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Gold and silver complexes with the diselenium ligand $[Ph_2P(Se)NP(Se)Ph_2]^-$

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Dedicated to Professor Rafael Usón

Abstract

The treatment of potassium diselenoimidodiphosphinato with silver(I) or gold(III) derivatives leads to the synthesis of three-coordinated, $[Ag\{(SePPh_2)_2N\}(PPh_3)]$, tetranuclear, $[Ag_4\{(SePPh_2)_2N\}_3]OTf$ (**4**) ($OTf = OSO_2CF_3$), or square-planar, $[Au(C_6F_5)_2\{(SePPh_2)_2N\}]$ (**5**), complexes. The crystal structures of $[Au_2\{(SePPh_2)_2N\}(PPh_3)_2]OTf$ (**2**), **4** and **5** have been established by X-ray diffraction. Complex **2** is associated by gold–gold interactions forming tetranuclear dimers. In complex **4** four silver atoms forming a distorted tetrahedron are bridged by three ligands, and **5** shows the expected square-planar coordination at gold.

Keywords: Crystal sturucture; Silver complexes; Gold complexes; Selenium complexes

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1. Introduction

Gold and silver have a remarkable affinity for selenium donor ligands and the number of known selenolate or selenide [1,2] and phosphineselenide [3,4] complexes is growing rapidly, probably as a consequence of their interesting structures or their potential applications in chemotherapy [5].

Recently, interest has been focussed on the coordination properties of the diselenoimidodiphosphinato anion $[Ph_2P(Se)NP(Se)Ph_2]^-$ as a flexible ligand, and a sizeable number of metal complexes have been reported [6]. However, not much work has been carried out in gold and silver chemistry with this ligand. Until recently the only such gold complex described was $[Au\{(SePPh_2)_2N\}\{PPh_2NHP(O)Ph_2\}]$ [7], but during the course of these studies, a parallel work by Schmidbaur et al. has appeared, reporting the synthesis of several gold complexes, $[Au\{(SePPh_2)_2N\}L]$ ($L = PMe_3$, PPh_3, $CNC_6H_3Me_2$), $[Au\{(SePPh_2)_2N\}(PMe_3)_2]$, $[Au_2\{(SePPh_2)_2N\}(PPh_3)_2]^+ [BF_4]^-$, $[Au_2\{(SePPh_2)_2N\}(dppm)]^+[OSO_2CF_3]^-$ and $[Au_2\{(SePPh_2)_2N\}_2]$ [8]. As part of an ongoing study of the coordination of ligands containing sulfur or selenium donor atoms, we present here the results of the reaction of $K[Ph_2P(Se)NP(Se)Ph_2]$ with silver(I) or gold(III) derivatives; these lead to three-coordinated, $[Ag\{(SePPh_2)_2N\}(PPh_3)]$, tetranuclear, $[Ag_4\{(SePPh_2)_2N\}_3](OTf)$, or square-planar, $[Au(C_6F_5)_2\{(SePPh_2)_2N\}]$, complexes. We also present the crystal structure of the dinuclear $[Au_2\{(SePPh_2)_2N\}(PPh_3)_2](OTf)$.

2. Results and discussion

We have studied the coordination behaviour of the anion $[Ph_2P(Se)NP(Se)Ph_2]^-$ in gold and silver complexes obtained according to Scheme 1.

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$K[Ph_2P(Se)NP(Se)Ph_2]$ reacts with $[AuCl(PPh_3)]$ to give $[Au\{(SePPh_2)_2N\}(PPh_3)]$ (**1**), which further reacts with $[Au(OTf)(PPh_3)]$ to give the dinuclear $[Au_2\{(SePPh_2)_2N\}(PPh_3)_2]OTf$ (**2**), both previously described by Schmidbaur [8]. We have obtained crystals of **2** and the crystal structure is described below.

