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Selenolate Gold Complexes with Aurophilic Au(I)–Au(I) and Au(I)–Au(III) Interactions

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The gold(I) selenolate compound [$Au_2(SePh)_2(\mu\text{-dppf})$] (dppf = 1,1′-bis(diphenylphosphino)ferrocene) has been prepared by reaction of [$Au_2Cl_2(\mu\text{-dppf})$] with $PhSeSiMe_3$ in a molar ratio 1:2. This complex reacts with gold(I) or gold(III) derivatives to give polynuclear gold(I)–gold(I) or gold(I)–gold(III) complexes of the type [$Au_4(\mu\text{-SePh})_2(PPh_3)_2(\mu\text{-dppf})$]$(OTf)_2$, [$Au_3(C_6F_5)_3(\mu\text{-SePh})_2(\mu\text{-dppf})$], or [$Au_4(C_6F_5)_6(\mu\text{-SePh})_2(\mu\text{-dppf})$], with bridging selenolate ligands. The reaction of [$Au_2(SePh)_2(\mu\text{-dppf})$] with 1 equiv of AgOTf leads to the formation of the insoluble Ag(SePh) and the compound [$Au_2(\mu\text{-SePh})(\mu\text{-dppf})$]OTf. The complexes [$Au_4(C_6F_5)_6(\mu\text{-SePh})_2(\mu\text{-dppf})$] and [$Au_2(\mu\text{-SePh})(\mu\text{-dppf})$]OTf (two different solvates) have been characterized by X-ray diffraction studies and show the presence of weak gold(I)–gold(III) interactions in the former and intra- and intermolecular gold(I)–gold(I) interactions in the later.

Introduction

Gold complexes with thiolate ligands have been thoroughly studied because of their importance in several applications such as in medicine, in the glass and ceramics industry, and in the field of nanoparticles.[1,2] However, it is surprising that the analogous gold selenolate chemistry has scarcely been studied until now, despite the great possibilities that the compounds can offer, and only a few complexes have been reported. These include mononuclear gold(I) complexes of the type [$Au(SeR)(PR_3)$] (R = Ph, naphthyl),[3,4] dinuclear gold(I) derivatives such as [$Au_2(\mu\text{-SeR})_2L_2$] (R = Ph, 4-$ClC_6F_4$, CH_2Ph, naphthyl, 4-$NH_2C_6H_4$, 4-ClC_6H_4; L = PPh_3, PPh_2Me, $PPhMe_2$; L_2 = dppm, dppe),[3−6] or heterodinuclear [$WCo(CO)_3Se(CH_2SiMe_3)AuPPh_3$]$SbF_6$.[7] Other oxidation states are even more poorly represented, with only one gold(II) [$Au_2Cl(SePh)\{\mu\text{-}(CH_2)_2PPh_2\}_2$][8] and no gold(III) derivatives having been described.

We are currently working on the chemistry of gold with selenium ligands, and thus, we have reported on gold complexes with a central selenido ligand,[9−11] phosphine selenides,[12,13] and selenoethers,[14] and recently on gold complexes with the *o*-carboranyl selenolate ligand.[15] Here we report on the synthesis of the dinuclear selenolate compound [$Au_2(SePh)_2(\mu\text{-dppf})$] and its reactivity with various metal fragments such as gold(I), gold(III), or silver salts, leading, as one example, to the synthesis of the first mixed gold(I)−gold(III) derivatives with selenolate ligands. The crystal

