Gold Complexes with Selenium Ligands, V [1]

Synthesis and Crystal Structure of $[(Ph_3PAu)_2Se(p\text{-}C_6F_4Cl)]^+SbF_6^-$

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Gold Complexes, X-Ray, Selenium Ligands

The binuclear complex $[(Ph_3PAu)_2Se(p\text{-}C_6F_4Cl)]^+SbF_6^-$ was prepared from Ph_3PAuCl and $(p\text{-}C_6F_4Cl)_2Se_2$ in the presence of $AgSbF_6$. The crystal structure shows a short intramolecular gold-gold interaction, which leads to an extreme distortion in the coordination geometry at selenium.

Introduction

We have recently reported the preparation and crystal structure of the binuclear, cationic phenylselenolato complex $[(Ph_3PAu)_2SePh]^+SbF_6^-$ [2]:

$$2\,Ph_3PAuCl + Ph_2Se_2 + 2\,AgSbF_6 \rightarrow [(Ph_3PAu)_2SePh]^+SbF_6^- + 2\,AgCl + \text{other products}$$

We have now begun to study a systematic extension of this reaction by varying the organic groups R of the diselenides. The mechanism of this reaction is not well understood, but it seems that the electronic properties of the selenolato ligand play an important role. We report here the synthesis and crystal structure of $[(Ph_3PAu)_2Se(p\text{-}C_6F_4Cl)]^+SbF_6^-$.

Experimental

^{31}P, ^{77}Se NMR spectroscopy: *Bruker* AC-200, – Elemental analyses: locally. The reactions were performed with dried solvents under N_2-atmosphere.

Preparation of $(p\text{-}C_6F_4Cl)_2Se_2$: This diselenide was prepared according to modified literature methods from $p\text{-}BrC_6F_4Cl$ and Li_2Se_2 [3, 4].

Preparation of $[(Ph_3PAu)_2Se(p\text{-}C_6F_4Cl)]^+SbF_6^-$: 686 mg $AgSbF_6$ (2 mmol) is added with stirring to a solution of 996 mg Ph_3PAuCl (2 mmol) and 525 mg $(p\text{-}C_6F_4Cl)_2Se_2$ (1 mmol) in 100 ml CH_2Cl_2/diethyl ether (3:2). After 1 h stirring, the brown precipitate is filtered off ($SiO_2/MgSO_4$) and the solution is concentrated to 30 ml. The product is precipitated with ether and recrystallised from CH_2Cl_2/ether. Yield 1,3 g (87%). – M.p. 153 °C (dec.).

Analysis

Calcd	C 35.6	H 2.1	P 4.4,
Found	C 34.1	H 2.1	P 4.1.

^{31}P NMR (CH_2Cl_2, C_6D_6 int. lock, Ph_3PSe int.): δ (ppm) 38.8 (s). – ^{77}Se NMR ($CDCl_3$:d_6-DMSO 5:1, Me_2Se ext.): δ (ppm) + 120 (s).

Crystal structure determination of $[(Ph_3PAu)_2Se(p\text{-}C_6F_4Cl)]^+SbF_6^-$. Crystal data: $C_{42}H_{30}Au_2ClF_{10}P_2SbSe$, M = 1416.5, space group $P\bar{1}$, a = 13.400(6), b = 13.930(6), c = 15.082(6) Å, α = 67.26(3)°, β = 73.35(3)°, γ = 62.95(3)°, U = 2291 Å^3, Z = 2, D_x = 2.03 Mg m^{-3}, F(000) = 1408, λ (MoKα) = 0.71069 Å, μ = 8.0 mm^{-1}, T = 173 K.

Data collection and reduction: A colourless tablet 0.72×0.48×0.14 obtained from liquid diffusion of ether into a CH_2Cl_2-solution was mounted on a glass fiber in inert oil. 10218 intensities were measured on a Siemens four-circle diffractometer with an LT-2 low temperature attachment using monochromated MoKα radiation ($2\theta_{max.}$ 50°). An absorption correction based on ψ-scans was applied, with transmission factors 0.38–1.00. Merging equivalents gave 8013 unique reflections (R_{int} 0.021), of which 6774 with $F > 4\sigma(F)$ were used for all calculations. Cell constants were refined from setting angles of 50 reflections in the range 2θ = 20–23°.

Structure solution and refinement: The structure was solved by the heavy-atom method and refined anisotropically on F to R 0.041, R_w 0.042. H atoms were included using a riding model. The weighting scheme was $w^{-1} = \sigma^2(F) + gF^2$, with g 0.0006. 560 parameters; max. Δ/σ 0.004; max. $\Delta\varrho$ 2.9 e Å^{-3} near Au 1; S 1.6. Final atomic coordinates are given in Table I, with derived molecular dimensions in Table II [5]. The crystallographic program system used was "Siemens SHELXTL PLUS".