The gold atoms exhibit almost linear geometries [Se(1)–Au(1)–P(3) = 177.340(17) Se(2)–Au(2)–P(4) = 178.008(17)°] (Fig. 1, Table 1). The Au···Au distance (> 5 Å) rules out any intramolecular metallic interaction. Both in **2** and $[Au_2\{(SePPh_2)_2N\}(dppm)]OTf$ [8] tetranuclear cationic dimers are formed, although in $[Au_2\{(SePPh_2)_2N\}(dppm)]OTf$ they are formed through Au···Se interactions of different cations (Au···Se = 3.447(1), 3.331(1) Å), whereas in **2** gold···gold contacts over an inversion centre (Au(1)··· Au(2)# = 3.1712 Å) are responsible; this distance is shorter than the intramolecular contacts found in $[Au_2\{(SePPh_2)_2N\}(dppm)]OTf$ (3.2687(4) Å). Au–Se distances (2.4231(3), 2.4352(3) Å) are of the same order as Au(I)–Se found in other complexes, with the same or different ligands, in which the gold atom displays linear coordination ($[Au_2\{(SePPh_2)_2N\}(dppm)]OTf$ (2.4280(7), 2.4209(8) Å), $[Se\{AuPPh_3)\}_2\{\mu\text{-}Au(C_6F_5)_2\}_2]$ 2.4225(9) Å [9]). The Au–P distances (2.2788(6), 2.2737(6) Å) are very close to those in $[Au\{(SePPh_2)_2N\}(PPh_3)]$ [8] (2.2786(9) Å) (trigonal geometry at gold) or the Au(I)–P distance in $[\{Se(AuPPh_3)\}_2\{\mu\text{-}Au(C_6F_5)_2\}_2]$ [9] (2.273(2) Å), and somewhat longer than those in $[Au_2\{(SePPh_2)_2N\}(dppm)]OTf$ (2.265(2), 2.263(2) Å). Weak interactions of the hydrogen bonding type C–H···O also form a feature of the packing, with H···O distances from 2.33 to 2.59 Å (Table 2) involving the triflate oxygen atoms and three phenyl hydrogens.

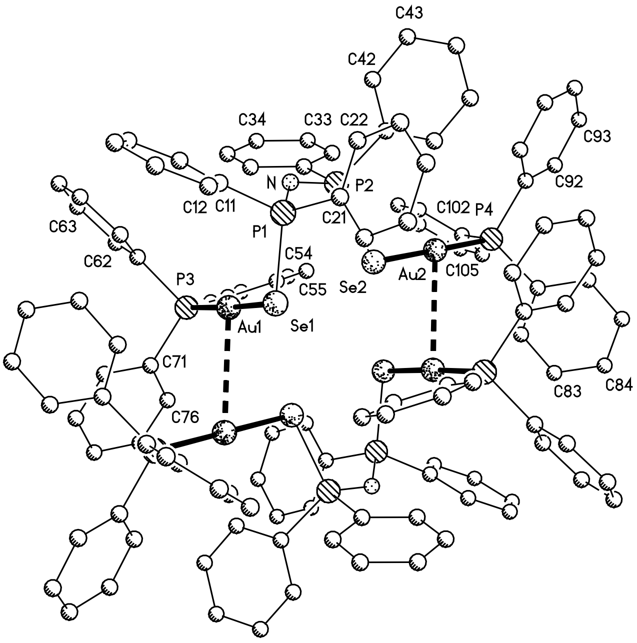
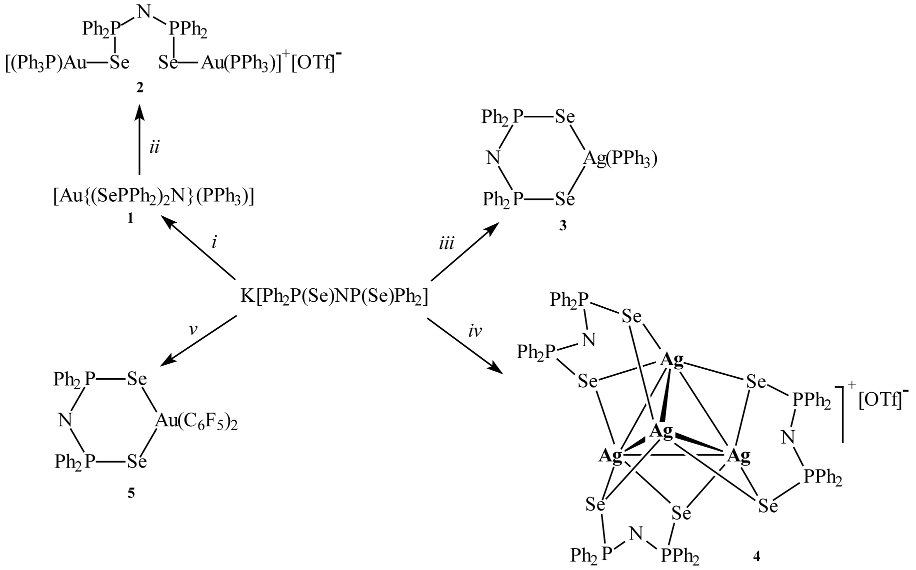


Fig. 1. Structure of the cation in **2**. Radii are arbitrary and hydrogen atoms have been omitted for clarity.