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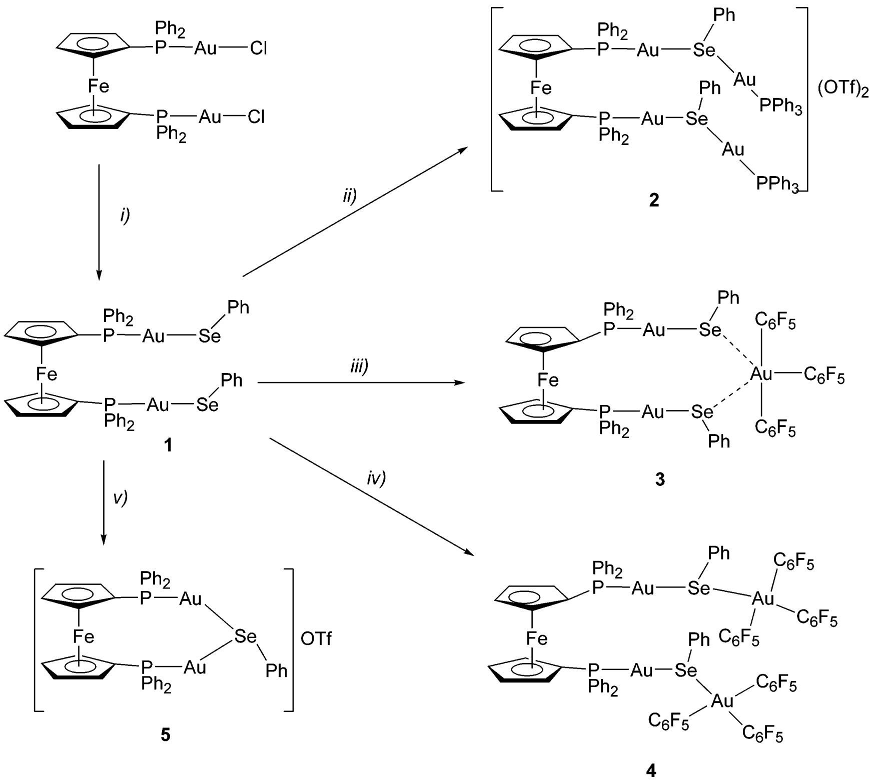
Scheme 1 [a]



[a] (i) 2PhSeSiMe$_3$, (ii) 2[Au(OTf)(PPh$_3$)], (iii) [Au(C$_6$F$_5$)$_3$(OEt$_2$)], (iv) 2[Au(C$_6$F$_5$)$_3$(OEt$_2$)], (v) Ag(OTf).

structures of two of these complexes reveal the presence of gold(I)−gold(I) and weak gold(I)−gold(III) interactions.

Results and Discussion

Synthesis of the Complexes. The reaction of [Au$_2$Cl$_2$-(μ-dppf)] with 2 equiv of PhSeSiMe$_3$ in tetrahydrofuran gives the dinuclear selenolate compound [Au$_2$(SePh)$_2$(μ-dppf)] (**1**) (see Scheme 1). Complex **1** is an air- and moisture-stable solid that behaves as a nonconductor in acetone solution. The ^{1}H NMR spectrum displays two multiplets at 4.14 and 4.45 ppm for the α and β protons of the cyclopentadienyl rings, respectively, and a broad multiplet for the phenyl protons around 7.5 ppm. The ^{31}P(^{1}H) NMR spectrum shows one singlet for the two equivalent phosphorus atoms at 33.0 ppm. The liquid secondary-ion positive mass spectrum (LSIMS+) does not show the presence of the molecular peak, but the fragment arising from the loss of one selenolate ligand appears at $m/z = 1105$ (60%). The loss of one anionic ligand such as a halogen or pseudo-halogen in the LSIMS+ spectra is a relatively common feature in neutral complexes.[15−17]

Complex **1** can react with gold(I) or gold(III) derivatives leading to gold(I)−gold(I) or mixed gold(I)−gold(III) complexes with a bridging selenolate ligand. Thus, the reaction of **1** with 2 equiv of [Au(OTf)(PPh$_3$)] affords the tetranuclear derivative [Au$_4$(μ-SePh)$_2$(PPh$_3$)$_2$(μ-dppf)](OTf)$_2$ (**2**). Compound **2** is an air- and moisture-stable orange solid that behaves as a 1:2 electrolyte in acetone solution. The IR spectrum shows the typical absorptions for the triflate anion. The ^{1}H NMR spectrum presents the two multiplets for the α and β protons of the substituted cyclopentadienyl rings at 4.21 and 4.56 ppm and also a multiplet around 7.4 ppm for the phenyl protons. The ^{31}P(^{1}H) NMR spectrum shows two singlets corresponding to the two different phosphorus environments; the phosphorus of the dppf ligand appears at 31.0 and the phosphorus of the PPh$_3$ at 36.2 ppm. The assignment has been made by comparison with other “Se−Au−PPh$_3$” or “Au−dppf” complexes.[10]

