123(3)
C(193)	4 664(3)	5 681(5)	5 132(4)
C(194)	4 437(3)	5 940(5)	4 760(4)
C(199)	4 580(2)	6 098(3)	4 380(3)
C(200)	4 949(2)	5 996(3)	4 372(3)
C(198)	5 092(3)	6 154(5)	3 992(4)
C(197)	4 865(4)	6 413(5)	3 620(4)
C(196)	4 495(4)	6 514(5)	3 629(4)
C(195)	4 353(3)	6 357(5)	4 008(4)
C(201)	7 282(3)	5 872(5)	5 245(5)
C(202)	7 426(4)	5 700(5)	4 872(4)
C(203)	7 791(4)	5 815(5)	4 851(4)
C(204)	8 012(3)	6 102(5)	5 204(5)
C(209)	7 868(3)	6 274(4)	5 577(4)
C(210)	7 503(3)	6 159(4)	5 598(4)
C(208)	7 359(4)	6 331(5)	5 971(5)
C(207)	7 580(5)	6 618(6)	6 324(4)
C(206)	7 944(5)	6 733(5)	6 304(5)
C(205)	8 088(3)	6 561(5)	5 930(5)
C(211)	7 658(3)	4 303(4)	4 822(4)
C(212)	7 496(3)	4 516(4)	5 162(4)
C(213)	7 129(3)	4 404(4)	5 175(4)
C(214)	6 924(3)	4 080(5)	4 847(4)

Table 8 (*continued*)

Atom	x	y	z
C(219)	7 085(2)	3 867(3)	4 507(3)
C(220)	7 452(2)	3 979(3)	4 495(3)
C(218)	7 613(3)	3 766(4)	4 154(4)
C(217)	7 408(4)	3 441(4)	3 827(4)
C(216)	7 041(4)	3 330(4)	3 839(4)
C(215)	6 879(3)	3 542(4)	4 179(4)
C(221)	9 760(3)	4 262(4)	5 455(4)
C(222)	9 929(3)	4 438(4)	5 105(4)
C(223)	10 295(3)	4 307(4)	5 107(4)
C(224)	10 493(3)	4 000(4)	5 460(4)
C(229)	10 324(2)	3 825(3)	5 810(3)
C(230)	9 958(2)	3 956(3)	5 808(3)
C(228)	9 789(3)	3 780(5)	6 158(4)
C(227)	9 987(4)	3 473(5)	6 511(4)
C(226)	10 353(4)	3 342(4)	6 513(4)
C(225)	10 522(3)	3 518(4)	6 163(4)
Sb(1)	5 000	7 667.1(8)	2 500
F(1)	4 554(6)	7 643(9)	2 078(11)
F(2)	5 154(8)	8 137(7)	2 155(9)
F(3)	4 831(7)	7 196(7)	2 844(7)
Sb(2)	5 000	7 282.1(8)	7 500
F(4)	4 644(6)	6 828(8)	7 519(6)
F(5)	5 347(5)	7 759(7)	7 495(6)
F(6)	5 154(4)	7 274(5)	8 164(5)
Sb(3)	7 431.5(4)	2 177.1(6)	2 547.4(5)
F(7)	6 916(4)	2 181(9)	2 346(8)
F(8)	7 441(7)	2 637(7)	2 087(6)
F(9)	7 388(5)	2 652(6)	2 987(5)
F(10)	7 435(5)	1 727(6)	3 018(6)
F(11)	7 460(4)	1 693(6)	2 100(6)
F(12)	7 947(4)	2 203(8)	2 727(6)
C(1)	9 163(8)	2 866(12)	3 297(11)
Cl(1)	9 241(2)	2 948(4)	3 904(3)
Cl(2)	8 765(2)	2 544(3)	3 052(3)
C(2)	5 494(10)	3 011(14)	1 277(13)
Cl(3)	5 511(4)	3 430(4)	840(4)
Cl(4)	5 922(4)	2 766(5)	1 534(7)