The reaction of the diselenoimidodiphosphinato salt with $[Ag(OTf)(PPh_3)]$, in a molar ratio 1:1 and at room temperature, gives the new complex $[Ag\{(SePPh_2)_2N\}(PPh_3)]$ (**3**). It is a white, air- and moisture-stable solid and behaves as non-conducting in acetone solution. The IR spectrum shows the $\nu(P=Se)$ vibration at 543 cm^{-1}. The positive-ion LSI MS exhibits a peak corresponding to the molecular cation $[M]^+$ at $m/z = 913$ (5%). The ^1H NMR spectrum shows a multiplet at 7.6 ppm (Ph) and the $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 27.6 ppm [2P, PPh_2, J(PSe) 562 Hz] and a doublet [1P, PPh_3, J_{ave}(PAg) 459 Hz].



Scheme 1. (i) $[AuCl(PPh_3)]$; (ii) $[Au(OTf)(PPh_3)]$; (iii) $[Ag(OTf)(PPh_3)]$; (iv) $[Ag(OTf)]$; (v) $[Au(C_6F_5)_2Cl]_2$.

Table 1
Selected bond lengths (Å) and bond angles (°) for **2**

Bond lengths			
Au(1)–P(3)	2.2788(6)	Se(1)–P(1)	2.1980(7)
Au(1)–Se(1)	2.4352(3)	Se(2)–P(2)	2.2034(7)
Au(1)–Au(2)#1	3.1712(3)	P(1)–N	1.598(2)
Au(2)–P(4)	2.2737(6)	P(2)–N	1.590(2)
Au(2)–Se(2)	2.4231(3)		
Bond angles			
P(3)–Au(1)–Se(1)	177.340(17)	N–P(2)–C(31)	105.39(11)
P(3)–Au(1)–Au(2)#1	97.702(16)	N–P(2)–C(41)	111.01(11)
Se(1)–Au(1)–Au(2)#1	84.468(8)	N–P(2)–Se(2)	111.59(8)
P(4)–Au(2)–Se(2)	178.008(17)	C(51)–P(3)–Au(1)	114.50(8)
P(4)–Au(2)–Au(1)#1	106.615(16)	C(71)–P(3)–Au(1)	114.28(8)
Se(2)–Au(2)–Au(1)#1	73.524(7)	C(61)–P(3)–Au(1)	109.58(8)
P(1)–Se(1)–Au(1)	98.169(18)	C(81)–P(4)–Au(2)	114.24(8)
P(2)–Se(2)–Au(2)	103.821(19)	C(91)–P(4)–Au(2)	111.12(8)
N–P(1)–C(11)	105.34(11)	C(101)–P(4)–Au(2)	113.45(8)
N–P(1)–C(21)	111.96(12)	P(2)–N–P(1)	132.64(13)
N–P(1)–Se(1)	118.00(8)		

Symmetry transformations used to generate equivalent atoms: #1 $-x+1$, $-y+1$, $-z+1$.

Table 2
Hydrogen bonds (Å, °) for **2**

	d(C–H)	d(H···O)	d(C···O)	∠(C–H···O)
C(53)–H(53)···O(1)#2	0.95	2.33	3.246(4)	161.3
C(94)–H(94)···O(1)#3	0.95	2.42	3.363(3)	171.2
C(75)–H(75)···O(2)#4	0.95	2.59	3.439(3)	149.3
C(84)–H(84)···O(3)	0.95	2.38	3.191(3)	143.7

Symmetry transformations used to generate equivalent atoms: #2 $-x$, $-y+1$, $-z+1$; #3 x, $y-1$, z; #4 x, y, $z-1$.

The treatment of K[$Ph_2P(Se)NP(Se)Ph_2$] with Ag(OTf), in the molar ratio 1:1 or 3:4, gives the ionic tetranuclear [$Ag_4\{(SePPh_2)_2N\}_3$]OTf (**4**) derivative as a white solid. It behaves as a 1:1 electrolyte in acetone solution. The positive-ion LSI MS shows the cation molecular peak $[M-\text{OTf}]^+$ [$m/z = 2060$ (55%)]. Other peaks appear at $m/z = 1409$ (70%), $[Ag_3\{(SePPh_2)_2N\}_2]^+$, and $m/z = 752$ (100%), $[Ag_2\{(SePPh_2)_2N\}]^+$. The IR spectrum shows, apart from the bands arising from the diselenoimidodiphosphinato ligand, those of the triflate at 1254(s), 1225(s), 1178(m), 1038(s) cm^{-1} and those corresponding to $\nu(P=Se)$ at 529(s) cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum at room temperature shows two broad signals at 24.4 and 22.5 ppm, although at −55 °C they split to give four singlets at 24.8 [J(PSe) 541 Hz], 23.7 (br), 22.9 (br), and 22.1 (br) ppm.