The reaction of complex **1** with 1 equiv of [Au(C$_6$F$_5$)$_3$-(OEt$_2$)] leads to the complex [Au$_3$(C$_6$F$_5$)$_3$(μ-SePh)$_2$(μ-dppf)] (**3**). Complex **3** is an air- and moisture-stable orange solid that behaves as a nonconductor in acetone solution. The IR spectrum shows the typical absorptions for pentafluorophenyl units bonded to gold(III). The ^{1}H NMR spectrum shows broad signals at 4.17 and 4.42 ppm for the α and the β protons of the cyclopentadienyl rings, respectively, and also for the phenyl protons. In the ^{31}P(^{1}H) spectrum, only one resonance for the two phosphorus atoms is present. The ^{19}F NMR spectrum shows the presence of two different types of pentafluorophenyl groups, and five signals appear, which are overlapped; two for the *ortho*, two for the *para*, in a ratio 1:2, and only one signal for the *meta* fluorine. The NMR spectra were also recorded at −85 °C but showed no difference from those at room temperature. With respect to the coordination of the gold(III) center to the selenolate ligands, we can thus propose either a rare pentacoordination of the gold atom bonded to both selenium atoms, or, more probably,

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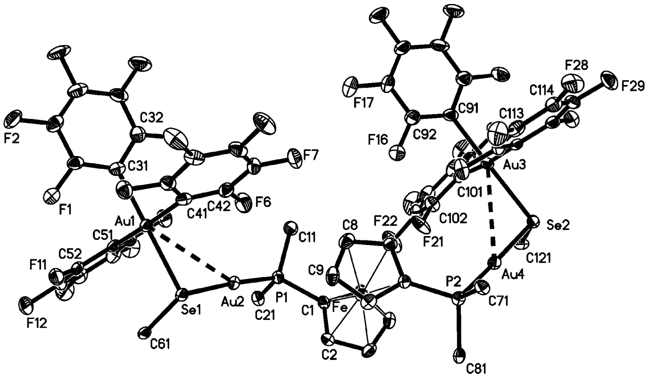

Figure 1. Molecular structure of compound **4** showing the atom numbering scheme. Displacement parameter ellipsoids represent 50% probability surfaces. Phenyl carbon atoms with the exception of the ipso carbon and hydrogen atoms omitted for clarity.

Table 1. Bond Distances (Å) and Lengths (deg) for Compound **4**

Au(1)−C(31)	2.036(3)	Au(4)−P(2)	2.2722(11)
Au(1)−C(51)	2.066(3)	Au(4)−Se(2)	2.4392(5)
Au(1)−C(41)	2.076(3)	Se(2)−C(121)	1.941(4)
Au(1)−Se(1)	2.4878(4)	P(1)−C(1)	1.794(4)
Au(2)−P(1)	2.2647(11)	P(1)−C(21)	1.812(4)
Au(2)−Se(1)	2.4408(5)	P(1)−C(11)	1.816(4)
Se(1)−C(61)	1.933(4)	P(2)−C(6)	1.792(4)
Au(3)−C(91)	2.051(4)	P(2)−C(71)	1.816(4)
Au(3)−C(101)	2.054(3)	P(2)−C(81)	1.820(4)
Au(3)−C(111)	2.061(3)		
Au(3)−Se(2)	2.4896(4)		

P(1)−Au(1)−Se(1)	175.36(8)	Au(2)−Au(3)−Au(4)	137.01(2)
P(1)−Au(1)−Au(2)	123.88(7)	P(4)−Au(4)−Se(2)	177.54(8)
Se(1)−Au(1)−Au(2)	52.28(3)	P(4)−Au(4)−Au(3)	125.25(7)
P(2)−Au(2)−Se(1)	170.03(7)	Se(2)−Au(4)−Au(3)	52.97(3)
P(2)−Au(2)−Au(3)	101.38(7)	C(51)−Se(1)−Au(1)	108.3(6)
Se(1)−Au(2)−Au(3)	87.44(3)	C(51′)−Se(1)−Au(1)	101.2(6)
P(2)−Au(2)−Au(1)	119.13(7)	C(51)−Se(1)−Au(2)	94.9(6)
Se(1)−Au(2)−Au(1)	51.78(3)	C(51′)−Se(1)−Au(2)	109.9(8)
Au(3)−Au(2)−Au(1)	139.18(2)	Au(1)−Se(1)−Au(2)	75.94(3)
P(3)−Au(3)−Se(2)	170.32(7)	C(111)−Se(2)−Au(4)	103.2(3)
P(3)−Au(3)−Au(2)	96.54(7)	C(111)−Se(2)−Au(3)	101.7(3)
Se(2)−Au(3)−Au(2)	91.59(3)	Au(4)−Se(2)−Au(3)	74.62(3)
P(3)−Au(3)−Au(4)	117.98(7)		
Se(2)−Au(3)−Au(4)	52.41(3)		

a rapid exchange of the Au(C_6F_5)$_3$ fragment between both coordination sites. The presence of a four-coordinate fast exchange derivative is also supported for the small differences in the ^{19}F NMR chemical shifts of **3** compare with those of the complex with two Au(C_6F_5)$_3$ groups (**4**, see below).

