Gold complexes with selenium ligands
3. Cationic gold(I) complexes with phosphine selenide ligands

Peter G. Jones and **Carsten Thöne**

Institut für Anorganische und Analytische Chemie der Technischen Universität, Hagenring 30, 3300 Braunschweig (F.R.G.)

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Abstract

The cationic gold complexes $[(Ph_3PSe)_2Au]^+$ (**1**) and $[(Ph_3P)Au(SePPh_3)]^+$ (**2**) are obtained in good yield as their SbF_6^- salts from the appropriate reaction between LAuCl, $AgSbF_6$ and L′. Attempts to prepare other cationic complexes $[L''Au(SePPh_3)]^+$ (where L″ is a phosphine other than PPh_3) led to some decomposition to metallic gold, and concomitantly poorly characterised or uncharacterised products, but the isolation in low yield of $[(Ph_3P)Au(SePPhMe_2)]^+$ (**3**) from a corresponding reaction with Ph_3PSe and $PhMe_2PAuCl$ demonstrates that selenium is exchanged between phosphines. Complexes **1** and **3** were characterised by X-ray structure determination; complex **2** is severely disordered.

Introduction

We have recently begun a systematic investigation of gold complexes with selenium ligands [1, 2]. Here we describe attempts to prepare cationic gold(I) complexes involving the ligand triphenylphosphine selenide, Ph_3PSe. The preparation and structure of $Ph_3PSeAuCl$ have already been described [3].

Experimental

X-ray structure determination of compound 1

Crystal data

$C_{36}H_{30}AuF_6P_2SbSe_2$, $M=1114.7$, triclinic, $P\bar{1}$, $a=13.058(2)$, $b=10.589(2)$, $c=14.047(3)$ Å, $\alpha=89.60(2)$, $\beta=86.77(2)$, $\gamma=72.23(2)°$, $U=1846.7$ Å^3, $Z=2$, $D_x=2.00$ Mg m^{-3}, λ(Mo Kα)$=0.71069$ Å, $\mu=6.6$ mm^{-1}, $F(000)=1056$, $T=18$ °C.

Data collection and reduction

A colourless prism $0.35\times0.2\times0.2$ mm was mounted in a glass capillary. A total of 9319 intensities were measured on a Stoe–Siemens four-circle diffractometer using monochromated Mo Kα radiation ($2\theta_{max}=50°$). An absorption correction based on ψ-scans was applied (transmissions 0.80–0.92). Averaging equivalents gave 6499 unique reflections (R_{int} 0.018), of which 5328 with $F>4\sigma(F)$ were used for all calculations (program system XLS, written by G. M. Sheldrick). Cell constants were refined from 2θ values of 52 reflections in the range 20–23°.

Structure solution and refinement

The structure was solved by the heavy-atom method and subjected to anisotropic full-matrix least-squares refinement on F. H atoms were included using a riding model. The final R value was 0.029, with R_W 0.026. The weighting scheme was $w^{-1}=\sigma^2(F)+gF^2$, with $g=0.0001$. 433 parameters; $S=1.4$; max. $\Delta/\sigma=0.001$; max. $\Delta\rho=0.6$ eÅ^{-3}. Final atom coordinates are given in Table 1, with derived bond lengths and angles in Table 2.

Attempted X-ray structure determination of compound 2

The apparent cell is I-centred tetragonal, with cell constants (at room temperature) $a=14.323$, $c=17.530$ Å, $Z=4$. An ordered structure is inconsistent with the Z value; the structure appears to be severely disordered, with triphenylphosphine ligands defining a cage within which no single chemically sensible arrangement of heavy atoms could be distinguished. A check for possible halved axes or incorrect Laue symmetry proved negative.

X-ray structure determination of compound 3

Crystal data

$C_{26}H_{26}AuF_6P_2SbSe$, $M=912.1$, triclinic, $P\bar{1}$, $a=10.195(6)$, $b=10.800(6)$, $c=13.661(8)$ Å, $\alpha=98.47(5)$, $\beta=102.49(4)$, $\gamma=93.46(4)°$, $U=1446$ Å^3, $Z=2$, $D_x=2.10$ Mg m^{-3}, μ(Mo Kα)$=7.3$ mm^{-1}, $F(000)=860$, $T=-95$ °C.