The X-ray stucture determination shows that the cation contains four silver atoms bridged by three ligands. The atoms Ag(2), Ag(3) and Ag(4) are bridged by two selenium atoms of the same and one from a different ligand, affording distorted trigonal geometries in each case. The trigonal geometry at Ag(1) arises from coordination by selenium atoms from three different ligands. The extended structure of the complex consists of an Ag_4Se_6 adamantane-type cluster and can be considered as a tetrahedron of silver atoms inscribed in a distorted octahedron of selenium atoms (Fig. 2). This atom framework is known in the structures of [$Cu_4(SMe)_6$] [10], [$Cu_4(SPh)_6$] [10,11] and also in other silver clusters as $[Ag_4(SCH_2C_6H_4CH_2S)_3]^{2-}$ [12], $[Ag_4\{Te(SC_4H_3)\}_6]^{2-}$ [13] or $[Ag_4(Se_4)_3]^{2-}$ [14] but only in one which includes Ag–Se bonding, $[Ag_4(SePh)_6]^{2-}$ [2b]. A different geometry has been described for $[Ag_4(Se_4)_4]^{2-}$ [14], it consists of a planar rhombus of four silver atoms, symmetrically disposed around an inversion centre, which is held together by four Se_4^{2-} ligands, two silver atoms are tetrahedrally coordinated, whereas the other display trigonal planar coordination. The Ag···Ag distances (Table 3) average in **4** 3.12 Å (2.9889(10)–3.3101(13) Å), similar values have been reported for $[Ag_4\{Te(SC_4H_3)\}_6]^{2-}$ (3.13 Å). A narrower range of distances was found in $[Ag_4(SePh)_6]^{2-}$ (2.958(1)–3.151(1) Å), $[Ag_4(SCH_2C_6H_4CH_2S)_3]^{2-}$ (2.998(1)–3.085(1) Å, mean value 3.044 Å) or in $[Ag_4(Se_4)_3]^{2-}$ (2.990(1)–3.193(1) Å, mean value 3.05 Å). The Ag–Se distances in the cation vary from 2.5922(10) to 2.6446(12) Å, this range is narrower than in the species $[Ag_4(SePh)_6]^{2-}$ (2.704(1)–2.567(1) Å) and $[Ag_4(Se_4)_3]^{2-}$ (2.545(1)–2.710(1) Å).

The diselenoimidodiphosphinato salt reacts with the dimer $[Au(C_6F_5)_2Cl]_2$ to give the neutral gold(III) complex $[Au(C_6F_5)_2\{(SePPh_2)_2N\}]$ (**5**). It is an air- and moisture-stable, pale cream solid. It is non-conducting in acetone solution. The positive-ion LSI MS shows the

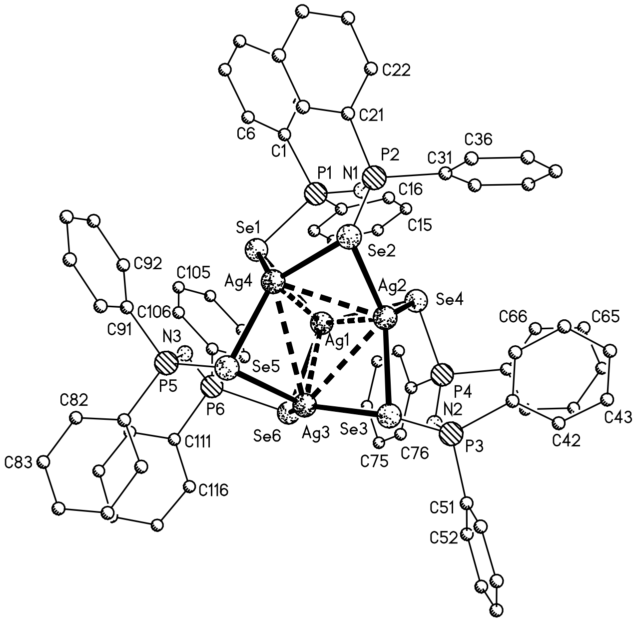


Fig. 2. Structure of the cation in **4**. Radii are arbitrary and hydrogen atoms have been omitted for clarity.

