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Coordination chemistry of 1,1′-bis(diphenylselenophosphoryl)ferrocene (dpspf) towards Group 11 elements. Crystal structures of $[Ag(dpspf)\{(SPPh_2)_2CH_2\}]OTf$ and $[Au(dpspf)][AuCl_2]$

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Abstract

The ligand 1,1′-bis(diphenylselenophosphoryl)ferrocene, dpspf, reacted with various Group 11 derivatives to afford the complexes [M(dpspf)]X (M = Cu, Ag, Au; X = OTf, ClO_4, $[AuCl_2]$). The crystal structure of $[Au(dpspf)][AuCl_2]$ revealed a *trans* coordination of the dpspf ligand and the presence of short Au–Au interactions in the cation. The complex [Ag(dpspf)]OTf can react further with bidentate ligands to give the four-coordinate complexes [M(dpspf)(L–L)]OTf (L–L = $(SPPh_2)_2CH_2$, $(SePPh_2)_2CH_2$, 2,2′-bipyridine or dpspf). The structure of the derivative with L–L = $(SPPh_2)_2CH_2$ was confirmed by X-ray diffraction. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: *Trans* coordination; Bidentate ligands; X-ray diffraction

1. Introduction

The diphosphine 1,1′-bis(diphenylphosphine)ferrocene (dppf) has been widely exploited in coordination chemistry during the last two decades [1]. It has a strong bonding ability because of the two PPh_2 groups and it is a very flexible ligand that can modify its steric bite in order to adapt to different geometric requirements of the metal centres. This has facilitated the synthesis of a great number of mono- or poly-nuclear gold or silver derivatives with different geometries [2,3].

The sulfuration product, bis(diphenylthiophosphoryl)ferrocene (dptpf), possesses a longer and more flexible backbone and can thus function as a *trans*-chelating ligand, as was confirmed recently in the species $[M(dptpf)]^+$ (M=Cu [4], Ag, Au [5,6]). The selenium analogue, bis(diphenylselenophosphoryl)ferrocene (dpspf), was similarly assigned as a *trans*-chelating ligand in the copper derivative $[Cu(dpspf)]BF_4$, on the basis of NMR spectroscopy [4] and it has been confirmed very recently, when this manuscript was in preparation, in the silver analog $[Ag(dpspf)]ClO_4$ [7]. The latter are the only known complexes of the Group 11 elements with the dpspf ligand. Here we report on the coordination chemistry of dpspf with Cu(I), Ag(I), Au(I) or Au(III) centres. Mono- and di-nuclear derivatives are reported in which the selenium donor ligand acts as bridging or chelating ligand and the metal centres display linear or tetrahedral geometry.

2. Results and discussion

The reaction of dpspf with the derivatives $[Cu(NCMe)_4]OTf$, AgOTf or $[Au(tht)_2]ClO_4$ (OTf = CF_3SO_3, tht = tetrahydrothiophene; molar ratio 1:1)

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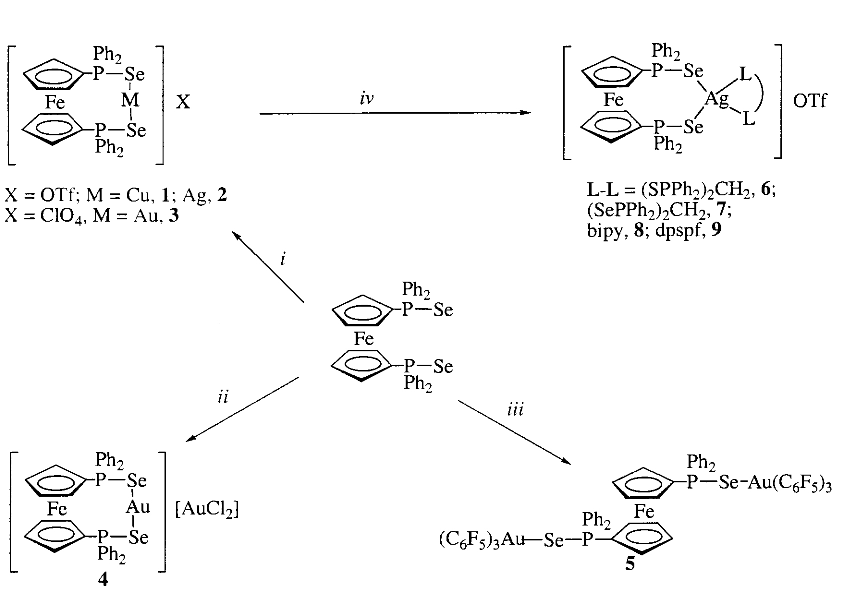
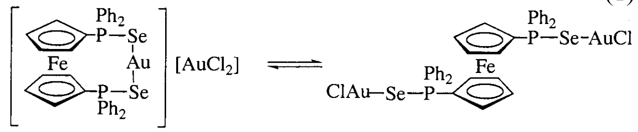


