

# Gold and silver complexes with the ligands $\text{Fc}(\text{SPh})_2$ and $\text{Fc}(\text{SePh})_2$ ( $\text{Fc} = (\eta^5\text{-C}_5\text{H}_4)_2\text{Fe}$ )

Silvia Canales,<sup>a</sup> Olga Crespo,<sup>a</sup> Angela Fortea,<sup>a</sup> M. Concepción Gimeno,<sup>a</sup> Peter G. Jones<sup>b</sup> and Antonio Laguna<sup>\*a</sup>

<sup>a</sup> Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, E-50009 Zaragoza, Spain

<sup>b</sup> Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, D-38023 Braunschweig, Germany

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The reaction of  $\text{Fc}(\text{Li})_2$  with diphenyl disulfide or diselenide gives the ferrocene derivatives  $\text{Fc}(\text{XPh})_2$  ( $\text{X} = \text{S}, \text{Se}$ ). These react with various gold or silver species to afford complexes where the ligand can act in either a bridging or a chelating mode. Thus gold(I) or gold(III) derivatives of the type  $[\text{Au}(\text{PPh}_3)\{\text{Fc}(\text{XPh})_2\}]\text{OTf}$  or  $[\{\text{Au}(\text{C}_6\text{F}_5)_3\}_2\{\text{Fc}(\text{XPh})_2\}]$  have been obtained by treatment of the ligands with the appropriate starting material. The reaction of  $\text{Fc}(\text{XPh})_2$  with  $\text{AgOTf}$  in 1 : 1 or 2 : 1 molar ratio leads to  $[\text{Ag}(\text{OTf})\{\text{Fc}(\text{XPh})_2\}]$  or  $[\text{Ag}\{\text{Fc}(\text{XPh})_2\}_2]\text{OTf}$ , respectively. Starting from  $[\text{Ag}(\text{OTf})(\text{PPh}_3)]$  the compounds  $[\text{Au}(\text{PPh}_3)\{\text{Fc}(\text{XPh})_2\}]\text{OTf}$  have been prepared. Finally, substitution of the triflate in  $[\text{Ag}(\text{OTf})\{\text{Fc}(\text{XPh})_2\}]$  by other ligands such as phenanthroline gives  $[\text{Ag}(\text{phen})\{\text{Fc}(\text{XPh})_2\}]\text{OTf}$ . The crystal structures of some of these complexes have been established by X-ray diffraction studies.

## Introduction

Although the ferrocene molecule was discovered nearly fifty years ago, its chemistry and the design of new compounds containing the ferrocene unit is currently attracting great interest because of their increasing role in the rapidly growing areas of materials science, organic synthesis or catalysis.<sup>1–3</sup> Ferrocene species in which the cyclopentadienyl rings are substituted with donor heteroatoms are well known. Studies of these ligands are important because the complexes thus obtained may present interesting redox properties or unusual structures.

As part of our studies of ferrocene derivatives as ligands,<sup>4</sup> we report here on the coordination chemistry of the ligands 1,1'-bis(phenylthio)ferrocene and 1,1'-bis(phenylseleno)ferrocene with gold and silver centres. Several alkyl or aryl thio- or seleno-ferrocenes have been previously described; these are usually obtained by reaction of 1,1'-dilithioferrocene with the corresponding disulfide or diselenide,<sup>5–7</sup> although some unsymmetrically disubstituted derivatives have been prepared by cleavage of the trisulfur bridge in 1,2,3-trithia[3]ferrocenophane.<sup>8,9</sup> The coordination chemistry of these ligands has been studied mainly with palladium and platinum; some silver complexes have been recently reported.<sup>5–7,9,10</sup> As far as we are aware the only gold compounds described with ferrocenylthio derivatives have been recently reported by us, using the ligand 1,1-bis(pyridylthio)ferrocene,<sup>11</sup> and no gold or silver compounds have been described with ferrocenylseleno derivatives.

## Results and discussion

Ferrocenyl sulfide or selenide compounds of the type  $\text{Fc}(\text{XPh})_2$  ( $\text{X} = \text{S}$  (**1**) or  $\text{Se}$  (**2**)) have been prepared in a general high-yield synthesis by reaction of  $\text{FcLi}_2$  (prepared from ferrocene, *n*-butyllithium and tetramethylethylenediamine) with  $\text{S}_2\text{Ph}_2$  or  $\text{Se}_2\text{Ph}_2$ . We have studied the reaction of these ligands with gold or silver derivatives.

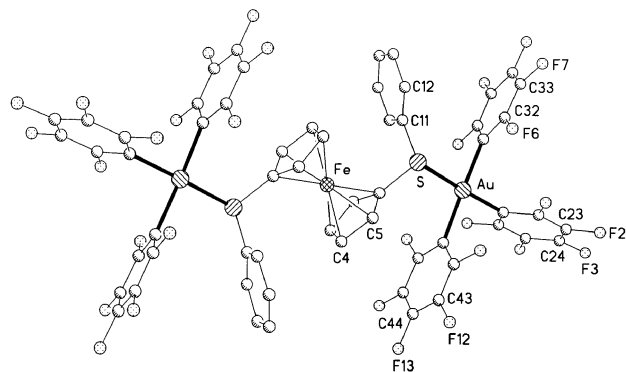
Usually ligands of the type  $\text{SR}_2$  or  $\text{SeR}_2$  do not coordinate strongly to gold(I) centres, indeed we usually use tetrahydrothiophene, tht, as an easily displaced ligand. We have carried

out the reactions with  $[\text{Au}(\text{OTf})(\text{PPh}_3)]$  as a suitable starting material because of the presence of the labile trifluoromethanesulfonate. Thus the reaction of  $\text{Fc}(\text{XPh})_2$  with  $[\text{Au}(\text{OTf})(\text{PPh}_3)]$  in a 1 : 1 molar ratio gives rise to the three-coordinate gold(I) derivatives,  $[\text{Au}(\text{PPh}_3)\{\text{Fc}(\text{XPh})_2\}]\text{OTf}$  ( $\text{X} = \text{S}$  (**3**),  $\text{Se}$  (**4**), see Scheme 1). Complexes **3** and **4** are air- and moisture-stable orange solids that behave as 1 : 1 electrolytes in acetone solutions. In the IR spectra the absorptions arising from anionic triflate appear at 1265 (vs, br), 1223 (s), 1150 (s) and 1023 (s)  $\text{cm}^{-1}$ . The  $^1\text{H}$  NMR spectra show only one multiplet for the cyclopentadienyl protons, and typical resonances for the phenylic protons. The  $^{31}\text{P}$  ( $^1\text{H}$ ) NMR spectra present a singlet for the unique phosphorus atom. In the positive liquid secondary-ion mass spectra the cationic molecular peaks appear at  $m/z = 861$  (12%) and 957 (2%) for complexes **3** and **4**, respectively.