0020-1693/91/$3.50

TABLE 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\AA^2 \times 10^3$) for compound **1**

	x	y	z	U_{eq} [a]
Au(1)	1746.2(2)	712.4(2)	4205.2(1)	44(1)
Se(1)	29.5(4)	492.2(6)	3874.0(3)	52(1)
Se(2)	3464.6(4)	731.5(5)	4696.3(4)	54(1)
P(1)	168.6(9)	205(1)	2335.3(8)	37(1)
C(111)	−1108(4)	45(4)	2043(3)	42(2)
C(112)	−1731(4)	849(5)	1385(3)	49(2)
C(113)	−2713(4)	706(6)	1198(4)	65(2)
C(114)	−3078(5)	−224(7)	1647(5)	70(3)
C(115)	−2465(5)	−1028(6)	2307(5)	74(3)
C(116)	−1483(4)	−906(5)	2504(4)	61(2)
C(121)	1192(4)	−1268(4)	1898(3)	42(2)
C(122)	992(4)	−1976(5)	1133(3)	54(2)
C(123)	1803(5)	−3036(6)	734(4)	69(3)
C(124)	2814(5)	−3386(6)	1087(5)	74(3)
C(125)	3011(5)	−2697(6)	1842(5)	79(3)
C(126)	2202(4)	−1640(5)	2260(4)	58(2)
C(131)	405(3)	1602(5)	1719(3)	41(2)
C(132)	1087(4)	1407(5)	912(4)	59(2)
C(133)	1264(5)	2475(7)	451(5)	73(3)
C(134)	773(5)	3731(7)	792(5)	76(3)
C(135)	76(6)	3932(6)	1570(5)	89(3)
C(136)	−105(5)	2864(5)	2044(4)	70(3)
P(2)	3675(1)	2389(1)	3872.5(8)	40(1)
C(211)	3877(4)	2077(5)	2602(3)	43(2)
C(212)	3731(4)	951(5)	2211(4)	57(2)
C(213)	3883(5)	756(7)	1231(4)	74(3)
C(214)	4198(5)	1651(7)	659(4)	73(3)
C(215)	4359(5)	2743(6)	1046(4)	64(2)
C(216)	4207(4)	2962(5)	2026(3)	55(2)
C(221)	4894(4)	2629(4)	4267(3)	40(2)
C(222)	5850(4)	2087(6)	3760(4)	58(2)
C(223)	6803(4)	2143(7)	4089(4)	71(3)
C(224)	6811(5)	2758(6)	4936(5)	65(3)
C(225)	5857(5)	3301(7)	5453(5)	81(3)
C(226)	4908(4)	3242(6)	5122(4)	66(2)
C(231)	2537(3)	3870(5)	4073(3)	44(2)
C(232)	2115(4)	4212(6)	5013(4)	59(2)
C(233)	1257(5)	5336(6)	5181(5)	72(3)
C(234)	799(5)	6125(6)	4451(6)	76(3)
C(235)	1196(5)	5773(6)	3528(5)	75(3)
C(236)	2067(4)	4657(5)	3338(4)	62(2)
Sb	3492.7(3)	4471.6(4)	8169.1(2)	53(1)
F(1)	4497(3)	4816(4)	7295(3)	103(2)
F(2)	2540(3)	4131(5)	9075(3)	129(3)
F(3)	2664(4)	4208(5)	7231(3)	131(3)
F(4)	4363(4)	4703(6)	9114(3)	137(3)
F(5)	4261(3)	2696(4)	8134(4)	133(3)
F(6)	2748(4)	6235(4)	8235(4)	147(3)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

TABLE 2. Selected bond lengths (Å) and angles (°) for compound **1**

Au(1)–Se(1)	2.395(1)
Au(1)–Se(2)	2.390(1)
Se(1)–P(1)	2.174(1)
Se(2)–P(2)	2.173(1)
P(1)–C(111)	1.796(5)
P(1)–C(121)	1.801(4)
P(1)–C(131)	1.806(5)
P(2)–C(211)	1.806(5)
P(2)–C(221)	1.804(5)
P(2)–C(231)	1.812(4)
Se(1)–Au(1)–Se(2)	172.6(1)
Au(1)–Se(1)–P(1)	102.6(1)
Au(1)–Se(2)–P(2)	100.3(1)
Se(1)–P(1)–C(111)	104.6(2)
Se(1)–P(1)–C(121)	115.5(2)
C(111)–P(1)–C(121)	107.2(2)
Se(1)–P(1)–C(131)	111.9(2)
C(111)–P(1)–C(131)	109.9(2)
C(121)–P(1)–C(131)	107.5(2)
Se(2)–P(2)–C(211)	114.2(2)
Se(2)–P(2)–C(221)	105.1(2)
C(211)–P(2)–C(221)	106.9(2)
Se(2)–P(2)–C(231)	111.6(2)
C(211)–P(2)–C(231)	107.8(2)
C(221)–P(2)–C(231)	111.1(2)