If the same reaction is carried out in molar ratio 1:2, the complex [$Au_4(C_6F_5)_6(\mu$-SePh$)_2(\mu$-dppf)] (**4**) is isolated. Compound **4** is an air- and moisture-stable orange solid that behaves as a nonconductor in acetone solution. The ^{1}H NMR spectrum shows multiplets at 4.37 and 4.71 ppm, which are assigned at the α and β protons of the cyclopentadienyl units, and another multiplet ranging from 6.9 to 7.5 ppm for the phenyl protons. The ^{31}P(^{1}H) NMR spectrum presents only one signal at 32.6 ppm for the equivalent phosphorus atoms. The ^{19}F NMR spectrum shows the expected equivalence of the Au(C_6F_5)$_3$ groups. Consequently, six resonances appear, two in the *ortho*, two in the *meta*, and two in the *para* region with a ratio 1:2, which is a consequence of the equivalence of the pentafluorophenyl groups in *trans* position in the Au(C_6F_5)$_3$ groups.

The treatment of **1** with the silver salt Ag(OTf) involves the elimination of one selenolate group as [Ag(SePh)]$_n$ and formation of a cyclic complex with a bridging selenolate ligand, [$Au_2(\mu$-SePh$)(\mu$-dppf)]OTf (**5**). Compound **5** is an air- and moisture-stable orange solid that behaves as a 1:1 electrolyte in acetone solution. The ^{1}H NMR spectrum shows two multiplets at 4.18 and 4.55 ppm that are assigned to the α and β protons of the substituted cyclopentadienyl rings. In the ^{31}P(^{1}H) NMR spectrum, one resonance appears at 31.1 ppm for the two equivalent phosphorus atoms. The LSIMS+ shows the cationic molecular peak at $m/z = 1105$ (75%).

Crystal Structures. The crystal structure of complex **4** has been established by X-ray diffraction; the molecule is shown in Figure 1. Selected bond lengths and angles are collected in Table 1. Compound **4** consists of a dppf ligand bridging two "Au(μ-SePh)Au(C_6F_5)$_3$" units, within each of which the selenolato ligand bridges the gold(I) and the gold(III) fragments. The cyclopentadienyl rings are staggered with a torsion angle C(1)−Cent−Cent−C(8) of 23.5° (Cent = ring centroid); the phosphorus substituents subtend a torsion angle of −167.5° across the centroids. The gold···gold distances between the gold(I) and the gold(III) centers, 3.693 Å for Au(1)−Au(2) and 3.578 Å for Au(3)−Au(4), together with very narrow Au−Se−Au angles, 74.62(3)° and 75.94(3)°, point out the presence of weak gold(I)−gold(III) interactions. Although these distances are long compared with those corresponding to Au(I)−Au(I) interactions, we have described several mixed valence derivatives with a central sulfur or selenium ligand in which we have postulated the presence of weak Au(I)−Au(III) contacts with bond distances ranging from 3.2 to 3.6 Å with corresponding interactions energies in the range 21−25 kJ mol^{-1}.[11,18] Theoretical studies at the HF and MP2 level have been carried out for these complexes[11,18] and others,[19,20] supporting the existence of Au(I)−Au(III) and even Au(III)−Au(III) interactions. These studies support the idea that the aurophilic interaction can exist for oxidation state Au(III), although it is much weaker than in gold(I) centers.[19] In the analogous pentafluorophenylthiolate derivative [$Au_4(C_6F_5)_6\{\mu$-S$(C_6F_5)\}_2(\mu$-dppf)], the gold(I)−gold(III) distance is 3.608(2) Å (despite the close similarity of cell constants, the two compounds are not isostructural; this can be seen in the widely differing ligand conformations, with a P−Cent−Cent−P torsion angle of 100.5° in the S(C_6F_5) derivative, and in the different space groups).[16] It is therefore reasonable to propose a weak interaction between the gold atoms in the mixed valence complex. The gold(III) centers display square-planar geometries; both of them lie in the plane formed by three carbons and a selenium donor atom. The Au−C distances range from 2.036(3) to 2.076(3) Å, the shorter values correspond to the Au−C bond *trans* to the selenium atoms (Au(1)−C(31) 2.036(3) Å, Au(3)−C(91) 2.051(4) Å), but the difference at Au(3) is scarcely significant. This fact may reflect the