We have also prepared gold(III) derivatives, which are as expected more stable with this type of ligand. Thus the treatment of  $\text{Fc}(\text{XPh})_2$  with 2 equiv. of  $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{OEt}_2)]$  gives the complexes  $[\{\text{Au}(\text{C}_6\text{F}_5)_3\}_2\{\text{Fc}(\text{XPh})_2\}]$  ( $\text{X} = \text{S}$  (**5**),  $\text{Se}$  (**6**)). Complexes **5** and **6** are orange air- and moisture-stable solids that behave as non-conductors in acetone solutions. The  $^1\text{H}$  NMR spectra of both compounds present a multiplet for the phenylic protons and complex **5** shows two multiplets for the  $\alpha$  and  $\beta$  cyclopentadienyl protons, whereas complex **6** shows eight multiplets corresponding to the eight inequivalent protons of the cyclopentadienyl rings. Usually, complexes with disubstituted ferrocene ligands show two multiplets in the  $^1\text{H}$  NMR spectra for the  $\alpha$  and  $\beta$  protons of the cyclopentadienyl rings, even though in the solid state (because of the different ring conformations) the eight protons are inequivalent. This is, however, seldom observed; sometimes when the temperature is lowered four proton signals, or in a few cases eight, are observed. We have previously observed the inequivalence of the eight protons at room temperature in gold complexes with disubstituted ferrocene ligands.<sup>12</sup> The  $^{19}\text{F}$  NMR spectra present the typical pattern for equivalent “ $\text{Au}(\text{C}_6\text{F}_5)_3$ ” groups, which consists of six signals in a 2 : 1 ratio for the mutually *trans* and *cis* pentafluorophenyl groups, respectively. In the LSIMS+ spectra the

molecular peaks do not appear, but the peaks arising from the loss of one  $\text{Au}(\text{C}_6\text{F}_5)_3$  group are present at  $m/z = 1100$  (4%, **5**) and 1196 (5%, **6**).

The crystal structure of **5** has been established by X-ray diffraction studies and is shown in Fig. 1, with a selection of bond lengths and angles in Table 1.



**Fig. 1** Structure of complex **5** in the crystal, showing the atom numbering scheme. H atoms are omitted for clarity.

Compound **5** possesses an inversion centre. The gold centre exhibits square planar geometry (angles from 88.18(15) to 91.44(11)°) with the gold atom essentially coplanar with the S, C(31), C(21) and C(41) atoms. The Au–C distances range from 2.028(4) to 2.073(4) Å; the shortest involves the pentafluorophenyl group *trans* to the sulfur atom. The larger values compare with those found in compound  $[\text{Au}_4(\mu_3\text{-SC}_6\text{F}_5)_2(\text{C}_6\text{F}_5)_6(\mu\text{-dppf})]^{13}$  (dppf = 1,1'-bis(diphenylphosphino)ferrocene)

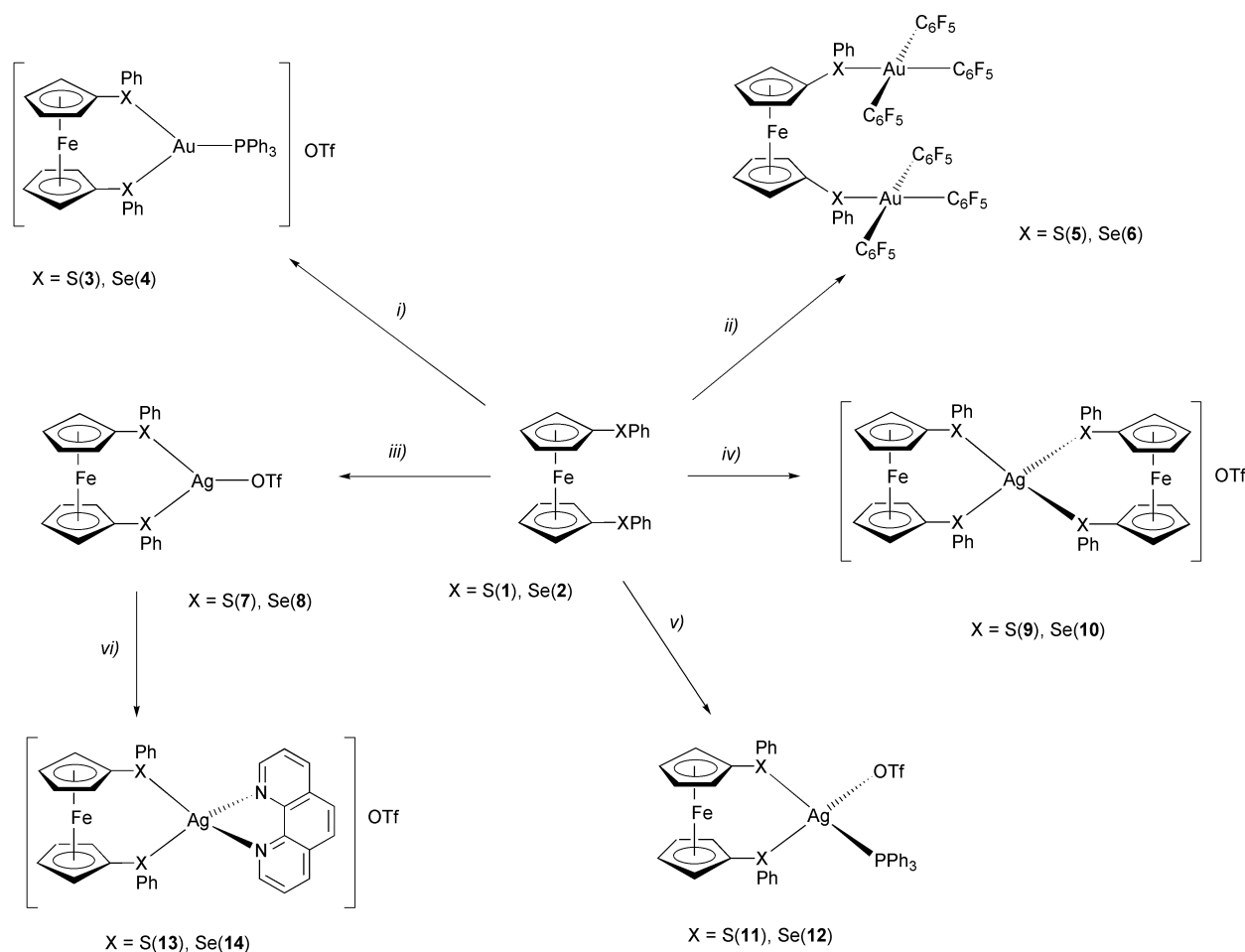
**Table 1** Selected bond lengths [Å] and angles [°] for complex **5**