Scheme 1. (i) $[Cu(NCMe)_4]OTf$, AgOTf or $[Au(tht)_2]ClO_4$; (ii) 2 $[AuCl(tht)]$; (iii) 2 $[Au(C_6F_5)_3(OEt_2)]$; (iv) M = Ag, $(SPPh_2)_2CH_2$, $(SePPh_2)_2CH_2$, bipy or dpspf (X = OTf).

gives the mononuclear complexes [M(dpspf)]X (X = OTf, M = Cu, **1**; Ag, **2** or X = ClO_4, M = Au, **3**) (see Scheme 1). They are pale brown (**1**) or orange (**2**, **3**) air- and moisture-stable solids and behave as 1:1 electrolytes in acetone solution. Their IR spectra show, apart from the bands arising from the dpspf ligand, those of the perchlorate at 1096(vs, br) and 625(m) cm^{-1} or triflate at 1265(vs, br), 1225(s) and 1155(s) cm^{-1}. The positive-ion LSIMS exhibit a peak corresponding to the cation $[M(dpspf)]^+$ at $m/z = 776$ (12%, **1**), 821 (100%, **2**) or 911 (35%, **3**).

The ^1H-NMR spectra show, apart from the multiplet from the phenyl protons, two multiplets for the α and β protons of the substituted cyclopentadienyl rings at approximately 4.3 and 4.7 ppm. The $^{31}P\{^1H\}$-NMR spectra at room temperature show a singlet at 33.0 (**1**), 34.9 (**2**) or 31.9 ppm (**3**). In complex **2** selenium satellites are observed [J(PSe) 605 Hz].

The treatment of dpspf with [AuCl(tht)] in the molar ratio 1:2 gives the ionic derivative $[Au(dpspf)][AuCl_2]$ (**4**) as an orange solid. It behaves as a 1:1 electrolyte but its conductivity is lower than that of complex **3**. The IR spectra present a band at 335(m) cm^{-1} from ν(Au–Cl). The positive-ion LSIMS exhibits a peak corresponding to the cation $[Au(dpspf)]^+$ [$m/z = 911(100\%)$]; the fragment $[Au_2(dpspf)]^+$ [$m/z = 1106(15\%)$] is also present. The $^{31}P\{^1H\}$-NMR spectrum at room temperature shows two singlets at 31.5 and 28.9 ppm; the second one being slightly more intense. At lower temperature (−55°C), the second peak (28.7 ppm) increases in intensity and selenium satellites [J(PSe) 684 Hz] can be observed. We surmise that this behavior is consistent with an equilibrium between complex **4** and the dinuclear isomer $[(\mu\text{-dpspf})(AuCl)_2]$ (Eq. (1)) that shifts to the right at lower temperature.