Table 9 Atom co-ordinates (× 10^4) for compound **7**

Atom	x	y	z
Au(1)	2 102.6(3)	4 732.3(4)	1 570.0(2)
Au(2)	2 051.1(3)	4 931.7(3)	3 375.8(2)
P(1)	67(2)	6 104(2)	858.6(14)
C(111)	−185(12)	7 703(9)	−65(7)
C(112)	892(10)	8 133(12)	−297(8)
C(113)	701(12)	9 314(13)	−965(8)
C(114)	−569(13)	10 067(10)	−1 403(7)
C(115)	−1 646(10)	9 637(11)	−1 171(8)
C(116)	−1 454(10)	8 456(11)	−503(8)
C(11′)	172(11)	7 533(9)	86(7)
C(12′)	1 416(9)	7 534(10)	−229(7)
C(13′)	1 498(10)	8 651(12)	−865(8)
C(14′)	336(12)	9 766(10)	−1 186(7)
C(15′)	−908(10)	9 765(9)	−871(8)
C(16′)	−990(9)	8 649(11)	−235(8)
C(121)	−1 234(5)	6 649(6)	1 559(3)
C(122)	−917(4)	7 192(6)	2 120(4)
C(123)	−1 870(5)	7 647(6)	2 666(3)
C(124)	−3 140(5)	7 560(6)	2 652(4)
C(125)	−3 457(4)	7 017(6)	2 091(4)
C(126)	−2 504(5)	6 561(6)	1 544(3)
C(1)	−534(8)	5 268(8)	296(5)
C(2)	−397(8)	4 814(8)	4 726(5)
P(2)	708(2)	3 841(2)	4 115.8(13)
C(211)	1 543(5)	2 246(5)	4 934(3)
C(212)	784(4)	1 491(6)	5 358(4)
C(213)	1 406(5)	280(5)	6 002(4)
C(214)	2 788(6)	−175(5)	6 222(4)
C(215)	3 547(4)	580(6)	5 797(4)
C(216)	2 924(5)	1 790(5)	5 154(4)
C(221)	−377(5)	3 535(6)	3 459(3)
C(222)	−1 776(5)	3 955(6)	3 495(3)
C(223)	−2 550(4)	3 689(6)	2 977(4)
C(224)	−1 925(5)	3 003(6)	2 422(4)
C(225)	−526(5)	2 584(6)	2 385(3)
C(226)	248(4)	2 850(6)	2 904(4)
Se(1)	4 229.6(10)	3 016.3(12)	2 247.5(7)
C(11)	4 791(7)	2 437(7)	1 279(4)
C(12)	4 821(7)	3 331(6)	470(4)
C(13)	5 279(9)	2 890(8)	−223(4)
C(14)	5 707(9)	1 555(9)	−106(5)
C(15)	5 677(9)	661(6)	704(6)
C(16)	5 219(8)	1 102(6)	1 396(4)
Se(2)	3 299.6(10)	6 316.9(10)	2 649.2(6)
C(21)	3 501(13)	6 831(12)	3 680(7)
C(22)	4 277(13)	5 886(9)	4 423(8)
C(23)	4 493(13)	6 255(12)	5 111(7)
C(24)	3 932(14)	7 569(13)	5 056(7)
C(25)	3 156(14)	8 514(10)	4 312(9)
C(26)	2 940(13)	8 145(11)	3 624(7)
C(21′)	3 145(12)	7 519(10)	3 224(7)
C(22′)	3 225(12)	8 733(11)	2 746(6)
C(23′)	3 143(13)	9 633(10)	3 152(8)
C(24′)	2 980(14)	9 321(12)	4 037(8)
C(25′)	2 901(14)	8 108(13)	4 515(6)
C(26′)	2 983(13)	7 207(10)	4 109(7)

interactions of 3.189 Å in the corresponding chlorogold complex [$(AuCl)_2$(dppe)] cause the formation of loose dimers.[14] In *trans*-[$(AuCl)_2(CHPPh_2)_2$] intermolecular Au ··· Au contacts of 3.043(1) Å are observed.[15] The Au–Se bond lengths in **7** are Au(1)–Se(1) 2.417(1) and Au(2)–Se(2) 2.412(1) Å and therefore not significantly different from the values in **6** (see above) and [$Au(PPh_3)(SePh)$] [2.422(1) Å].[6a] The angles at selenium are narrow for tetrahedral values [C(11)–Se(1)–Au(1) 97.1(2), C(21)–Se(2)–Au(2) 94.9(3)°].

Experimental

All syntheses were carried out in dried solvents under an N_2 atmosphere using conventional Schlenk techniques. NMR spectra were recorded on a Bruker AC 200 spectrometer (^1H at 200.1, ^{31}P at 81 and ^{77}Se at 38.2 MHz). Tetramethylsilane (^1H), H_3PO_4 (^{31}P) and $SeMe_2$ (^{77}Se) were used as external references. Mass spectra (FAB) were obtained on a Finnigan MAT 8430 instrument. Elemental analyses were performed locally and by Beller Lab., Göttingen, Germany.