Table 3
Selected bond lengths (Å) and bond angles (°) for **4**

Bond lengths			
Ag(1)–Se(4)	2.6170(11)	Ag(4)–Se(1)	2.5850(12)
Ag(1)–Se(6)	2.6259(11)	Ag(4)–Se(2)	2.5878(10)
Ag(1)–Se(1)	2.6446(12)	Ag(4)–Se(5)	2.5922(10)
Ag(1)–Ag(3)	3.0164(10)	Se(1)–P(1)	2.2118(18)
Ag(1)–Ag(4)	3.151(2)	Se(2)–P(2)	2.2199(17)
Ag(1)–Ag(2)	3.1597(12)	Se(3)–P(3)	2.216(2)
Ag(2)–Se(2)	2.5854(14)	Se(4)–P(4)	2.206(2)
Ag(2)–Se(3)	2.6019(9)	Se(5)–P(5)	2.209(2)
Ag(2)–Se(4)	2.6121(17)	Se(6)–P(6)	2.218(2)
Ag(2)–Ag(4)	2.9889(10)	P(1)–N(1)	1.584(6)
Ag(2)–Ag(3)	3.0979(11)	P(2)–N(1)	1.602(5)
Ag(3)–Se(6)	2.5866(14)	P(3)–N(2)	1.606(6)
Ag(3)–Se(3)	2.6077(10)	P(4)–N(2)	1.602(5)
Ag(3)–Se(5)	2.6103(16)	P(5)–N(3)	1.594(6)
Ag(3)–Ag(4)	3.3101(13)	P(6)–N(3)	1.611(6)
Bond angles			
Ag(3)–Ag(1)–Ag(4)	64.87(4)	Ag(2)–Se(2)–Ag(4)	70.59(3)
Se(2)–Ag(2)–Se(3)	122.98(4)	Ag(2)–Se(3)–Ag(3)	72.98(3)
Se(2)–Ag(2)–Se(4)	118.52(4)	Ag(4)–Se(5)–Ag(3)	79.03(4)
Se(3)–Ag(2)–Se(4)	118.50(4)	Ag(3)–Se(6)–Ag(1)	70.71(3)
Ag(4)–Ag(2)–Ag(3)	65.86(3)	P(1)–N(1)–P(2)	140.2(4)
Ag(4)–Ag(2)–Ag(1)	61.59(4)	P(4)–N(2)–P(3)	129.3(4)
Ag(3)–Ag(2)–Ag(1)	57.63(2)	P(5)–N(3)–P(6)	134.7(4)
Se(6)–Ag(3)–Se(3)	134.47(4)	N(1)–P(1)–Se(1)	118.5(2)
Se(6)–Ag(3)–Se(5)	117.71(5)	N(1)–P(2)–Se(2)	119.0(2)
Se(3)–Ag(3)–Se(5)	107.43(4)	N(2)–P(3)–Se(3)	115.5(2)
Ag(1)–Ag(3)–Ag(2)	62.21(3)	N(2)–P(4)–Se(4)	119.6(2)
Ag(1)–Ag(3)–Ag(4)	59.54(4)	N(3)–P(5)–Se(5)	119.1(2)
Ag(2)–Ag(3)–Ag(4)	55.49(2)	N(3)–P(6)–Se(6)	120.0(2)
Se(1)–Ag(4)–Se(2)	119.30(3)	P(1)–Se(1)–Ag(4)	101.97(5)
Se(1)–Ag(4)–Se(5)	121.15(3)	P(1)–Se(1)–Ag(1)	91.19(6)
Se(2)–Ag(4)–Se(5)	118.94(4)	P(2)–Se(2)–Ag(2)	95.53(7)
Se(2)–Ag(4)–Ag(1)	107.82(3)	P(2)–Se(2)–Ag(4)	99.80(6)
Se(5)–Ag(4)–Ag(1)	100.44(4)	P(3)–Se(3)–Ag(2)	91.56(6)
Ag(2)–Ag(4)–Ag(1)	61.87(3)	P(3)–Se(3)–Ag(3)	104.95(6)
Se(1)–Ag(4)–Ag(3)	102.66(4)	P(4)–Se(4)–Ag(2)	101.80(6)
Se(2)–Ag(4)–Ag(3)	108.18(3)	P(4)–Se(4)–Ag(1)	94.82(6)
Se(5)–Ag(4)–Ag(3)	50.73(4)	P(5)–Se(5)–Ag(4)	93.45(5)
Ag(2)–Ag(4)–Ag(3)	58.65(3)	P(5)–Se(5)–Ag(3)	100.60(7)
Ag(1)–Ag(4)–Ag(3)	55.59(3)	P(6)–Se(6)–Ag(3)	92.29(6)
Ag(4)–Se(1)–Ag(1)	74.10(5)	P(6)–Se(6)–Ag(1)	92.29(6)

cation molecular peak, ($[M]^+$, $m/z = 1076$ (10%)). The cation $[M-C_6F_5]^+$ is also observed at $m/z = 906$ (5%). The ν(P=Se) stretching vibration appears in the IR spectra at 547(s) cm^{-1}. Other bands arising from the pentafluorophenyl groups appear at 1511(s), 969(s), 805(m), 795(m) cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum presents only a singlet resonance at 29.7 ppm and the ^{19}F NMR corresponds to the presence of 2 equiv. C_6F_5 groups, with signals at −121.8 (m, 4F, *o*-F), −158.0 (t, 2F, *p*-F, *J*(FF) 18 Hz) and −162.2 (m, 4F, *m*-F) ppm.