Data collection and reduction

A colourless tablet 0.35×0.2×0.08 mm was mounted in inert oil and transferred to the cold gas stream of the diffractometer (Siemens R3 with LT-2 low temperature attachment). A total of 6044 intensities was measured to $2\theta_{max}$ 50°. An absorption correction was applied with DIFABS (transmissions 0.78–1.41). Cell constants were refined from setting angles of 50 reflections in the 2θ range 20–28°. Averaging equivalents gave 5038 unique reflections (R_{int} 0.026), of which 3732 with $F > 4\sigma(F)$ were used for all calculations (program system 'Siemens Shelxtl Plus').

Structure solution and refinement

As for compound **1**, with the following differences: R 0.042, R_w 0.040, 334 parameters, g 0.0003, S 1.4, max. Δ/σ 0.003, max. $\Delta\rho$ 2.4 e$\AA^{-3}$ near Sb. Final atomic coordinates are given in Table 3, with derived bond lengths and angles in Table 4.

See also 'Supplementary material'.

Preparation of [$(Ph_3PSe)_2Au$][SbF_6] (1)

Ph_3PSe (682 mg, 1 mmol) and (tht)AuCl (tht = tetrathiophene; 321 mg, 1 mmol) are dissolved in 50 ml CH_2Cl_2/ether (3:2). After 1 h stirring, the solution is concentrated to 20 ml, and a solution of Ph_3PSe (682 mg, 1 mmol) in the same solvent is added together with 343 mg (1 mmol) solid $AgSbF_6$. After 1 h stirring, the solution is filtered through SiO_2/$MgSO_4$ and the product precipitated with ether. After recrystallisation from CH_2Cl_2/petrol, the yield

TABLE 3. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^4) for compound **3**

	x	y	z	U_{eq}
Au(1)	3606.9(4)	3563.0(4)	9009.5(3)	205(1)
Se(1)	5221(1)	5006(1)	8578.6(7)	275(3)
P(1)	4160(3)	5110(2)	7035(2)	234(8)
C(111)	3812(9)	3585(9)	6224(6)	204(30)
C(112)	2653(12)	3316(14)	5470(9)	572(51)
C(113)	2412(13)	2176(14)	4836(10)	652(55)
C(114)	3297(14)	1291(12)	4953(9)	517(49)
C(115)	4466(14)	1590(11)	5697(9)	519(51)
C(116)	4728(12)	2715(10)	6349(8)	386(39)
C(121)	2615(11)	5824(11)	7011(9)	415(43)
C(131)	5255(11)	6069(10)	6525(8)	374(40)
P(2)	2223(2)	2131(2)	9460(2)	192(8)
C(211)	3116(10)	1484(8)	10555(7)	246(32)
C(212)	2413(10)	1058(10)	11243(7)	298(35)
C(213)	3105(12)	513(11)	12028(7)	392(41)
C(214)	4470(12)	402(11)	12164(8)	435(43)
C(215)	5170(11)	857(10)	11505(8)	393(40)
C(216)	4501(10)	1412(9)	10711(8)	279(34)
C(221)	1709(9)	771(9)	8451(7)	231(31)
C(222)	1245(9)	−379(8)	8662(7)	237(32)
C(223)	904(10)	−1402(9)	7885(7)	312(36)
C(224)	983(10)	−1284(9)	6915(7)	286(34)
C(225)	1416(11)	−146(10)	6701(7)	348(37)
C(226)	1800(10)	890(9)	7477(7)	262(33)
C(231)	697(9)	2680(8)	9773(6)	192(29)
C(232)	797(11)	3611(9)	10620(7)	284(34)
C(233)	−346(11)	4076(10)	10848(8)	348(38)
C(234)	−1602(11)	3609(10)	10233(8)	344(39)
C(235)	−1711(10)	2718(10)	9395(8)	325(37)
C(236)	−547(10)	2243(9)	9156(7)	276(34)
Sb(1)	8699(1)	3224(1)	6247(1)	601(4)
F(1)	7935(9)	1878(7)	6717(6)	766(35)
F(2)	7168(9)	3102(16)	5193(8)	1673(81)
F(3)	7909(9)	4305(9)	7065(10)	1121(55)
F(4)	10256(7)	3389(6)	7279(4)	455(24)
F(5)	9500(11)	2063(17)	5465(7)	1791(83)
F(6)	9452(10)	4458(19)	5734(13)	2492(120)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