(1)

The structure of complex **4** has been confirmed by an X-ray crystal diffraction study. A selection of bond lengths and angles are collected in Table 1. The asymmetric unit contains one and a half cations and one and a half anions, with the gold atom of the half cation lying on a twofold axis and that of the half anion on an inversion centre. The extended structure involves three $[Au(dpspf)]^+$ cations connected through gold–gold interactions (Fig. 1). The Au1···Au2 distance is short, 3.0915(6) Å, whereas the Au2···Au2 # 1 distance is much longer, 4.030 Å; the angle Au2–Au1–Au2 # 1 is

Table 1
Selected bond lengths (Å) and angles (°) for compound **4** [a]

Au(1)–Se(1)	2.4217(8)	Se(2)–P(2)	2.172(2)
Au(1)–Au(2)	3.0915(6)	Se(3)–P(3)	2.176(3)
Au(2)–Se(3)	2.4000(9)	Au(3)–Cl(1)	2.245(3)
Au(2)–Se(2)	2.4050(9)	Au(3)–Cl(2)	2.250(3)
Se(1)–P(1)	2.172(2)	Au(4)–Cl(3)	2.226(3)
Se(1)–Au(1)–Se(1) # 1	178.14(5)	Se(2)–Au(2)–Au(1)	94.48(2)
Se(1)–Au(1)–Au(2)	86.72(3)	P(1)–Se(1)–Au(1)	100.55(6)
Se(1) # 1Au(1)–Au(2)	94.70(2)	P(2)–Se(2)–Au(2)	98.81(7)
Au(2)–Au(1)–Au(2) # 1	81.36(2)	P(3)–Se(3)–Au(2)	98.93(7)
Se(3)–Au(2)–Se(2)	178.65(4)	Cl(1)–Au(3)–Cl(2)	179.19(11)
Se(3)–Au(2)–Au(1)	86.60(3)	Cl(3) # 2Au(4)–Cl(3)	180.00

[a] Symmetry transformations used to generate equivalent atoms: $-x+1$, y, $-z+3/2$, $-x+1/2$, $-y+1/2$, $-z+1$.

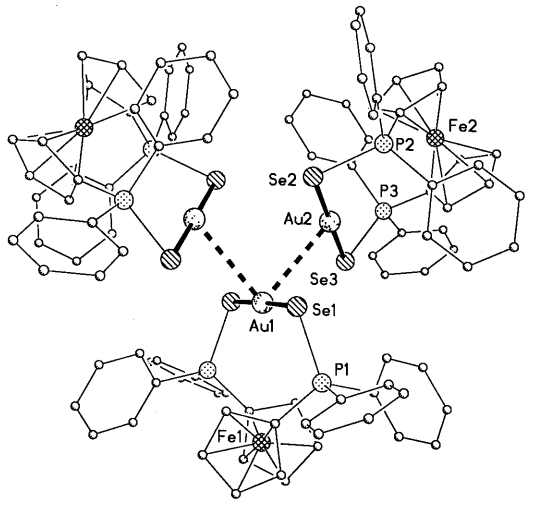


Fig. 1. The cation aggregate of compound **4** with the atom numbering scheme. Hydrogen atoms have been omitted for clarity. Radii are arbitrary.

Table 2
Selected bond lengths (Å) and angles (°) for compound **6**

Ag–S(1)	2.5919(12)	Ag–Se(2)	2.6753(6)
Ag–Se(1)	2.5936(6)	Se(1)–P(2)	2.1358(11)
Ag–S(2)	2.6012(11)	Se(2)–P(3)	2.1363(12)
S(1)–Ag–Se(1)	127.82(3)	Se(1)–Ag–Se(2)	108.897(18)
S(1)–Ag–S(2)	96.05(4)	S(2)–Ag–Se(2)	93.75(3)
Se(1)–Ag–S(2)	110.93(3)	P(2)–Se(1)–Ag	99.17(3)
S(1)–Ag–Se(2)	113.02(3)	P(3)–Se(2)–Ag	109.74(3)