The X-ray structure of **5** shows that the gold centre exhibits a significant distortion from square planar geometry (Fig. 3), attributable to the wide bite angle of the $[Ph_2P(Se)NPPh_2)]^-$ ligand [(Se(1)–Au–Se(2) = 102.718(9) °] (Fig. 3, Table 4) but also to its rigidity. The Se(1), Se(2), C(41) and C(42) atoms do not lie in exactly the same plane (the dihedral angle between C(41)/Au/C(51) and Se(1)/Au/Se(2) planes is 4.3°). The six-membered ring formed by Au, Se(1), P(1), N, P(2), Se(2) has a twist conformation, as was also described for $[Au\{(SePPh_2)_2N\}(PPh_3)]$ or $[Au\{(SePPh_2)_2N\}(PMe_3)_2]$ [8].

The Au–Se distances (2.4808(3), 2.4832(3) Å) lie in a similar range to those Au(III)–Se found in $[\{Se(AuPPh_3)\}_2\{\mu\text{-}Au(C_6F_5)_2\}_2]$ (2.4802(8)Å) or in $[Se\{Au_2(\mu\text{-}dppf)\}\{Au(C_6F_5)_3\}]$ (2.5038(13) Å [9]). The Au–C distances are very close to those obtained for $[\{Se(AuPPh_3)\}_2\{\mu\text{-}Au(C_6F_5)_2\}_2]$ or $[Se\{Au_2(\mu\text{-}dppf)\}\text{-}\{Au(C_6F_5)_3\}]$.

Concerning the diselenoimidodiphosphinato moiety, despite its different coordination pattern, i.e. monometallic biconnective (a) in **5**, bimetallic biconnective (bridging) (b) in **2**, or trimetallic tetraconnective (c) in **4** (Fig. 4), the P–Se bond lengths [range 2.195(1)–2.220(1) Å] within a ligand unit are not significantly different. They corresponds to single phosphorus–selenium bonds, while the P–N bonds [range 1.584(6)–1.611(6) Å] are intermediate between single and double phosphorus–nitrogen bonds [cf. the free acid $(Se{=}PPh_2)_2NH$ [6a]: P=Se 2.085(1), 2.101(1) Å, P–N 1.686(3), 1.678(4) Å; $[2\text{-}(Me_2NCH_2)C_6H_4]Te\text{-}S\text{-}PPh_2{=}N\text{-}PPh_2{=}S$ [15]: P–N 1.612(3), P=N 1.557(3) Å]. By contrast, magnitude of the P–N–P angle varies considerably with the coordination pattern, i.e. from 132.64(13)° in the dinuclear cation of **2**, to 116.46(7)° in the mononuclear **5** derivative.

3. Experimental

Infrared spectra were recorded on a Perkin–Elmer 883 spectrophotometer, over the range 4000–200 cm^{-1},

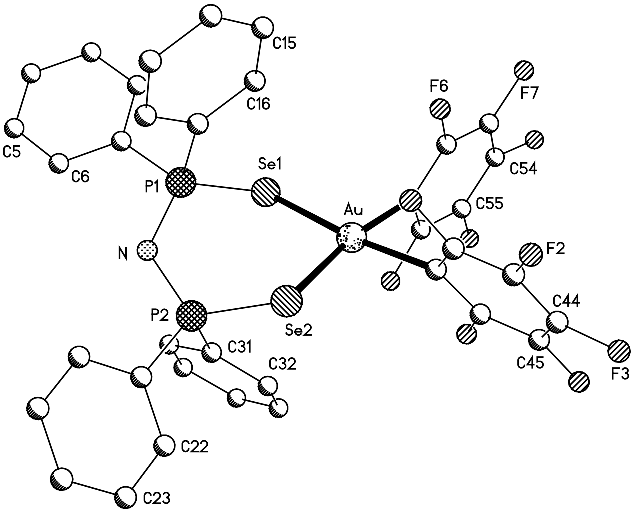


Fig. 3. Molecular structure of **5**. Radii are arbitrary and hydrogen atoms have been omitted for clarity.