is 920 mg of **1** as colourless crystals (83%); m.p. 221 °C (d). ^{31}P NMR ($CDCl_3$, H_3PO_4 ext.): δ 32.36 ppm (s, with satellites from P–Se coupling, J_{P-Se} 548 Hz); ^{77}Se NMR ($CDCl_3$, Me_2Se ext.): δ −77.25 ppm (d, J_{P-Se} 547 Hz). *Anal.* Calc. for $C_{36}H_{30}AuF_6P_2SbSe_2$: C, 38.8; H, 2.8; Au, 17.5. Found: C, 38.8; H, 2.7; Au, 17.7%.

Preparation of [(Ph$_3$P)Au(SePPh$_3$)][SbF$_6$] (2)

Ph_3PAuCl (498 mg, 1 mmol) is dissolved in 50 ml CH_2Cl_2/ether (3:2) and stirred with 343 mg (1 mmol) $AgSbF_6$ in the dark for 1 h. After filtration through $SiO_2/MgSO_4$, a solution of 341 mg (1 mmol) Ph_3PSe in 10 ml CH_2Cl_2 is added to the filtrate. After 1 h stirring, the solution is concentrated to 20 ml and the product precipitated with ether. Recrystallisation from CH_2Cl_2/ether gives 870 mg of **2** as white crystals (84%); m.p. 218 °C (d). ^{31}P NMR ($CDCl_3$, H_3PO_4 ext.): δ 34.65 ppm (s, Ph_3PSe, satellites from P–Se coupling, J_{P-Se} 549 Hz), 38.3 ppm (s, Ph_3PAu); ^{77}Se NMR ($CDCl_3$, Me_2Se ext.): δ −97.45 ppm (d, J_{P-Se} 551 Hz). *Anal.* Calc. for $C_{36}H_{30}AuF_6P_2SbSe$: C, 41.7; H, 2.9; Se, 7.7. Found: C, 41.5; H, 3.0; Se, 7.6%.

TABLE 4. Selected bond lengths (Å) and angles (°) for compound **3**

Au(1)–Se(1)	2.422(1)	Au(1)–P(2)	2.270(3)
Se(1)–P(1)	2.174(2)	P(1)–C(111)	1.813(9)
P(1)–C(121)	1.792(12)	P(1)–C(131)	1.792(12)
P(2)–C(211)	1.830(10)	P(2)–C(221)	1.825(9)
P(2)–C(231)	1.811(10)		
Se(1)–Au(1)–P(2)	175.8(1)	Au(1)–Se(1)–P(1)	99.1(1)
Se(1)–P(1)–C(111)	112.7(3)	Se(1)–P(1)–C(121)	111.6(4)
C(111)–P(1)–C(121)	109.4(4)	Se(1)–P(1)–C(131)	106.6(3)
C(111)–P(1)–C(131)	107.6(5)	C(121)–P(1)–C(131)	108.8(6)
Au(1)–P(2)–C(211)	110.9(3)	Au(1)–P(2)–C(221)	110.6(3)
C(211)–P(2)–C(221)	104.4(4)	Au(1)–P(2)–C(231)	116.4(3)
C(211)–P(2)–C(231)	106.8(5)	C(221)–P(2)–C(231)	107.0(4)

Results and discussion

General methods of preparation of gold(I) cations $[LAuL']^+$ are well-known [4] and usually involve the reaction of a chlorocomplex LAuCl with a silver salt such as $AgSbF_6$ in the presence of the second ligand L′. The reaction with $Ph_3PSeAuCl$ and Ph_3PSe proceeds smoothly to give the expected product $[(Ph_3PSe)_2Au][SbF_6]$ (**1**) in good yield. Similarly, $[(Ph_3P)Au(SePPh_3)][SbF_6]$ (**2**) can be obtained from Ph_3PAuCl and Ph_3PSe. The structure of **1** was determined by X-ray crystallography; **2** proved to be severely disordered (see above).