81.36(2)°. This structural framework is different from that in the related [Au(dptpf)]$^+$ derivative [5], in which loose dimers are formed (Au···Au 3.305, 3.370 Å). The coordination around the gold centres is linear (Se1–Au1–Se1 # 178.14(5)°, Se3–Au2–Se2 178.65(4)°), as in [Ag(dptpf)]ClO$_4$ [7] (Se–Ag–Se = 176.5(1)°). The almost ideal geometry shows the great flexibility of this *trans*-bidentate chelating ligand. The Au–Se distances (2.4000(9)–2.4217(8) Å) compare well with those found in [Se{Au$_2$(μ-dppf)}] [8] (2.4055(11), 2.4218(11) Å) and are longer than the values in [Se{Au(PPh$_3$)}$_2$] [9], which contains a bridging selenide centre. The intramolecular gold–iron contacts are 3.981 and 4.017 Å. The corresponding anions [AuCl$_2$]$^-$, which are not involved in noteworthy contacts, exhibit linear geometries (Cl1–Au3–Cl2 179.19(11)°, Cl3 # 2–Au4–Cl3 180° by symmetry) and the Au–Cl distances (2.226(3)–2.250(3) Å) are comparable to those obtained in other linear gold derivatives such as [(μ-dppf)(AuCl)$_2$] (three crystalline modifications, Au–Cl 2.2815(13)–2.300(3) Å) [3,10]. The cyclopentadienyl rings are staggered by 17.9° around the Cp···Cp axis (Cp = centre of the cyclopentadienyl ring) as defined by the torsion angle C(31)–Cp–Cp–C(37).

The gold(III) complex [(μ-dpspf){Au(C$_6$F$_5$)$_3$}$_2$] (**5**) has been obtained by reaction of dpspf with [Au(C$_6$F$_5$)$_3$(OEt$_2$)] in a 1:2 molar ratio. It is an orange, air- and moisture-stable solid and is non-conducting in acetone solutions. The mass spectrum shows the cation molecular peak at $m/z = 2109$ (25%).

The ^{1}H-NMR spectrum shows three multiplets for the phenyl and the α and β protons of the substituted cyclopentadienyl rings. The ^{31}P{^{1}H}-NMR spectrum presents only a singlet at 30.7 with selenium satellites [J(PSe) 576 Hz]. The ^{19}F-NMR spectrum shows six resonances corresponding to the two types of pentafluorophenyl groups, in a ratio 2:1.

Complex **2** can easily react further with other ligands, increasing the coordination number of the silver atom. Indeed, the reaction with bidentate ligands leads to the four co-ordinate complexes [Ag(dpspf)(L–L)]OTf [L–L = (SPPh$_2$)$_2$CH$_2$ (**6**), (SePPh$_2$)$_2$CH$_2$ (**7**), 2,2′-bipyridine (bipy) (**8**) or dpspf (**9**)] (Scheme 1). They are air- and moisture stable orange solids that behave as 1:1 electrolytes in acetone solutions. The positive-ion LSIMS do not show the cation molecular peak, [M–OTf]$^+$, except for complex **7** [$m/z = 1363$ (2%)]. The cation [Ag(dpspf)]$^+$ is observed in all the complexes [$m/z = 821$ (55%)].

The ^{31}P{^{1}H}-NMR spectrum presents only a singlet for complex **8** (34.8 ppm) or **9** [33.5 ppm, J(PSe) 630 Hz], and two singlets for complex **6** or **7** corresponding to the two different phosphorus of the two ligands. The ^{1}H-NMR spectra are in agreement with the proposed structures (see Section 3).