Au–C(21)	2.028(4)	Au–S	2.3786(11)
Au–C(31)	2.068(4)	S–C(11)	1.788(4)
Au–C(41)	2.073(4)		
C(21)–Au–C(31)	88.18(15)	C(31)–Au–S	91.16(12)
C(21)–Au–C(41)	89.30(15)	C(41)–Au–S	91.44(11)
C(31)–Au–C(41)	177.31(15)	C(1)–S–Au	107.63(13)
C(21)–Au–S	174.03(11)	C(11)–S–Au	109.11(13)

(Au–C 2.048(7)–2.056(7) Å),  $[\text{MeC}_6\text{H}_3\{\text{NHPPPh}_2\text{SAu}(\text{C}_6\text{F}_5)_3\}_2]$  (2.064(10)–2.088(9) Å),<sup>14</sup> or in  $[\text{C}_6\text{H}_4\{\text{NHPPPh}_2\text{Au}(\text{C}_6\text{F}_5)_3\}\text{-}\{\text{N}(\text{AuPPh}_3)\text{PPh}_2\text{Au}(\text{C}_6\text{F}_5)_3\}]^{14}$  (range 2.061(6)–2.079(6) Å). The Au–S distance (2.3786(11) Å) resembles that found in  $[\text{Au}_4(\mu_3\text{-SC}_6\text{F}_5)_2(\text{C}_6\text{F}_5)_6(\mu\text{-dppf})]$  (2.380(2) Å).<sup>13</sup> Slightly larger values have been described for  $[\text{MeC}_6\text{H}_3\{\text{NHPPPh}_2\text{SAu}(\text{C}_6\text{F}_5)_3\}_2]$  (2.400(5), 2.403(5) Å)<sup>14</sup> and shorter distances are shown in  $[\text{Au}_2\text{Cl}_4(\mu\text{-SPh})_2]$  (2.332(5), 2.339(5) Å).<sup>15</sup>

X-Ray diffraction studies have also been carried out for compound **6**. The compound crystallises in the monoclinic system, space group  $P2_1/n$ , with cell parameters:  $a = 21.4924$ ,  $b = 9.1778$ ,  $c = 28.9178$  Å,  $\beta = 94.085^\circ$ ,  $Z = 6$ . The geometry is analogous to that shown by complex **5**. Unfortunately the poor quality of the data does not allow a comparison of geometrical parameters.

The reaction of **1** or **2** with  $\text{Ag}(\text{OTf})$  affords the complexes  $[\text{Ag}(\text{OTf})\{\text{Fc}(\text{XPh})_2\}]$  ( $\text{X} = \text{S}(\mathbf{7})$ ,  $\text{Se}(\mathbf{8})$ ). Compounds **7** and **8** are air- and moisture-stable orange solids that behave as non-conductors in acetone solutions. Their IR spectra show absorptions of the triflate anion bonded to silver at 1245 (vs, br), 1223 (s), 1169 (s) and 1151 (s) for **7** and 1240 (vs, br), 1220 (s), 1163 (s), 1150 (s) and 1025 (s)  $\text{cm}^{-1}$  for **8**, which are characteristic of coordinated triflate.



**Scheme 1** Reagents and conditions; i)  $[\text{Au}(\text{OTf})(\text{PPh}_3)]$ ,  $\text{CH}_2\text{Cl}_2$ , 15 min, ii)  $2[\text{Au}(\text{C}_6\text{F}_5)_3(\text{OEt}_2)]$ ,  $\text{CH}_2\text{Cl}_2$ , 15 min, iii)  $[\text{Ag}(\text{OTf})]$ ,  $\text{CH}_2\text{Cl}_2$ , 30 min, iv)  $1/2[\text{Ag}(\text{OTf})]$ ,  $\text{CH}_2\text{Cl}_2$ , 30 min, v)  $[\text{Ag}(\text{OTf})(\text{PPh}_3)]$ ,  $\text{CH}_2\text{Cl}_2$ , 15 min, vi) phen,  $\text{CH}_2\text{Cl}_2$ , 15 min.

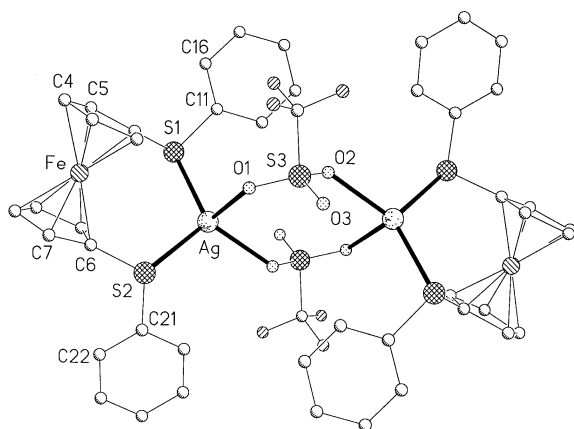
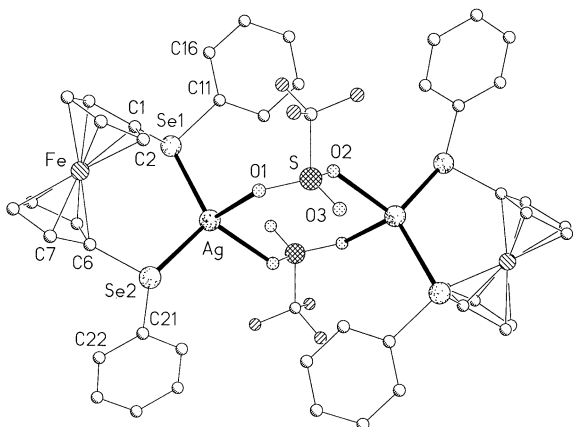
**Table 2** Selected bond lengths [Å] and angles [°] for complex **7**