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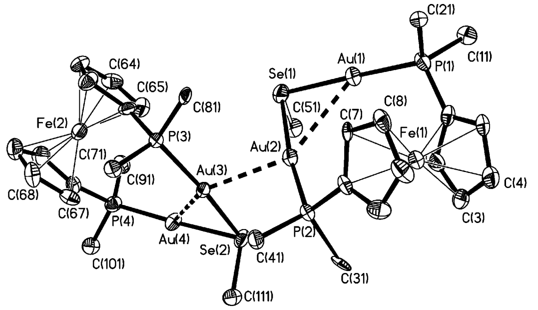

Figure 2. Structure of the two cations in **5** showing the atom numbering scheme. Displacement parameter ellipsoids represent 50% probability surfaces. Phenyl carbon atoms with the exception of the ipso carbon and hydrogen atoms omitted for clarity.

Table 2. Bond Distances (Å) and Lengths (deg) for Compound **5**

Au(1)−P(1)	2.273(3)	Au(3)−P(3)	2.288(3)
Au(1)−Se(1)	2.4454(12)	Au(3)−Se(2)	2.4706(11)
Au(1)−Au(2)	3.0193(7)	Au(3)−Au(4)	2.9839(7)
Au(2)−P(2)	2.275(3)	Au(4)−P(4)	2.274(3)
Au(2)−Se(1)	2.4621(13)	Au(4)−Se(2)	2.4523(12)
Au(2)−Au(3)	2.9238(7)		
P(1)−Au(1)−Se(1)	175.35(8)	Se(2)−Au(3)−Au(4)	52.41(3)
P(1)−Au(1)−Au(2)	123.88(7)	Au(2)−Au(3)−Au(4)	137.01(2)
Se(1)−Au(1)−Au(2)	52.28(3)	P(4)−Au(4)−Se(2)	177.54(8)
P(2)−Au(2)−Se(1)	170.03(7)	P(4)−Au(4)−Au(3)	125.25(7)
P(2)−Au(2)−Au(3)	101.38(7)	Se(2)−Au(4)−Au(3)	52.97(3)
Se(1)−Au(2)−Au(3)	87.44(3)	C(51)−Se(1)−Au(1)	108.3(6)
P(2)−Au(2)−Au(1)	119.13(7)	C(51′)−Se(1)−Au(1)	101.2(6)
Se(1)−Au(2)−Au(1)	51.78(3)	C(51)−Se(1)−Au(2)	94.8(6)
Au(3)−Au(2)−Au(1)	139.18(2)	C(51′)−Se(1)−Au(2)	109.8(8)
P(3)−Au(3)−Se(2)	170.32(7)	Au(1)−Se(1)−Au(2)	75.94(3)
P(3)−Au(3)−Au(2)	96.54(7)	C(111)−Se(2)−Au(4)	103.2(3)
Se(2)−Au(3)−Au(2)	91.59(3)	C(111)−Se(2)−Au(3)	101.7(3)
P(3)−Au(3)−Au(4)	117.98(7)	Au(4)−Se(2)−Au(3)	74.62(3)

lower *trans* influence of the $[PhSe]^-$ ligand. The values compare well with those found in other complexes with a bridging selenide ligand. Similar Au(III)−Se bond distances to those in **4** (2.4874(4), 2.4896(4) Å) have been found in $[\{Se(AuPPh_3)\}_2\{Au(C_6F_5)_2\}_2]$[11] (2.4802(8) Å), or in $[Se\{Au_2(\mu\text{-dppf})\}\{Au(C_6F_5)_3\}]$[11] (2.5038(13) Å). The gold(I) centers display distorted linear geometries, whereby the Au(I)−Se and Au(I)−P bond distances resemble those found in other selenolato gold complexes.