The structure of compound **6** has been established by an X-ray diffraction study, although the precision was somewhat limited by the presence of large amounts of poorly defined solvent. Selected bond lengths and angles are shown in Table 2. The silver atom displays a distorted tetrahedral geometry (Fig. 2) with ligand bite angles of 96.05(4) (S1–Ag–S2) and 108.897(18)° (Se1–Ag–Se2). These bite angles are very dissimilar: the first is similar to that found for the same ligand in the complex [Ag{(SPPh$_2$)$_2$CH$_2$}{(PPh$_2$)$_2$C$_2$B$_{10}$H$_{10}$}]ClO$_4$ (99.20(5)°) [12], whereas the second is much wider and can be attributed to the greater flexibily of the dpspf ligand, as is shown the synthesis of the *trans*-chelating complexes. The Ag–S bond lengths, 2.5916(15), 2.6013(15) Å, can be compared with the values found in complexes such as [AgBr([18]-aneS$_6$)] [11] ([18]-aneS$_6$ = 1,4,7,10,13,16-hexathiacyclooctadecane) (2.514(1)–2.636(1) Å), [Ag{(SPPh$_2$)$_2$CH$_2$}{(PPh$_2$)$_2$C$_2$B$_{10}$H$_{10}$}]ClO$_4$ (2.540(2), 2.588(2) Å) [12] or [Ag$_2${S$_2$C$_2$(CN)$_2$}(PPh$_3$)$_4$] [13] (2.568(7), 2.653(7) Å) for the silver atom in a tetrahedral geometry. Nevertheless, they are slightly longer than in the compound [Ag$_2$(μ-dptpf){(SPPh$_2$)$_2$CH$_2$}$_2$]ClO$_4$ [6] (2.514(2)–2.434(2) Å). The Ag–Se distances (2.5936(6), 2.6753(6) Å) are similar to those found in [Ag{MeSe(CH$_2$)$_2$SeMe}$_2$]$^+$ (2.626(2)–2.638(1)

Å) [14] or in $[AgL_2]^+$ (L = 1,5-diselenacyclooctane) (2.636(4)–2.695(4) Å) [15]. This structure is also different from that of the complex $[Ag_2(\mu\text{-dptpf}\{(SPPh_2)_2CH_2\}_2]ClO_4$ which arose from the reaction of $[Ag(dptpf)]ClO_4$ and $(SPPh_2)_2CH_2$, in a molar relation 1:1, and consists of a polymeric chain [6]. The cyclopentadienyl rings are staggered by 21.4° around the Cp···Cp axis as defined by the torsion angle C(1)–Cp–Cp–C(7).

3. Experimental

Infrared spectra were recorded on a Perkin–Elmer 883 spectrophotometer, over the range 4000–200 cm^{-1}, using Nujol mulls between polyethylene sheets. Conductivities were measured in approximately 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 (LSIMS) technique, using nitrobenzyl alcohol as matrix. ^1H-, ^{19}F- and $^{31}P\{^1H\}$-NMR spectra were recorded on a Varian UNITY 300, Bruker ARX·300 or GEMINI 2000 apparatus in $CDCl_3$ solutions (kept with Na_2CO_3), if no other solvent is stated; chemical shifts are quoted relative to $SiMe_4$ (external, ^1H), $CFCl_3$ (external, ^{19}F) and 85% H_3PO_4 (external, ^{31}P).

The starting materials [AuCl(tht)] [16], $[Au(tht)_2]ClO_4$ [17], $[Au(C_6F_5)_3(OEt_2)]$ [18], $[Cu(NCMe)_4]OTf$ [19], dpspf [5], $(SPPh_2)_2CH_2$ [20] and $(SePPh_2)_2CH_2$ [20] were prepared by published procedures. CAUTION: perchlorate salts with organic cations may be explosive.

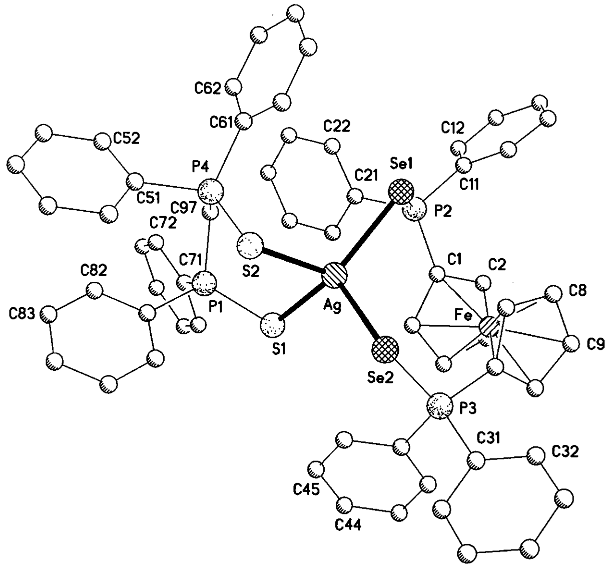


Fig. 2. The cation of compound **6** with the atom numbering scheme. Hydrogen atoms have been omitted for clarity. Radii are arbitrary.