Ag–O(2)#1	2.312(2)	Ag–O(1)	2.521(2)
Ag–S(1)	2.5037(8)	Ag–S(2)	2.5558(8)
O(2)#1–Ag–S(1)	135.24(7)	C(1)–S(1)–Ag	99.70(10)
O(2)#1–Ag–O(1)	88.64(8)	C(11)–S(1)–Ag	107.15(10)
S(1)–Ag–O(1)	103.25(6)	C(6)–S(2)–Ag	104.04(10)
O(2)#1–Ag–S(2)	109.14(6)	C(21)–S(2)–Ag	110.22(11)
S(1)–Ag–S(2)	112.01(3)	S(3)–O(1)–Ag	133.81(15)
O(1)–Ag–S(2)	96.55(6)	S(3)–O(2)–Ag#1	124.51(14)

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

The  $^1\text{H}$  NMR spectra present the resonances due to the phenylic protons and for complex **7** two multiplets for the  $\alpha$  and  $\beta$  protons of the cyclopentadienyl units; compound **8** presents only a broad multiplet for all the Cp protons.

The structures of complexes **7** and **8** have been established by X-ray diffraction studies. The complexes are isostructural; the molecule of **7** is shown in Fig. 2 and that of **8** in Fig. 3. A selection of bond lengths and angles for **7** is collected in Table 2

**Fig. 2** Perspective view of complex **7**, with the atom labelling scheme; H atoms are omitted for clarity.**Fig. 3** Structure of complex **8** in the crystal, showing the atom numbering scheme. H atoms are omitted for clarity.

and for **8** in Table 3. The molecules display crystallographic inversion symmetry; they are dimers in which the two silver centres are tetracoordinated, being bridged by two oxygen atoms of the triflate ligands and chelated by an  $\text{Fc}(\text{SPh})_2$  or  $\text{Fc}(\text{SePh})_2$  ligand, respectively.

In complexes **7** and **8** the geometry around the silver centres is distorted tetrahedral; the main distortions arise at the narrow angles formed by O(1)–Ag–O(2)#1, which are 88.64(8)° for complex **7** and 89.40(6)° for complex **8** (#1  $-x + 1, -y + 1, -z + 1$ ) and the wide O(2)#1–Ag–S(1) or O(2)#1–Ag–Se(1)

**Table 3** Selected bond lengths [Å] and angles [°] for complex **8**

Ag–O(2)#1	2.3267(17)	Ag–Se(1)	2.5888(4)
Ag–O(1)	2.4999(18)	Ag–Se(2)	2.6339(3)
O(2)#1–Ag–O(1)	89.40(6)	C(1)–Se(1)–Ag	96.33(7)
O(2)#1–Ag–Se(1)	132.32(4)	C(11)–Se(1)–Ag	104.03(7)
O(1)–Ag–Se(1)	104.62(4)	C(6)–Se(2)–Ag	100.97(7)
O(2)#1–Ag–Se(2)	109.39(4)	C(21)–Se(2)–Ag	106.50(7)
O(1)–Ag–Se(2)	96.55(4)	S–O(1)–Ag	133.41(11)
Se(1)–Ag–Se(2)	113.744(10)	S–O(2)–Ag#1	124.07(10)

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

angles of 135.24(7) or 132.32(4)°, respectively. The Ag–O distances are very similar at 2.312(2) and 2.521(2) Å for complex **7** and 2.327(2) and 2.500(2) Å for complex **8**, indicating a weaker bond to the second triflate unit. The silver atom lies only 0.26 Å out of the plane formed by the atoms O(2)#1, S(1) and S(2) in **7** and 0.30 Å out of the plane formed by O(2)#1, Se(1) and Se(2) in **8**. The Ag–S bond lengths are 2.5037(8) and 2.5558(8) Å, which lie between the values for three-coordinated complexes such as  $[\text{Ag}_2\{\text{S}_2\text{C}_2(\text{CN})_2\}(\text{PPh}_3)_4]$  (2.478(7) Å)<sup>16</sup> and four-coordinated complexes such as  $[\text{AgBr}(18\text{S}_6)]$  ( $18\text{S}_6 = 1,4,7,10,13,16$ -hexathiacyclooctadecane) (2.514(1)–2.636(1) Å)<sup>17</sup> or  $[\text{Ag}\{\text{SPPPh}_2\text{CH}_2\}\{\text{PPh}_2\text{C}_2\text{B}_{10}\text{H}_{10}\}]\text{ClO}_4$  (2.540(2), 2.588(2) Å).<sup>18</sup> The Ag–Se bond distances are 2.5888(4) and 2.6339(3) Å and are similar to those found in the complex  $[\text{Ag}_6(6\text{-Me}_3\text{SipySe})_6]$  (2.5943(14)–2.6044(13) Å),<sup>19</sup> where the silver centre is tricoordinated, but shorter than those in selenoether complexes with Ag–Se bond distances in the range 2.610–2.695 Å.<sup>20</sup>

In both structures there are several intermolecular hydrogen bonds of the type C–H  $\cdots$  O, of which the shortest are O(3)  $\cdots$  H2 2.50 Å for complex **7** and O(3)  $\cdots$  H14 2.44 Å for compound **8**.

The treatment of **1** or **2** with  $\text{Ag}(\text{OTf})$  in a 2 : 1 molar ratio leads to the tetracoordinated complexes  $[\text{Ag}\{\text{Fc}(\text{XPh})_2\}_2]\text{OTf}$  (X = S (**9**), Se (**10**)) in good yield. They are air- and moisture-stable orange solids that behave as 1 : 1 electrolytes in acetone solutions. Their IR spectra present the absorptions for ionic trifluoromethanesulfonate at 1237 (s), 1222 (s), 1154 (s) and 1024 (s)  $\text{cm}^{-1}$ .