The structure of complex **5** has been confirmed by X-ray diffraction of its acetone solvate (Figure 2). Selected bond lengths and angles are collected in Table 2. The asymmetric unit consists of two independent formula units, which show intra- and intermolecular interaction (and also two acetone molecules); it is analogous to the complex with the thiolate ligand.[16] One discrete cation of **5** consists of two gold centers doubly bridged by a $[PhSe]^-$ ligand and a dppf diphosphine. The torsion angles in the ferrocene units are 19.5° (C(1)−Cent−Cent−C(7)) and 18.7° (C(61)−Cent−Cent−C(67)), with the relative phosphorus positions expressed by P1−Cent−Cent−P2, 89.0°, and P3−Cent−Cent−P4, −87.7°. The intramolecular Au···Au distances in the two dinuclear units are 3.0193(7) and 2.9839(7) Å, longer than the intermolecular Au···Au distance of 2.9237(7) Å, despite the narrow Au−Se−Au angles of 75.94(3)° and 74.62(3)°. However, in the analogous thiolate complex $[Au_2(\mu\text{-}SC_6F_5)(\mu\text{-dppf})]OTf$ both intermolecular (2.9610(16) and 2.9788(14) Å) and intramolecular (2.9666(14) Å) distances are very similar, and the Au−S−Au angles are slightly wider, 77.59(17)° and 78.75(16)°. This is consistent with that observed in isostructural $[E(AuPPh_3)_4](OTf)_2$ (E = S, Se) where narrow Au−E−Au angles and longer Au−Au distances are observed for the selenium derivative.[9,21]

The four gold centers in the resulting tetranuclear array show distorted linear geometries. The major distortion corresponds to the connected gold centers of different units [P(2)−Au(2)−Se(1), 170.03(7)°; P(3)−Au(3)−Se(2), 170.32(7)°].

The Au−Se bond distances (2.4454(12)−2.4706(11) Å) are in the range of those found in other complexes in which the selenium atom acts as a triply bridging ligand, as in $[Au_2(\mu\text{-dppf})\{Se\{Au_2(\mu\text{-dppf})\}_2](OTf)_2$ (2.4240(10)−2.704(10) Å).[10] The Au(I)−P bond lengths, 2.273(3)−2.288(3) Å, are shorter than in $[Au_2(\mu\text{-dppf})\{Se\{Au_2(\mu\text{-dppf})\}_2](OTf)_2$ (2.259(3)−2.280(3) Å).[10] A second solvate of complex **5**, **5′**, with two independent formula units plus three dichloromethane molecules in the asymmetric unit, was also analyzed and displays a closely similar structure with analogous Au···Au contacts (however, despite similar cells, the two forms are not isostructural because the motif of chains of cations in the regions $x \approx 0.25$ is mutually shifted parallel to the *z* axis). Data for **5′** are summarized in Table 4 and may be found in full in the Supporting Information.

Experimental Section

Instrumentation. Infrared spectra were recorded in the range 4000−200 cm^{-1} on a Perkin-Elmer 883 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured in ca. 5×10^{-4} mol dm^{-3} solutions with a Philips 9509 conductometer. C, H, N, and S analyses were carried out with a Perkin-Elmer 2400 microanalyzer. Mass spectra were recorded on a VG Autospec, with the liquid secondary-ion mass spectra (LSIMS) technique, using nitrobenzyl alcohol as matrix. NMR spectra were recorded on a Varian Unity 300 spectrometer and a Bruker ARX 300 spectrometer in $CDCl_3$. Chemical shifts are cited relative to $SiMe_4$ (^1H, external), $CFCl_3$ (^{19}F, external), and 85% H_3PO_4 (^{31}P, external).

Starting Materials. The starting materials $[Au_2Cl_2(\mu\text{-dppf})]$[22] and $[Au(C_6F_5)_3(OEt_2)]$[23] were prepared according to published procedures. $[Au(OTf)(PPh_3)]$ has been obtained by reaction of $[AuCl(PPh_3)]$[24] with Ag(OTf) in dichloromethane and used in situ. All other reagents were commercially available.

Synthesis of $[Au_2(SePh)_2(\mu\text{-dppf})]$ (1). To a solution of $[Au_2Cl_2(\mu\text{-dppf})]$ (0.102 g, 0.1 mmol) in 20 mL of tetrahydrofuran was added $PhSeSiMe_3$ (0.046 g, 0.2 mmol), and the mixture was stirred for 1 h. The solution was concentrated to ca. 5 mL, and then, by addition of diethyl ether (10 mL) an orange solid of **1** was isolated. Yield 80%. $\Lambda_M = 0.4\ \Omega^{-1}\ cm^2\ mol^{-1}$. Elemental Analysis (%) Found: C, 43.47; H, 2.89. Calcd for $C_{46}H_{38}Au_2FeP_2Se_2$: C, 43.81; H, 3.01. NMR data. ^1H, δ: 4.14 (m, 4H, C_5H_4), 4.45 (m, 4H, C_5H_4), 7.24−7.65 (m, 30H, Ph). $^{31}P(^1H)$, δ: 33.0 (s, 2P, PPh_2) ppm.