Discussion

The title compound can be easily prepared by the reaction of Ph_3PAuCl and $(p\text{-}C_6F_4Cl)_2Se_2$ with solid $AgSbF_6$, analogous to the preparation of $[(Ph_3PAu)_2SePh]^+SbF_6^-$. The mechanism of this reaction is not clear. Fackler *et al.* proposed an induced reduction of $PhCh_2SSCH_2Ph$ through gold(I) centers for the similar thiolato complex $[(Ph_3PAu)_2SCH_2Ph]^+NO_3^-$ [6], but the by-prod-

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Table I. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^4$).

	x	y	z	U(eq)
Au(1)	931.2(3)	53.7(3)	3341.3(2)	258(2)
Au(2)	75.8(3)	1816.1(3)	4380.8(2)	274(2)
Se(1)	1509.0(7)	− 130.3(6)	4825.3(5)	251(4)
C(11)	2959(7)	− 49(7)	4272(5)	261(37)
C(12)	3257(7)	749(7)	4358(6)	337(41)
C(13)	4310(8)	742(8)	4028(7)	405(47)
C(14)	5127(8)	− 27(9)	3586(7)	437(50)
C(15)	4849(7)	− 829(8)	3492(6)	401(44)
C(16)	3802(7)	− 828(7)	3828(6)	323(40)
F(12)	2473(4)	1525(4)	4801(4)	484(29)
F(13)	4539(5)	1550(6)	4126(5)	746(44)
Cl(14)	6440(2)	19(3)	3129(2)	711(18)
F(15)	5630(5)	−1590(5)	3042(4)	615(34)
F(16)	3558(4)	−1582(4)	3673(4)	478(29)
Sb(1)	3208.0(6)	2496.2(6)	1326.3(5)	469(3)
F(1)	1805(5)	2614(5)	1213(4)	600(34)
F(2)	3674(6)	947(5)	1870(4)	684(36)
F(3)	2595(6)	2697(5)	2559(5)	746(39)
F(4)	2745(6)	4054(6)	758(7)	946(45)
F(5)	3758(6)	2314(7)	92(5)	915(42)
F(6)	4593(7)	2382(7)	1449(9)	1209(64)
P(1)	529(2)	134(2)	1943(1)	252(9)
C(111)	− 662(6)	1371(6)	1459(5)	259(36)
C(112)	− 652(8)	2434(7)	1280(6)	345(43)
C(113)	−1521(8)	3414(7)	863(6)	375(43)
C(114)	−2432(8)	3350(8)	640(7)	414(45)
C(115)	−2461(8)	2291(8)	859(7)	424(47)
C(116)	−1584(7)	1319(7)	1251(6)	335(41)
C(121)	208(7)	−1074(7)	2128(6)	290(39)
C(122)	− 517(7)	−1364(7)	2931(6)	309(40)
C(123)	− 799(9)	−2275(8)	3098(7)	465(52)
C(124)	− 323(8)	−2883(8)	2449(7)	441(50)

Table I (continued).

	x	y	z	U(eq)
C(125)	421(8)	−2614(7)	1656(6)	401(47)
C(126)	703(8)	−1715(7)	1486(6)	351(43)
C(131)	1716(7)	107(7)	994(6)	286(37)
C(132)	1576(7)	708(7)	30(6)	367(43)
C(133)	2485(8)	625(8)	− 666(7)	444(51)
C(134)	3569(9)	− 32(8)	− 443(7)	500(53)
C(135)	3718(8)	− 628(10)	499(8)	604(59)
C(136)	2794(7)	− 559(8)	1236(7)	439(47)
P(2)	−1406(2)	3519(2)	4097(2)	300(10)
C(211)	−2700(8)	3368(7)	4103(7)	378(43)
C(212)	−3692(8)	3771(8)	4700(9)	592(60)
C(213)	−4649(9)	3696(10)	4627(12)	832(83)
C(214)	−4620(10)	3246(9)	3930(12)	803(81)
C(215)	−3621(11)	2798(10)	3377(9)	644(72)
C(216)	−2657(9)	2848(8)	3481(7)	462(52)
C(221)	−1712(7)	4205(7)	5000(6)	356(42)
C(222)	−1993(9)	3653(9)	5972(7)	529(53)
C(223)	−2248(9)	4147(11)	6687(8)	659(67)
C(224)	−2172(11)	5151(11)	6460(9)	718(75)
C(225)	−1891(16)	5689(12)	5516(10)	1009(110)
C(226)	−1648(12)	5228(9)	4777(9)	750(78)
C(231)	−1247(7)	4516(7)	2916(6)	320(40)
C(232)	− 222(8)	4317(8)	2331(7)	408(46)
C(233)	− 156(9)	5062(8)	1406(7)	444(50)
C(234)	−1085(9)	5996(8)	1080(7)	469(55)
C(235)	−2096(9)	6207(8)	1651(7)	479(51)
C(236)	−2188(8)	5473(8)	2578(7)	430(47)
C(1)	5369(12)	5801(13)	1566(10)	901(97)
Cl(1)	4768(3)	6520(3)	2411(2)	710(17)
Cl(2)	4494(3)	5369(5)	1279(3)	1171(33)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table II. Selected bond lengths (Å) and angles (°).