The  $^1\text{H}$  NMR spectra show multiplets for the protons of the phenyl groups and also for the protons of the cyclopentadienyl rings. In the LSIMS+ spectra the cation molecular peaks appear at  $m/z = 912$  (5%, **9**) or 1100 (18%, **10**).

We have also carried out the reaction of **1** or **2** with other silver salts such as  $[\text{Ag}(\text{OTf})(\text{PPh}_3)]$  in a 1 : 1 molar ratio to give the complexes  $[\text{Ag}(\text{OTf})(\text{PPh}_3)\{\text{Fc}(\text{XPh})_2\}]$  (X = S (**11**), Se (**12**)). Their IR spectra show the bands arising for the covalent trifluoromethanesulfonate at 1241 (s), 1221 (s), 1165 (s), 1153 (s) and 1025 (s)  $\text{cm}^{-1}$  for compound **12**.

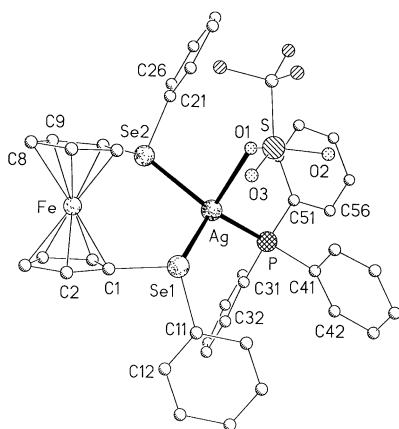
The  $^1\text{H}$  NMR spectra present the resonances for the cyclopentadienyl and phenylic protons in the appropriate ratio for one coordinated  $\text{AgPPh}_3$ . The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of complex **11** at room temperature consists of a broad multiplet that splits at  $-55^\circ\text{C}$  into two doublets as a consequence of the coupling of phosphorus atoms with both silver nuclei,  $^{107}\text{Ag}$  and  $^{109}\text{Ag}$ . For compound **12** only a broad doublet is observed at room temperature, that also splits, at  $-55^\circ\text{C}$ , into two doublets.

In the positive-ion mass spectra the cation molecular peaks arising from the loss of one triflate anion appear for complex **11** at  $m/z = 773$  (21%) and for complex **12** at  $m/z = 867$  (12%).

The crystal structure of complex **12** has been established by an X-ray diffraction study. The molecule is shown in Fig. 4 and a selection of bond lengths and angles is collected in Table 4. The silver centre has a tetrahedral geometry and is bonded to the 1,1'-bis(phenylseleno)ferrocene ligand, acting as a chelate,

**Table 4** Selected bond lengths [Å] and angles [°] for complex **12**

Ag–P	2.443(3)	Ag–Se(2)	2.645(2)
Ag–O(1)	2.473(12)	Ag–Se(1)	2.7347(18)
P–Ag–O(1)	108.7(4)	C(1)–Se(1)–Ag	100.1(4)
P–Ag–Se(2)	124.12(11)	C(6)–Se(2)–Ag	105.5(5)
O(1)–Ag–Se(2)	94.1(4)	C(21)–Se(2)–Ag	107.7(5)
P–Ag–Se(1)	119.34(10)	C(51)–P–Ag	114.6(5)
O(1)–Ag–Se(1)	95.8(3)	C(41)–P–Ag	112.2(4)
Se(2)–Ag–Se(1)	107.58(6)	C(31)–P–Ag	114.3(4)
C(11)–Se(1)–Ag	106.1(3)	S–O(1)–Ag	132.7(8)

**Fig. 4** Perspective view of complex **12**, with the atom labelling scheme; H atoms are omitted for clarity.

to the triphenylphosphine and the oxygen atom of the triflate. The angles Se(1)–Ag–Se(2) and O(1)–Ag–P are very regular, 107.58(6) and 108.7(4)°, whereas the O(1)–Ag–Se(2) and P–Ag–Se(1) angles are 94.1(4) and 119.34(10)°, respectively. The Ag–Se bond distances are also somewhat dissimilar, 2.645(2) and 2.7347(18) Å, and slightly longer than those found in compound **8**, but of the same order as those found in selenoether derivatives.<sup>20</sup>

Complexes **7** and **8** possess a weakly coordinated ligand in trifluoromethanesulfonate and thus can react further with other ligands such as 1,10-phenanthroline (phen) to give the complexes [Ag(phen){Fc(XPh)<sub>2</sub>}]OTf (X = S (**13**), Se (**14**)), presumably with the silver centres in a tetrahedral geometry. Complexes **13** and **14** are orange and moisture-stable solids that behave as 1 : 1 electrolytes in acetone solutions.

The <sup>1</sup>H NMR spectra of **13** and **14** present only two multiplets for the phenyl and cyclopentadienyl protons and four signals for the phenanthroline protons. In the mass spectra (LSIMS+) the cation molecular peaks appear at *m/z* = 691 (19%, **13**) and 785 (14%, **14**), respectively.

## Experimental

### Instrumentation

Infrared spectra were recorded on a Perkin-Elmer 883 spectrophotometer, over the range 4000–200 cm<sup>-1</sup>, using Nujol mulls between polyethylene sheets. Conductivities were measured in *ca.* 5 × 10<sup>-4</sup> mol dm<sup>-3</sup> solutions with a Philips 9509 conductimeter. C, H, and N 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 3-nitrobenzyl alcohol as matrix. NMR spectra were recorded on a Varian UNITY 300 or Bruker ARX 300 apparatus in CDCl<sub>3</sub> solutions. Chemical shifts are quoted relative to SiMe<sub>4</sub> (external, <sup>1</sup>H), CFCl<sub>3</sub> (<sup>19</sup>F, external), and 85% H<sub>3</sub>PO<sub>4</sub> (external, <sup>31</sup>P).

## Materials

The starting materials Fc(SPh)<sub>2</sub>,<sup>5</sup> Fc(SePh)<sub>2</sub>,<sup>5</sup> [Au(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-(OEt<sub>2</sub>)<sub>2</sub>]<sup>21</sup> were prepared by published procedures. [Au(OTf)-(PPh<sub>3</sub>)] was obtained by reaction of [AuCl(PPh<sub>3</sub>)]<sup>22</sup> with Ag(OTf) in dichloromethane and [Ag(OTf)(PPh<sub>3</sub>)] by reaction of Ag(OTf) with PPh<sub>3</sub> in diethyl ether. All other chemicals used were commercially available and used without further purification.