3.1. Syntheses

3.1.1. [Cu(dpspf)]OTf (**1**)

To a solution of dpspf (0.071 g, 0.1 mmol) in tetrahydrofurane under argon atmosphere (20 cm^3) was added $[Cu(NCMe)_4]OTf$ (0.037 g, 0.1 mmol) and the mixture stirred for 30 min. Concentration of the solution to approximately 5 cm^3 and addition of diethyl ether (10 cm^3) gave complex **1** as a pale brown solid. Yield 70%. Λ_M 110 Ω^{-1} cm^2 mol^{-1}. Anal Found (%): C, 45.09; H, 3.43; S, 3.89. Calc. for $C_{35}H_{28}CuF_3FeO_3P_2SSe_2$: C, 45.40; H, 3.03; S, 3.46. ^1H-NMR, δ: 4.33 (m, 4H), 4.71 (m, 4H), 7.3–7.8 (m, 20H, Ph). $^{31}P\{^1H\}$-NMR, δ: 33.0 (s).

3.1.2. [Ag(dpspf)]OTf (**2**)

To a solution of dpspf (0.071 g, 0.1 mmol) in dichloromethane (20 cm^3) was added AgOTf (0.026 g, 0.1 mmol) and the mixture stirred for 30 min. Concentration of the solution to approximately 5 cm^3 and addition of diethyl ether (10 cm^3) gave complex **2** as an orange solid. Yield 50%. Λ_M 67 Ω^{-1} cm^2 mol^{-1}. Anal. Found (%): C, 42.98; H, 2.90; S, 3.85. Calc. for $C_{35}H_{28}AgF_3FeO_3P_2SSe_2$: C, 43.34; H, 2.89; S, 3.30. ^1H-NMR, δ: 4.27 (m, 4H), 4.68 (m, 4H), 7.3–7.9 (m, 20H, Ph). $^{31}P\{^1H\}$-NMR, δ: 34.9 [s, J(SeP) 605 Hz].

3.1.3. [Au(dpspf)]X (X = ClO_4, **3**; $[AuCl_2]$, **4**)

To a solution of dpspf (0.071 g, 0.1 mmol) in dichloromethane (20 cm^3) was added $[Au(tht)_2]ClO_4$ (0.047 g, 0.1 mmol) or [AuCl(tht)] (0.064 g, 0.2 mmol) and the mixture stirred for 30 min. Concentration of the solution to approximately 5 cm^3 and addition of diethyl ether (10 cm^3) gave complexes **3** or **4** as orange solids. Complex **3**: yield 60%. Λ_M 147 Ω^{-1} cm^2 mol^{-1}. Anal. Found (%): C, 40.10; H, 2.40. Calc. for $C_{34}H_{28}AuClFeO_4P_2Se_2$: C, 40.47; H, 2.77. ^1H-NMR, δ: 4.39 (m, 4H), 4.65 (m, 4H), 7.4–7.8 (m, 20H, Ph). $^{31}P\{^1H\}$-NMR, δ: 31.9 (s). Complex **4**: yield 76%. Λ_M 106 Ω^{-1} cm^2 mol^{-1}. Anal. Found (%): C, 34.19; H, 2.62. Calc. for $C_{34}H_{28}Au_2Cl_2FeP_2Se_2$: C, 34.66; H, 2.38. ^1H-NMR, δ: (r.t.) 4.65 (m, 4H), 4.75 (m, 4H), 7.4–7.8 (m, 20H, Ph); (−55°C) 4.60 (m, 4H), 4.70 (m, 4H), 7.4–7.8 (m, 20H, Ph). $^{31}P\{^1H\}$-NMR, δ: (r.t.) 28.9 (s), 31.5 (s); (−55°C) 28.7 [s, J(SeP) 684 Hz], 30.3 (s).