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Synthesis of [Au_4(*μ*-SePh)$_2$(PPh_3)$_2$(*μ*-dppf)](OTf)$_2$ (2). To a solution of [Au_2(SePh)$_2$(*μ*-dppf)] (0.126 g, 0.1 mmol) in 20 mL of dichloromethane was added [Au(OTf)(PPh_3)] (0.122 g, 0.2 mmol), and the mixture was stirred for 1 h. Concentration of the solvent to ca. 5 mL and addition of diethyl ether (10 mL) gave an orange solid of **2**. Yield 67%. $\Lambda_M = 210\ \Omega^{-1}\ cm^2\ mol^{-1}$. Elemental Analysis (%) Found: C, 40.76; H, 3.17; S, 2.53. Calcd for $C_{84}H_{68}Au_4FeO_6P_4S_2Se_2$: C, 40.71; H, 2.75; S, 2.58. NMR data. ^1H, δ: 4.21 (m, 4H, C_5H_4), 4.56 (m, 4H, C_5H_4), 7.19−7.69 (m, 60H, Ph). $^{31}P\{^1H\}$, δ: 33.0 (s, 2P, PPh_2), 36.2 (s, 2P, PPh_3) ppm.

Synthesis of [Au_3(C_6F_5)$_3$(*μ*-SePh)$_2$(*μ*-dppf)] (3). To a solution of [Au_2(SePh)$_2$(*μ*-dppf)] (0.126 g, 0.1 mmol) in 20 mL of dichloromethane was added [Au(C_6F_5)$_3$OEt$_2$] (0.077 g, 0.1 mmol), and the mixture was stirred for 30 min. Concentration of the solvent to ca. 5 mL and addition of hexane (10 mL) gave an orange solid of **3**. Yield 62%. $\Lambda_M = 3.4\ \Omega^{-1}\ cm^2\ mol^{-1}$. Elemental Analysis (%) Found: C, 39.45; H, 2.41. Calcd for $C_{64}H_{38}Au_3F_{15}FeP_2Se_2$: C, 39.22; H, 1.95. NMR data. ^1H, δ: 4.17 (m, 4H, C_5H_4), 4.42 (m, 4H, C_5H_4), 6.71−7.59 (m, 30H, Ph). $^{31}P\{^1H\}$, δ: 30.5 (s, 2P, PPh_2). ^{19}F, δ: −119.2 (m, 4F, *o*-F), −121.5 (m, 2F, *o*-F), −160.0 (t, 1F, *p*-F, ^3J(FF) 18.0 Hz), −160.7 (m, 2F, *p*-F), −163.0 (m, 6F, *m*-F) ppm.

Synthesis of [Au_4(C_6F_5)$_6$(*μ*-SePh)$_2$(*μ*-dppf)] (4). To a solution of [Au_2(SePh)$_2$(*μ*-dppf)] (0.126 g, 0.1 mmol) in 20 mL of dichloromethane was added [Au(C_6F_5)$_3$OEt$_2$] (0.154 g, 0.2 mmol), and the mixture was stirred for 30 min. Concentration of the solvent to ca. 5 mL and addition of hexane (10 mL) gave an orange solid of **4**. Yield 70%. $\Lambda_M = 4.0\ \Omega^{-1}\ cm^2\ mol^{-1}$. Elemental Analysis (%) Found: C, 37.45; H, 1.47. Calcd for $C_{82}H_{38}Au_4F_{30}FeP_2Se_2$: C, 37.05; H, 1.44. NMR data. ^1H, δ: 4.37 (m, 4H, C_5H_4), 4.71 (m, 4H, C_5H_4), 6.97−7.56 (m, 30H, Ph). $^{31}P\{^1H\}$, δ: 32.6 (s, 2P, PPh_2). ^{19}F, δ: −122.2 (m, 4F, *o*-F), −119.1 (m, 8F, *o*-F), −158.1 (t, 4F, *p*-F, ^3J(FF) 19.1 Hz), −157.9 (t, 2F, *p*-F, ^3J(FF) 21.0 Hz), −161.9 (m, 4F, *m*-F), −161.5 (m, 8F, *m*-F) ppm.