## Syntheses

**Synthesis of [Au(PPh<sub>3</sub>)<sub>2</sub>]{Fc(XPh)<sub>2</sub>}OTf (X = S (**3**), Se (**4**)).** To a solution of [Fc(XPh)<sub>2</sub>] (0.040 g, 0.1 mmol, **3**; 0.049 g, 0.1 mmol, **4**) in 20 mL of dichloromethane was added the corresponding amount of [Au(OTf)(PPh<sub>3</sub>)] (0.061 g, 0.1 mmol) and the mixture stirred for 15 min. Concentration of the solution to *ca.* 5 mL and addition of diethyl ether (10 mL) gave complexes **3** and **4** as orange solids. Complex **3**: Yield 76%. *A<sub>M</sub>* 117 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. Elemental analysis (%). Found: C, 49.98; H, 3.54; S, 9.45. Calc. for C<sub>41</sub>H<sub>33</sub>AuF<sub>3</sub>FeO<sub>3</sub>S<sub>3</sub>: C, 50.41; H, 3.37; S, 9.80. <sup>31</sup>P{<sup>1</sup>H}, δ: 34.2 (s) ppm. <sup>1</sup>H, δ: 7.5–7.1 (m, 25H, C<sub>6</sub>H<sub>5</sub>), 4.52 (m, 8H, C<sub>5</sub>H<sub>4</sub>) ppm. Complex **4**: Yield 54%. *A<sub>M</sub>* 108 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. Elemental analysis (%). Found: C, 45.52; H, 2.74; S, 2.75. Calc. for C<sub>41</sub>H<sub>33</sub>AuF<sub>3</sub>FeO<sub>3</sub>Se<sub>2</sub>: C, 45.85; H, 3.07; S, 2.98. <sup>31</sup>P{<sup>1</sup>H}, δ: 34.8 (s) ppm. <sup>1</sup>H, δ: 7.59–7.12 (m, 25H, C<sub>6</sub>H<sub>5</sub>), 4.55 (m, 8H, C<sub>5</sub>H<sub>4</sub>) ppm.

**Synthesis of [{Au(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>}<sub>2</sub>]{Fc(XPh)<sub>2</sub>} (X = S (**5**), Se (**6**)).** To a solution of [Fc(XPh)<sub>2</sub>] (0.040 g, 0.1 mmol, **5**; 0.049 g, 0.1 mmol, **6**) in 20 mL of dichloromethane was added [Au(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>(OEt<sub>2</sub>)] (0.154 g, 0.2 mmol) and the mixture stirred for 15 min. Concentration of the solution to *ca.* 5 mL and addition of hexane (10 mL) gave complexes **5** or **6** as orange solids. Complex **5**: Yield 57%. *A<sub>M</sub>* 0.5 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. Elemental analysis (%). Found: C, 38.98; H, 1.33; S, 3.61. Calc. for C<sub>58</sub>H<sub>18</sub>Au<sub>2</sub>F<sub>30</sub>FeS<sub>2</sub>: C, 38.71; H, 1.00; S, 3.56. <sup>1</sup>H, δ: 7.63–7.43 (m, 10H, C<sub>6</sub>H<sub>5</sub>), 4.06 (m, 4H, C<sub>5</sub>H<sub>4</sub>), 3.94 (m, 4H, C<sub>5</sub>H<sub>4</sub>) ppm. <sup>19</sup>F, δ: -121.8 (m, 8F, *o*-F), -122.3 (m, 4F, *o*-F), -155.9 [t, 4F, *p*-F, <sup>3</sup>J(FF) 20 Hz], -156.0 [t, 2F, *p*-F, <sup>3</sup>J(FF) 20 Hz], -160.5 (m, 8F, *m*-F), -160.9 (m, 4F, *m*-F) ppm. Complex **6**: Yield 70%. *A<sub>M</sub>* 0 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. Elemental analysis (%). Found: C, 37.14; H, 1.17. Calc. for C<sub>58</sub>H<sub>18</sub>Au<sub>2</sub>F<sub>30</sub>FeSe<sub>2</sub>: C, 36.78; H, 0.95. <sup>1</sup>H, δ: 7.61–7.30 (m, 10H, C<sub>6</sub>H<sub>5</sub>), 4.32 (s, 1H, C<sub>5</sub>H<sub>4</sub>), 4.23 (s, 1H, C<sub>5</sub>H<sub>4</sub>), 4.13 (s, 1H, C<sub>5</sub>H<sub>4</sub>), 4.10 (s, 1H, C<sub>5</sub>H<sub>4</sub>), 4.02 (s, 1H, C<sub>5</sub>H<sub>4</sub>), 3.98 (s, 1H, C<sub>5</sub>H<sub>4</sub>), 3.94 (s, 1H, C<sub>5</sub>H<sub>4</sub>), 3.63 (s, 1H, C<sub>2</sub>H<sub>4</sub>) ppm. <sup>19</sup>F, δ: -121.2 (m, 8F, *o*-F), -122.4 (m, 4F, *o*-F), -155.8 [t, 4F, *p*-F, <sup>3</sup>J(FF) 20 Hz], -155.9 [t, 2F, *p*-F, <sup>3</sup>J(FF) 20 Hz], -160.4 (m, 8F, *m*-F), -161.0 (m, 4F, *m*-F) ppm.