Table 4
Selected bond lengths (Å) and bond angles (°) for **5**

Bond lengths			
Au–C(41)	2.052(2)	P(1)–N	1.604(2)
Au–C(51)	2.055(2)	P(1)–Se(1)	2.1970(6)
Au–Se(2)	2.4808(3)	P(2)–N	1.596(2)
Au–Se(1)	2.4832(3)	P(2)–Se(2)	2.1953(7)
Bond angles			
C(41)–Au–C(51)	88.25(10)	C(11)–P(1)–Se(1)	110.07(8)
C(41)–Au–Se(2)	84.11(6)	N–P(2)–C(21)	108.09(11)
C(51)–Au–Se(2)	171.39(7)	N–P(2)–C(31)	111.07(11)
C(41)–Au–Se(1)	172.90(7)	N–P(2)–Se(2)	115.31(8)
C(51)–Au–Se(1)	85.06(7)	C(21)–P(2)–Se(2)	104.05(8)
Se(2)–Au–Se(1)	102.718(9)	C(31)–P(2)–Se(2)	109.54(8)
N–P(1)–C(1)	107.07(11)	P(2)–N–P(1)	121.37(12)
N–P(1)–C(11)	111.64(10)	P(1)–Se(1)–Au	102.050(19)
N–P(1)–Se(1)	116.46(7)	P(2)–Se(2)–Au	101.465(18)
C(1)–P(1)–Se(1)	106.65(8)		

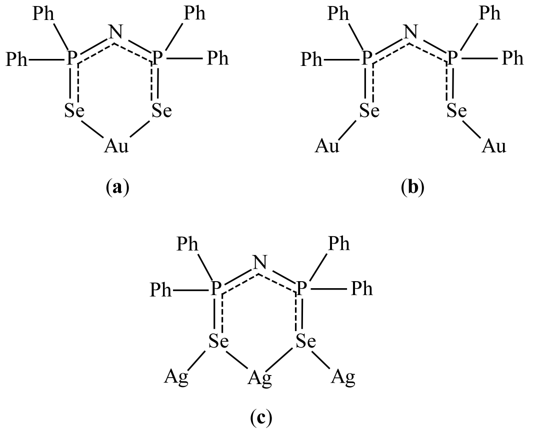


Fig. 4. Different coordination modes of the $[Ph_2P(Se)NP(Se)Ph_2]^-$ anion.

using Nujol mulls between polyethylene sheets. Conductivities were measured in ca. 5×10^{-4} mol dm^{-3} solutions with a Philips 9509 conductimeter. C, H, N and S analyses were carried out with a Perkin Elmer 2400 microanalyser. Mass spectra were recorded on a VG Autospec, with the liquid secondary-ion mass spectra (LSI MS) technique, using 3-nitrobenzyl alcohol as matrix. NMR spectra were recorded on a Varian UNITY 300 or Bruker ARX 300 apparatus in $CDCl_3$ solutions. Chemical shifts are quoted relative to $SiMe_4$ (external, ^{1}H), $CFCl_3$ (^{19}F, external), and 85% H_3PO_4 (external, ^{31}P).

AgOTf was purchased from Aldrich and used as given. [Ag(OTf)(PPh_3)] was obtained by reaction of equimolecular amounts of [AgCl(PPh_3)] [16] and AgOTf. Compound $[Au(C_6F_5)_2Cl]_2$ [17], the potassium diselenoimidodiphosphinato, $K[Ph_2P(Se)NP(Se)Ph_2]$ [6b], and compounds **1** and **2** [8] were prepared according to literature methods.

3.1. Syntheses

3.1.1. [Ag{($SePPh_2)_2N$}(PPh_3)] (3)

[Ag(OTf)(PPh_3)] (0.0519 g, 0.1 mmol) was added to a solution of $K[Ph_2P(Se)NP(Se)Ph_2]$ (0.0581 g, 0.1 mmol) in dichloromethane (20 cm^3) and the mixture was stirred for 30 min. After separation of the KOTf formed, concentration of the solution to ca. 5 cm^3 and addition of diethyl ether (10 cm^3) gave complex **3** as a white solid. Yield 75%. Λ_M 16 Ω^{-1} cm^2 mol^{-1}. Elemental analysis: *Anal*. Found: C, 55.40; H, 3.04; N, 1.43. Calc. for $C_{42}H_{35}AgNP_3Se_2$: C, 55.26; H, 3.84; N, 1.53%. ^{1}H NMR, −55 °C, δ: 6.8–8.2 (m, Ph) ppm.

3.1.2. [Ag_4{($SePPh_2)_2N$}$_3$](OTf) (4)

Ag(OTf) (0.0519 g, 0.1 mmol) was added to a solution of $K[Ph_2P(Se)NP(Se)Ph_2]$ (0.0581 g, 0.1 mmol) in dichloromethane (20 cm^3) and the mixture was stirred for 30 min. After separation of the KOTf formed, concentration of the solution to ca. 5 cm^3 and addition of diethyl ether (10 cm^3) gave complex **4** as a white solid. Yield 78%. Λ_M 84 Ω^{-1} cm^2 mol^{-1}. Elemental analysis: *Anal.* Found: C, 39.26; H, 2.95; N, 1.77; S, 1.87. Calc. for $C_{73}H_{60}Ag_4F_3NO_3P_6SSe_2$: C, 39.69; H, 2.71; N, 1.90; S, 1.45%. ^{1}H NMR, −55 °C, δ: 7.2–8. (m, Ph) ppm.