Synthesis of [Au_2(*μ*-SePh)(*μ*-dppf)]OTf (5). To a solution of [Au_2(SePh)$_2$(*μ*-dppf)] (0.126 g, 0.1 mmol) in 20 mL of dichloromethane was added Ag(OTf) (0.026 g, 0.1 mmol), and the mixture was stirred for 1 h. The solid [Ag(SePh)]$_n$ was filtered off and the solution concentrated to ca. 5 mL. Addition of diethyl ether (10 mL) afforded an orange solid of **5**. Yield 65%. $\Lambda_M = 83\ \Omega^{-1}\ cm^2\ mol^{-1}$. Elemental Analysis (%) Found: C, 39.08; H, 2.73; S, 2.54. Calcd for $C_{41}H_{33}Au_2F_3FeO_3P_2SSe$: C, 39.26; H, 2.63; S, 2.55. NMR data. ^1H, δ: 4.18 (m, 4H, C_5H_4), 4.55 (m, 4H, C_5H_4), 7.19−7.60 (m, 25H, Ph). $^{31}P\{^1H\}$, δ: 31.1 (s, 2P, PPh_2).

Table 3. Details of Data Collection and Structure Refinement for Complexes **4**, **5**, and **5′**

	4	**5**	**5′**
chemical formula	$C_{82}H_{38}Au_4F_{30}FeP_2Se_2$	$C_{44}H_{36}Au_2F_3FeO_4P_2SSe$	$C_{42.5}H_{36}Au_2F_3Cl_3FeO_3P_2SSe$
cryst habit	pale yellow hexagonal plate	yellow trapezoidal plate	yellow prism
cryst size/mm^3	0.21 × 0.16 × 0.04	0.24 × 0.14 × 0.04	0.40 × 0.16 × 0.13
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
a/Å	13.2844(11)	23.974(4)	27.294(3)
b/Å	21.8735(16)	13.384(2)	13.0289(16)
c/Å	27.1159(18)	27.686(4)	27.574(3)
α/deg	90	90	90
β/deg	96.923(3)	106.126(6)	116.23(2)
γ/deg	90	90	90
U/Å^3	7821.8(10)	8534(2)	8795.8(18)
Z	4	8	8
D_c/g cm^{-3}	2.256	2.042	2.085
M	2656.70	2622.99	1380.81
F(000)	4960	5008	5256
T/°C	−130	−130	−130
$2\theta_{max}$/deg	60	52	50
μ(Mo Kα)/mm^{-1}	8.747	8.228	8.163
no. reflns measured	147698	71386	127381
no. unique reflns	22884	17470	16458
R_{int}	0.0954	0.1827	0.1204
R^a ($F > 4\sigma(F)$)	0.0269	0.0490	0.0606
$R_w{}^b$ (F^2, all reflns)	0.0503	0.1267	0.1589
no. reflns used	22884	17470	16458
no. params	1090	1052	1039
no. restraints	344	1069	883
S^c	0.900	0.939	1.064
max $\Delta\rho$/e Å^{-3}	1.240	1.791	3.552

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F^2) = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum\{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and a and b are constants adjusted by the program. [c] $S = [\sum\{w(F_o^2 - F_c^2)^2\}/(n - p)]^{0.5}$, where n is the number of data and p the number of parameters.

Crystallography. Crystals were mounted in inert oil on glass fibers and transferred to the cold gas stream of a Bruker Smart 1000 CCD diffractometer equipped with a low-temperature attachment. Data were collected using monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Scan type was ω (**5**) or ω and ϕ (**4**, **5′**). Absorption corrections were performed by face indexing (**4**, **5**) or were based on multiple scans, program SADABS (**5′**). The structures were refined on F^2 using the program SHELXL-97.[25] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included using a riding model. Special refinement details for **4** follow: One phenyl ring (C51−56) at Se1 is disordered over two position with half occupancies. One of the triflate anions is also disordered over two positions with 0.64 and 0.36 occupancies. Acetone hydrogens were not located. Further details of the data collection and refinement are given in Table 3.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for complexes **4**, **5**, and **5′**. This material is available free of charge via the Internet at http://pubs.acs.org.

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