**Synthesis of [Ag(OTf)]{Fc(XPh)<sub>2</sub>} (X = S (**7**), Se (**8**)).** To a solution of [Fc(XPh)<sub>2</sub>] (0.040 g, 0.1 mmol, **7**; 0.049 g, 0.1 mmol, **8**) in 20 mL of dichloromethane was added the corresponding amount of [Ag(OTf)] (0.026 g, 0.1 mmol) and the mixture stirred for 30 min. Concentration of the solution to *ca.* 5 mL and addition of diethyl ether (10 mL) gave complexes **7** and **8** as orange solids. Complex **7**: Yield 84%. *A<sub>M</sub>* 10 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. Elemental analysis (%). Found: C, 41.23; H, 2.40; S, 13.92. Calc. for C<sub>23</sub>H<sub>18</sub>AgF<sub>3</sub>FeO<sub>3</sub>S<sub>3</sub>: C, 41.50; H, 2.70; S, 14.43. <sup>1</sup>H, δ: 7.5–7.18 (m, 10H, C<sub>6</sub>H<sub>5</sub>), 4.51 (m, 4H, C<sub>5</sub>H<sub>4</sub>), 4.48 (m, 4H, C<sub>5</sub>H<sub>4</sub>) ppm. Complex **8**: Yield 63%. *A<sub>M</sub>* 2 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. Elemental analysis (%). Found: C, 36.01; H, 2.30; S, 4.03. Calc. for C<sub>23</sub>H<sub>18</sub>AgF<sub>3</sub>FeO<sub>3</sub>Se<sub>2</sub>: C, 36.65; H, 2.39; S, 4.25. <sup>1</sup>H, δ: 7.22–7.18 (m, 10H, C<sub>6</sub>H<sub>5</sub>), 4.46 (m, 8H, C<sub>5</sub>H<sub>4</sub>) ppm.

**Synthesis of [Ag{Fc(XPh)<sub>2</sub>}<sub>2</sub>](OTf) (X = S (**9**), Se (**10**)).** To a solution of [Fc(XPh)<sub>2</sub>] (0.080 g, 0.2 mmol, **9**; 0.098 g, 0.2 mmol, **10**) in 20 mL of dichloromethane was added the corresponding amount of [Ag(OTf)] (0.026 g, 0.1 mmol) and the mixture stirred for 30 min. Concentration of the solution to *ca.* 5 mL and addition of diethyl ether (10 mL) gave complexes **9** or **10** as

**Table 5** Details of data collection and structure refinement for complexes **5**, **7**, **8** and **12**

Compound	<b>5</b>	<b>7</b>	<b>8</b>	<b>12</b>
Chemical formula	C <sub>58</sub> H <sub>18</sub> Au <sub>2</sub> F <sub>30</sub> FeS <sub>2</sub>	C <sub>23</sub> H <sub>18</sub> AgF <sub>3</sub> FeO <sub>3</sub> S <sub>3</sub>	C <sub>23</sub> H <sub>18</sub> AgF <sub>3</sub> FeO <sub>3</sub> SSe <sub>2</sub>	C <sub>41</sub> H <sub>33</sub> AgF <sub>3</sub> FeO <sub>3</sub> PSSe <sub>2</sub>
<i>M</i>	1798.63	659.27	753.07	1015.34
Crystal habit	Orange lath	Orange prism	Orange prism	Orange prism
Crystal size/mm	0.48 × 0.12 × 0.04	0.70 × 0.70 × 0.50	0.22 × 0.15 × 0.14	0.60 × 0.50 × 0.40
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>Pna</i> 2(1)
<i>a</i> /Å	10.6032(12)	10.715(1)	10.7367(8)	24.083(8)
<i>b</i> /Å	9.6844(10)	16.222(2)	16.0702(14)	16.552(5)
<i>c</i> /Å	27.385(3)	14.125(1)	14.2622(12)	9.808(3)
$\beta$ /°	94.836(3)	109.916(6)	109.167(3)	—
<i>U</i> /Å <sup>3</sup>	2802.0(5)	2308.4(4)	2324.4(3)	3910(2)
<i>Z</i>	2	4	4	4
<i>F</i> (000)	1704	1312	1456	2008
<i>T</i> /°C	−130	−100	−130	−100
$\mu$ (Mo-K $\alpha$ )/mm <sup>−1</sup>	5.694	1.798	4.738	2.881
No. of reflections measured	44196	5190	19087	6484
No. of unique reflections	6940	4030	6578	4068
<i>R</i> <sub>int</sub>	0.091	0.032	0.0333	0.055
<i>R</i> <sup><i>a</i></sup> ( <i>F</i> > 4 $\sigma$ ( <i>F</i> ))	0.028	0.032	0.0252	0.058
<i>wR</i> <sup><i>b</i></sup> ( <i>F</i> <sup>2</sup> , all reflections)	0.066	0.082	0.0479	0.156
No. of parameters	421	307	307	478
No. of restraints	132	0	0	81
<i>S</i> <sup><i>c</i></sup>	1.008	1.0	0.879	1.049

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

orange solids. Complex **9**: Yield 75%. *A<sub>M</sub>* 102 Ω<sup>−1</sup> cm<sup>2</sup> mol<sup>−1</sup>. Elemental analysis (%). Found: C, 50.24; H, 3.28; S, 1.49. Calc. for C<sub>45</sub>H<sub>36</sub>AgF<sub>3</sub>Fe<sub>2</sub>O<sub>3</sub>S<sub>5</sub>: C, 50.89; H, 3.39; S, 1.51. <sup>1</sup>H,  $\delta$ : 7.20–7.10 (m, 20H, C<sub>6</sub>H<sub>5</sub>), 4.41 (m, 8H, C<sub>5</sub>H<sub>4</sub>) ppm. Complex **10**: Yield 67%. *A<sub>M</sub>* 118 Ω<sup>−1</sup> cm<sup>2</sup> mol<sup>−1</sup>. Elemental analysis (%). Found: C, 42.77; H, 2.66; S, 2.61. Calc. for C<sub>45</sub>H<sub>36</sub>AgF<sub>3</sub>Fe<sub>2</sub>O<sub>3</sub>SSe<sub>4</sub>: C, 43.23; H, 2.88; S, 2.56. <sup>1</sup>H,  $\delta$ : 7.19 (m, 20H, C<sub>6</sub>H<sub>5</sub>), 4.58 (m, 8H, C<sub>5</sub>H<sub>4</sub>) ppm.