Attempts to prepare similar complexes using other phosphines and Ph_3PSe were essentially unsuccessful, but the results were nonetheless instructive.

The reaction between $Me_2PhPAuCl$, Ph_3PSe and $AgSbF_6$ led to considerable decomposition to metallic gold and an oily product. ^{31}P NMR spectra indicated the presence of Ph_3PSe as the major species in solution (δ 35.6, J_{P-Se} 745 Hz), with a small amount of another species with δ 21.9 ppm. Fractional crystallisation yielded a small amount of a gold-containing product, which was characterised by X-ray methods (see below) as $[(Ph_3P)Au(SePPhMe_2)]^+[SbF_6]^-$ (**3**); the selenium atom has thus been transferred from one phosphine residue to the other.

The reaction between Et_3PAuCl, Ph_3PSe and $AgSbF_6$ also led to some decomposition to metallic gold. After filtration, the solution was crystallised to yield at first unchanged Ph_3PSe. The remaining solution was evaporated to dryness. ^{31}P NMR spectra of the residue indicated the presence of more free Ph_3PSe, plus a signal of approximately equal intensity with δ 54.8 ppm. J_{P-Se} 541 Hz. This signal does not belong to free Et_3P, Et_3PAuCl or $[(Et_3P)_nAu]^+$ [5]; if we assume that P–Se coupling constants of *c.* 550 Hz are typical of the P–Se–Au moiety, then an as yet unknown gold–(phosphine selenide) complex must be present in solution. It is clear that the reactions and equilibria in solution are complicated; in future experiments, in particular NMR studies, we hope to resolve some of these problems.

The X-ray structure determinations of **1** and **3** both reveal the expected linear coordination at gold (Figs. 1 and 2), although slight deviations from ideal linearity are observed (Se–Au–P 172.6, 175.8°). No short Au...Au contacts are observed. The Au–Se bonds in **1** (2.390, 2.395 Å) are somewhat longer than in $Ph_3PSeAuCl$ (2.371 Å) [3]). In **3** the Au–Se bond is longer still (2.422 Å), a typical value for Au(I)–Se *trans* to P [1, 6] and presumably due to the *trans* influence of the phosphine ligand. The P–Se bond lengths are all similar (2.173, 2.174 Å in **1**, 2.174 Å in **3**, 2.187(5) Å in $Ph_3PSeAuCl$ [3]), as are the P–Se–Au angles (100.3, 102.6° in **1**, 99.1° in **3**, 100.1° in $Ph_3PSeAuCl$). The relative conformation of the ligands in **1** is described by the torsion angle P(1)–Se(1)...Se(2)–P(2) of 59°.

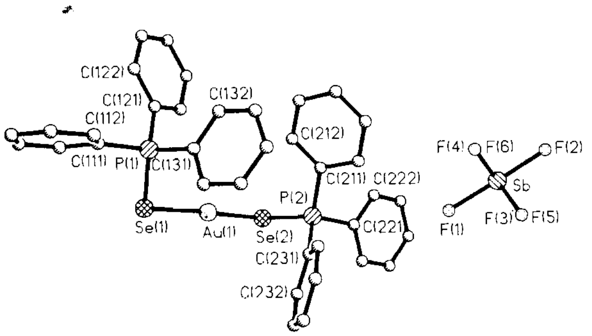

Fig. 1. The structure of compound **1** in the crystal. Radii are arbitrary; H atoms omitted for clarity. Two F atoms of the anion are eclipsed.

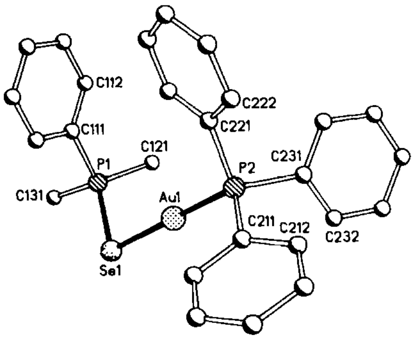

Fig. 2. The cation of compound **3** in the crystal. Radii are arbitrary; H atoms omitted for clarity.

Supplementary material

Further details of the structure determinations (complete bond lengths and angles, H atom coordinates, structure factors, temperature factors) have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany. Any request for this material should quote a full literature citation and the reference number CSD54932.

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