Au(1)···Au(2)	3.031(1)	Au(1)−Se(1)	2.458(2)
Au(1)−P(1)	2.272(3)	Au(2)−Se(1)	2.467(1)
Au(2)−P(2)	2.274(2)	Se(1)−C(11)	1.919(9)
C(14)−Cl(14)	1.717(11)	P(1)−C(111)	1.801(7)
P(1)−C(121)	1.823(11)	P(1)−C(131)	1.806(8)
P(2)−C(211)	1.836(12)	P(2)−C(221)	1.807(12)
P(2)−C(231)	1.813(8)		
Au(2)···Au(1)−Se(1)	52.1(1)	Au(2)···Au(1)−P(1)	131.4(1)
Se(1)−Au(1)−P(1)	175.8(1)	Au(1)···Au(2)−Se(1)	51.9(1)
Au(1)···Au(2)−P(2)	128.1(1)	Se(1)−Au(2)−P(2)	172.8(1)
Au(1)−Se(1)−Au(2)	76.0(1)	Au(1)−Se(1)−C(11)	98.1(3)
Au(2)−Se(1)−C(11)	107.0(2)	C(12)−C(11)−C(16)	115.9(8)
Au(1)−P(1)−C(111)	115.0(3)	Au(1)−P(1)−C(121)	110.5(3)
C(111)−P(1)−C(121)	106.1(4)	Au(1)−P(1)−C(131)	111.1(4)
C(111)−P(1)−C(131)	106.1(3)	C(121)−P(1)−C(131)	107.7(4)
Au(2)−P(2)−C(211)	111.2(3)	Au(2)−P(2)−C(221)	112.3(3)
C(211)−P(2)−C(221)	107.1(5)	Au(2)−P(2)−C(231)	114.8(2)
C(211)−P(2)−C(231)	103.2(4)	C(221)−P(2)−C(231)	107.5(5)

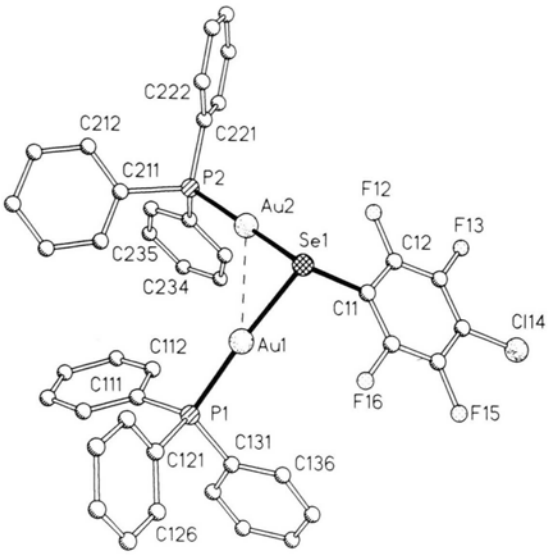

Fig. 1. The cation of the title compound in the crystal, showing the atom numbering scheme. Radii are arbitrary; H atoms are omitted for clarity.

ucts in both cases have not been determined. Interestingly, the reaction of Ph_3PAuCl and MeSeSeMe with $AgSbF_6$ leads to an oily mixture, which decomposes very fast under the same conditions. Thus the electronic properties of the organic diselenide substituents probably play an important role.

The title compound crystallises with one formula unit and one dichloromethane molecule per asymmetric unit. As expected, both gold atoms show only slight deviations from a linear coordination [Se–Au–P 175.8(1), 172.8(1)°]. In contrast to the phenylselenolato complex, only an intramolecular gold–gold interaction can be observed [Au–Au 3.031(1) Å]. Such interactions are well documented [7–9]. In this case, they give rise to an extreme distortion from ideal geometry at selenium [Au–Se–Au 76.0(1)°]. The other bond angles at selenium are similar to those in $[(Ph_3PAu)_2SePh]^+SbF_6^-$ [Au–Se–C 98.1(3), 107.0(2)°], in which the second value is probably due to the steric demand of the halogenated phenyl group.

The Au–Se bond lengths of 2.458(2), 2.467(1) Å are somewhat longer than the 2.445(2) Å (av. of two Au–Se bonds) observed in $[(Ph_3PAu)_2SePh]^+SbF_6^-$, which may reflect the greater group electronegativity of the C_6F_4Cl substituent.

As in many metal-pentafluorophenyl complexes the *ipso* angle of the C_6F_4Cl ring is narrow [115.9(8)°] [10].

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