**Synthesis of [Ag(OTf)(PPh<sub>3</sub>)<sub>2</sub>]{Fc(XPh)<sub>2</sub>}** (*X* = S (**11**), Se (**12**)). To a solution of [Fc(XPh)<sub>2</sub>] (0.040 g, 0.1 mmol, **11**; 0.049 g, 0.1 mmol, **12**) in 20 mL of dichloromethane was added the corresponding amount of [Ag(OTf)(PPh<sub>3</sub>)<sub>2</sub>] (0.052 g, 0.1 mmol) and the mixture stirred for 15 min. Concentration of the solution to *ca.* 5 mL and addition of diethyl ether (10 mL) gave complexes **11** or **12** as orange solids. Complex **11**: Yield 78%. *A<sub>M</sub>* 112 Ω<sup>−1</sup> cm<sup>2</sup> mol<sup>−1</sup>. Elemental analysis (%). Found: C, 52.98; H, 3.62; S, 9.93. Calc. for C<sub>41</sub>H<sub>33</sub>AgF<sub>3</sub>FeO<sub>3</sub>S<sub>3</sub>: C, 53.42; H, 3.58; S, 10.42. <sup>31</sup>P{<sup>1</sup>H}, rt,  $\delta$ : 11.0 (m, br). <sup>1</sup>H, rt,  $\delta$ : 7.4–7.0 (m, 25H, C<sub>6</sub>H<sub>5</sub>), 4.46 (m, 4H, C<sub>5</sub>H<sub>4</sub>), 4.42 (m, 4H, C<sub>5</sub>H<sub>4</sub>) ppm. <sup>31</sup>P{<sup>1</sup>H}, (−55 °C):  $\delta$  10.9 [2d, *J*(<sup>107</sup>AgP) 514 Hz, *J*(<sup>109</sup>AgP) 585 Hz]. Complex **12**: Yield 71%. *A<sub>M</sub>* 108 Ω<sup>−1</sup> cm<sup>2</sup> mol<sup>−1</sup>. Elemental analysis (%). Found: C, 48.15; H, 2.87; S, 3.11. Calc. for C<sub>41</sub>H<sub>33</sub>AgF<sub>3</sub>FeO<sub>3</sub>SSe<sub>2</sub>: C, 48.47; H, 3.25; S, 3.15. <sup>31</sup>P{<sup>1</sup>H}, rt,  $\delta$ : 11.0 [d, br, *J*<sub>av</sub>(AgP) 531 Hz] ppm. <sup>1</sup>H, rt,  $\delta$ : 7.37–7.04 (m, 25H, C<sub>6</sub>H<sub>5</sub>), 4.47 (m, 8H, C<sub>5</sub>H<sub>4</sub>) ppm. <sup>31</sup>P{<sup>1</sup>H}, −55 °C,  $\delta$ : 9.5 [2d, br, *J*(<sup>107</sup>AgP) 501 Hz, *J*(<sup>109</sup>AgP) 569 Hz], <sup>1</sup>H, −55 °C,  $\delta$ : 7.48–7.02 (m, 25H, C<sub>6</sub>H<sub>5</sub>), 4.56 (m, 4H, C<sub>5</sub>H<sub>4</sub>), 4.44 (m, 4H, C<sub>5</sub>H<sub>4</sub>) ppm.

**Synthesis of [Ag(phen){Fc(XPh)<sub>2</sub>}](OTf)** (*X* = S (**13**), Se (**14**)). To a solution of [Ag(OTf){Fc(XPh)<sub>2</sub>}] (0.066 g, 0.1 mmol, **13**; 0.075 g, 0.1 mmol, **14**) in 20 mL of dichloromethane was added the corresponding amount of phenanthroline (0.018 g, 0.1 mmol) and the mixture stirred for 15 min. Concentration of the solution to *ca.* 5 mL and addition of diethyl ether (10 mL) gave complexes **13** or **14** as orange solids. Complex **13**: Yield 71%. *A<sub>M</sub>* 125 Ω<sup>−1</sup> cm<sup>2</sup> mol<sup>−1</sup>. Elemental analysis (%). Found: C, 49.69; H, 3.12; N, 2.88; S, 10.90. Calc. for C<sub>35</sub>H<sub>26</sub>AgF<sub>3</sub>FeN<sub>2</sub>O<sub>3</sub>S<sub>3</sub>: C, 50.05; H, 3.10; N, 3.33; S, 11.44. <sup>1</sup>H,  $\delta$ : 9.25 (s, br, 2H, C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>), 8.60 [d, 2H, <sup>3</sup>*J*(HH) 11.22 Hz, C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>], 8.32 (s, 2H, C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>), 8.02 (m, 2H, C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>), 7.2–

7.5 (m, 10H, C<sub>6</sub>H<sub>5</sub>), 4.65 (m, 8H, C<sub>5</sub>H<sub>4</sub>) ppm. Complex **14**: Yield 68%. *A<sub>M</sub>* 135 Ω<sup>−1</sup> cm<sup>2</sup> mol<sup>−1</sup>. Elemental analysis (%). Found: C, 44.14; H, 2.10; S, 3.05. Calc. for C<sub>35</sub>H<sub>26</sub>AgF<sub>3</sub>FeN<sub>2</sub>O<sub>3</sub>SSe<sub>2</sub>: C, 45.01; H, 2.78; S, 3.00. <sup>1</sup>H,  $\delta$ : 8.85 (s, br, 2H, C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>), 8.40 (d, 2H, <sup>3</sup>*J*(HH) 12 Hz, C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>), 7.90 (s, 2H, C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>), 7.75 (m, 2H, C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>), 7.20 (m, 10H, C<sub>6</sub>H<sub>5</sub>), 4.50 (m, 8H, C<sub>5</sub>H<sub>4</sub>) ppm.

### Crystallography

The crystals were mounted in inert oil on glass fibres and transferred to the cold gas stream of a Bruker Smart 1000 CCD diffractometer (**5**, **8**) or a Siemens P4 diffractometer (**7**, **12**) equipped with the corresponding low temperature attachment. Data were collected using monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Absorption corrections were applied on the basis of  $\psi$ -scans (XEMP; **7**, **12**),<sup>23</sup> face-indexing (XPREF; **5**)<sup>24</sup> or multi-scans (SADABS; **8**).<sup>23</sup> Structures were solved by direct or heavy-atom methods and refined on *F*<sup>2</sup> using the program SHELXL-97.<sup>25</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using a riding model. Systems of restraints to light-atom displacement-factor components and local ring symmetry were used (**5**, **12**). Further crystallographic details are given in Table 5.

CCDC reference numbers 176348–176351.

See <http://www.rsc.org/suppdata/dt/b1/b111459j/> for crystallographic data in CIF or other electronic format.

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