The following chemicals were prepared according to established or slightly modified literature methods: [$Au(PPh_3)Cl$],[16] [$(AuCl)_2$(dppe)],[17] [$Au(PMePh_2)Cl$],[18] [$Au(PMe_2Ph)Cl$],[18] $Se_2(C_6H_4NH_2)_2$,[19] $Se_2(C_6H_4Cl)_2$,[19] $Se_2(CH_2Ph)_2$[20] and $PhSeSiMe_3$;[21] Se_2Ph_2 was purchased from Aldrich.

Synthesis of [$(AuPR^1R^2R^3)_2(SeR^4)$]SbF_6 (*General Procedure*) (**1**–**5**) *and of* [$(AuPPh_3)_2(SeC_{10}H_7)$]SbF_6·[$Au(PPh_3)(SeC_{10}H_7)$].—To the phosphinegold(I) complex (2 mmol) dissolved in CH_2Cl_2–diethyl ether (100 cm^3, 3 : 2) was added the diselenide (1 mmol) and solid $AgSbF_6$ (2 mmol). After stirring for 3 h under exclusion of light, the precipitate was filtered off ($MgSO_4/SiO_2$) and the solution concentrated to 20 cm^3. The product was precipitated with diethyl ether and recrystallized from CH_2Cl_2–diethyl ether. In the case of the naphthylselenolate complex [Au(PPh$_3$)Cl] (0.6 mmol, 297 mg), AgSbF$_6$ (0.6 mmol, 206 mg) and Se$_2$(C$_{10}$H$_7$)$_2$[22] (0.3 mmol, 124 mg) were employed.

Synthesis of [(AuSePh)$_2$(dppe)] **7**.—The compound PhSeSiMe$_3$ (458 mg, 2 mmol) was added with stirring to a solution of [(AuCl)$_2$(dppe)] (863 mg, 1 mmol) in MeCN–dmf (60 cm^3 5:1). The solution was refluxed for 3 h, after which the solvent was removed. The residue was recrystallized from dichloromethane–light petroleum.

For analytical and NMR data see Tables 1 and 2.

Crystallography.—Crystals of [(AuPPh$_3$)$_2$Se(CH$_2$Ph)]SbF$_6$·2.5CDCl$_3$ **1**·2.5CDCl$_3$, [(AuPPh$_3$)$_2$(SeC$_{10}$H$_7$)]SbF$_6$·[Au(PPh$_3$)(SeC$_{10}$H$_7$)]·CH$_2$Cl$_2$ **6**·CH$_2$Cl$_2$ and [(AuSePh)$_2$(dppe)] **7** were mounted on glass fibres in inert oil and transferred to the cold gas stream (− 100 °C) of the diffractometer (Siemens R3, equipped with an LT-2 low-temperature attachment). Mo-Kα radiation (λ = 0.710 73 Å, graphite monochromator) was used to collect the intensity data with the ω-scan technique. Cell constants were refined from setting angles of 50 reflections in the 2θ range 20–23°. Absorption corrections were based on ψ-scans.

The crystallographic program system used was Siemens SHELXTL PLUS or SHELXL 92.[23] The structures were solved by direct methods (**1**, **6**) or by the Patterson method (**7**) and refined by a full-matrix least-squares procedure on F (**1**) or on F^2 (**6**, **7**). The following atoms were refined anisotropically: **1** Au, Se, Sb, P, F; **6** Au, Se, Sb, P, F, Cl; **7** Au, Se, P. All hydrogen atoms were included using a riding model. Idealized phenyl groups were employed. Weighting schemes were of the form $w^{-1} = \sigma^2(F) + gF^2$ (**1**) and $w^{-1} = [\sigma^2(F_o)^2 + (aP)^2 + bP]$ with $P = (F_o^2 + 2F_c^2)/3$ (**6**, **7**), respectively.

Special features of refinement. Compound **1** crystallizes with 2.5 CDCl$_3$ molecules per formula unit. The D atoms were not included in the refinements. In compound **7**, the phenyl groups C(111)–C(116) and C(21)–C(26) are statically disordered. For both rings, two alternative positions were refined.

A summary of crystal data is presented in Table 6; fractional atomic coordinates are given in Tables 7–9. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

This work was supported by the Fonds der Chemischen Industrie. We thank Riedel de Haën, Seelze, Germany for a gift of perfluoro-polyether oil. Technical assistance in diffractometer maintenance by A. Weinkauf is gratefully acknowledged.

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Received 14*th June* 1993; *Paper* 3/03414C