3.1.4. [(μ-dpspf){Au(C_6F_5)$_3$}$_2$] (**5**)

To a solution of $[Au(C_6F_5)_3(OEt_2)]$ (0.154 g, 0.2 mmol) in dichloromethane (20 cm^3) was added dpspf (0.071 g, 0.1 mmol) and the mixture stirred for 30 min. Concentration of the solution to approximately 5 cm^3 and addition of hexane (10 cm^3) gave complex **5** as an orange solid. Yield 73%. Λ_M 7 Ω^{-1} cm^2 mol^{-1}. Anal. Found (%): C, 39.80; H, 2.22. Calc. for $C_{70}H_{28}Au_2F_{30}FeP_2Se_2$: C, 39.84; H, 1.40. ^1H-NMR, δ:

Table 3
Details of data collection and structure refinement for complexes **4** and **6**

Compound	**4** 5/3 CH_2Cl_2	**6**·3CH_2Cl_2
Empirical formula	$C_{35.67}H_{31.33}Au_2$-$Cl_{5.33}FeP_2Se_2$	$C_{63}H_{56}AgCl_6F_3FeO_3$-$P_4S_3Se_2$
Crystal habit	Yellow prism	Yellow prism
Crystal size (mm^{-1})	0.26 × 0.13 × 0.08	0.41 × 0.28 × 0.12
Crystal system	Monoclinic	Triclinic
Space group	*C*2/*c*	$P\bar{1}$
a (Å)	29.615(3)	14.2813(12)
b (Å)	17.6644(18)	16.3269(14)
c (Å)	23.448(2)	16.5422(14)
α (°)	90	63.307(3)
β (°)	106.537(3)	84.146(3)
γ (°)	90	81.568(3)
U (Å^3)	11759(2)	3406.0(5)
Z	12	2
D_{calc} (g cm^{-3})	2.235	1.631
M	1318.65	1672.48
F(000)	7416	1672
T (°C)	−130	−130
$2\theta_{max}$ (°)	53	57
μ(Mo–K$_\alpha$) (mm^{-1})	10.16	2.04
Transmission	0.745, 0.928	0.488, 0.792
Reflections measured	67080	67140
Unique reflections	16866	16876
R_{int}	0.1051	0.0518
R [a] ($F>4\sigma(F)$)	0.0529	0.0574
wR_2 [b](F^2, all reflections)	0.1584	0.1929
Reflections used	16866	16876
Parameters	787	767
Restraints	620	199
S [c]	1.052	0.756
Max. $\Delta\rho$ (e Å^{-3})	3.299	3.399

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

[b] $wR(F^2)=[\Sigma\{w(F_o^2-F_c^2)^2\}/\{w(F_o^2)^2\}]^{1/2}$; $w^{-1}=\sigma^2(F_o^2)+(aP)^2+bP$, 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.

4.40 (m, 4H), 4.68 (m, 4H), 7.3–7.9 (m, 20H, Ph). $^{31}P\{^1H\}$-NMR, δ: 30.7 [s, *J*(SeP) 576 Hz]. ^{19}F-NMR, δ: −119.7 (m, 4F, *o*-F), −157.5 [t, 2F, *p*-F, *J*(FF) 20.1 Hz], −161.3 (m, 4F, *m*-F); −122.5 (m, 2F, *o*-F), −157.4 [t, 1F, *p*-F, *J*(FF) 20.2 Hz], −161.4 (m, 2F, *m*-F).

3.1.5. [Ag(dpspf)(L–L)]OTf [L–L = $(SPPh_2)_2CH_2$, **6**; $(SePPh_2)_2CH_2$, **7**; bipy, **8**; dpspf, **9**]