3.1.3. [Au($C_6F_5)_2${($SePPh_2)_2N$}] (5)

$[Au(C_6F_5)_2Cl]_2$ (0.1133 g, 0.1 mmol) was added to a solution of $K[Ph_2P(Se)NP(Se)Ph_2]$ (0.1162 g, 0.2 mmol) in dichloromethane (20 cm^3) and the mixture was stirred for 30 min. Concentration of the solution to ca. 5 cm^3 and addition of hexane (10 cm^3) gave complex **5** as a pale orange solid. Yield 60%. Λ_M 5.0 Ω^{-1} cm^2 mol^{-1}. Elemental analysis: *Anal*. Found: C, 40.43; H, 1.72; N, 1.19. Calc. for $C_{36}H_{20}AuF_{10}NP_2Se_2$: C, 40.26; H, 1.86; N, 1.30%. ^{1}H NMR, δ: 7.4–8 (m, Ph) ppm.

3.2. Crystallography

The crystals were mounted in inert oil on a glass fibre and transferred to the cold gas stream of a Siemens Smart 1000 CCD diffractometer equipped with a Siemens LT-2 low temperature attachment. Data were collected using monochromated Mo Kα radiation (λ = 0.71073 Å). Scan type ω and ϕ. Absorption corrections were based on multiple scans (program SADABS). The structures were refined on F^2 using the program SHELXL-97 [18]. All non hydrogen atoms were refined anisotropically. Hydrogen atoms were included using a riding model.

Special refinement details: **2**—the complex crystallises with two molecules of dichloromethane. One dichloromethane molecule is disordered over an inversion centre, the other over two general positions with half occupancies. **4**—the structure contains three poorly resolved acetone molecules, a further region of feature-

Table 5
Details of data collection and structure refinement for the complexes **2**, **4** and **5**

Compound	**2**$\cdot$1.5CH$_2$Cl$_2$	**4**$\cdot$3(CH$_3$)$_2$CO	**5**
Chemical formula	$C_{62.5}H_{53}Au_2Cl_3F_3NO_3P_4SSe_2$	$C_{82}H_{78}Ag_4F_3N_3O_6P_6SSe_6$	$C_{36}H_{20}AuF_{10}NP_2Se_2$
Crystal habit	colourless prism	colourless prism	colourless tablet
Crystal size (mm^3)	0.37 × 0.20 × 0.17	0.37 × 0.11 × 0.04	0.24 × 0.16 × 0.06
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a (Å)	14.8441(10)	14.188(3)	16.4622(12)
b (Å)	15.4681(12)	18.222(4)	21.4322(16)
c (Å)	16.0972(12)	20.273(4)	10.2734(8)
α (°)	91.915(3)	108.08(3)	90
β (°)	107.702(3)	99.58(3)	106.177(3)
γ (°)	117.158(3)	109.21(3)	90
U (Å^3)	3067.5(4)	4489.4(16)	3481.2(5)
Z	2	2	4
D_{calc} (g cm^{-3})	1.881	1.762	2.048
M	1737.20	2381.59	1073.36
$F(000)$	1678	2352	2040
T (°C)	−130	−130	−130
$2\theta_{max}$ (°)	60	53	60
μ(Mo Kα) (mm^{-1})	6.28	3.48	6.492
Transmission	0.620–0.928	0.743–0.972	0.505–0.930
No. of reflections measured	65100	64212	74906
No. of unique reflections	17883	18355	10194
R_{int}	0.0266	0.0519	0.0482
R [a] $(F > 4\sigma(F))$	0.0214	0.0467	0.0222
wR [b] (F^2, all reflections)	0.0536	0.1483	0.0510
No. of reflections used	17883	18335	10194
No. of parameters	751	940	469
No. of restraints	661	137	144
S [c]	1.002	1.029	0.973
Max. $\Delta\rho$ (e Å^{-3})	1.418	2.474	1.225

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR(F^2) = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and a and b are constants adjusted by the program.

[c] $S = [\Sigma\{w(F_o^2 - F_c^2)^2\}/(n-p)]^{0.5}$, where n is the number of data and p the number of parameters.

less electron density probably corresponds to further solvent. Further crystallographic details are given in Table 5.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 179894–179896 for compounds **2**, **4** and **5**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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