To a solution of [Ag(dpspf)]OTf (0.097 g, 0.1 mmol) in dichloromethane (20 cm^3) was added $(SPPh_2)_2CH_2$ (0.045 g, 0.1 mmol), $(SePPh_2)_2CH_2$ (0.054 g, 0.1 mmol), bipy (0.015 g, 0.1 mmol) or dpspf (0.071 g, 0.1 mmol), respectively and the mixture stirred for 30 min. Concentration of the solution to approximately 5 cm^3 and addition of diethyl ether (10 cm^3) gave complexes **6**–**9** as orange solids. Complex **6**: yield 63%. Λ_M 117 Ω^{-1} cm^2 mol^{-1}. Anal. Found (%): C, 50.80; H, 3.54; S, 6.89. Calc. for $C_{60}H_{50}AgF_3FeO_3P_4S_3Se_2$: C, 50.81; H, 3.52; S, 6.77. ^1H-NMR, δ: 4.40 (m, 4H), 4.54 (m, 4H), 4.14 (t, 2H, *J*(PH) = 13 Hz), 7.3–8 (m, 40H, Ph). $^{31}P\{^1H\}$-NMR, δ: 37.3 (s, 2P, dpspf), 32.5 [s, 2P, $(SPPh_2)_2CH_2$]. Complex **7**: yield 74%. Λ_M 139 Ω^{-1} cm^2 mol^{-1}. Anal. Found (%): C, 47.3; H, 3.51; S, 2.54. Calc. for $C_{60}H_{50}AgF_3FeO_3P_4SSe_4$: C, 47.65; H, 3.31; S, 2.12. ^1H-NMR, δ: 4.41 (m, 4H), 4.48 (m, 6H, $C_5H_4+CH_2$), 7.4–7.8 (m, 40H, Ph). $^{31}P\{^1H\}$-NMR, δ: 26.3 [s, 2P, $(SePPh_2)_2CH_2$], 32.2 (s, 2P, dpspf). Complex **8**: yield 64%. Λ_M 120 Ω^{-1} cm^2 mol^{-1}. Anal. Found (%): C, 47.58; H, 3.24; S, 3.04; N, 2.20. Calc. for $C_{45}H_{36}AgF_3FeN_2O_3P_2SSe_2$: C, 48.0; H, 3.20; S, 2.84; N, 2.48. ^1H-NMR, δ: 4.31 (m, 4H), 4.69 (m, 4H), 7.5–7.7 (m, 20H, Ph), 8.64 (m, 1H, bipy), 8.37 [d, 1H, bipy, *J*(HH) 7.8 Hz], 7.94 [t, 1H, bipy, *J*(HH) 6.2 Hz], 7.40 (m, 1H, bipy). $^{31}P\{^1H\}$-NMR, δ: 34.8 (s). Complex **9**: yield 51%. Λ_M 147 Ω^{-1} cm^2 mol^{-1}. Anal. Found (%): C, 48.96; H, 3.23; S, 2.07. Calc. for $C_{69}H_{56}AgF_3Fe_2O_3P_4SSe_4$: C, 49.25; H, 3.33; S, 1.90. ^1H-NMR, δ: 4.36 (m, 8H), 4.62 (m, 8H), 7.4–7.8 (m, 40H, Ph). $^{31}P\{^1H\}$-NMR, δ: 33.5 [s, *J*(SeP) 630 Hz].

3.2. Crystallography

The crystals were mounted in inert oil on a glass fibre and transferred to the cold gas stream of a Bruker SMART 1000 CCD area detector equipped with an LT-3 low temperature attachment. Absorption corrections were based on multiple scans (program SADABS). Crystallographic data are summarised in Table 3. Structures were solved by direct methods and refined against F^2 (program SHELXL-97, G.M. Sheldrick, University of Göttingen, Germany).

3.2.1. Special refinement details

The asymmetric unit of compound **4** contains four dichloromethane sites, three of which are disordered (half occupied). The overall stoichiometry is thus one formula unit of the complex to 5/3 molecules of dichloromethane. The ring C72–C76 is disordered over two positions. All rings were refined isotropically with idealised geometry. The poor *R* values obtained for compound **6** are associated with the ill-defined or disordered solvent and anion; an extensive system of restraints to light atom temperature factors and local ring symmetry was employed to improve refinement stability.

4. Supplementary material

Complete crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre under the CCDC nos. 143 500 (**4**) and 143 501 (**6**). Copies can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

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