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Group 11 Complexes with Imidazoline-2-thione or Selone Derivatives

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The reactions of the organodichalcogenone ligands Bbit [1,1′-(butane-1,4-diyl)bis(3-methylimidazoline-2-thione)], Mbis [1,1′-methylenebis(3-methylimidazoline-2-selone)], Ebis [1,1′-(ethane-1,2-diyl)bis(3-methylimidazoline-2-selone)] and Pbis [1,1′-(pentane1,5-diyl)bis(3-methylimidazoline-2-selone)] with gold(I/III), silver(I) and copper(I) have been studied by elemental analysis, multinuclear (^{1}H, ^{13}C, ^{19}F, ^{31}P and ^{77}Se) NMR spectroscopy and for several products obtained the molecular structures were also established by single-crystal X-ray diffraction analysis. In most cases the organodichalcogenone coordinates to two metallic fragments as a bidentate bridging ligand but the ligand Mbis coordinates to silver(I) in an unprecedented tetradentate bridging-chelate mode.

Introduction

The coordination chemistry of organochalcogenone compounds featuring two or more 3-methylimidazole-2-thione/selone groups has not been studied in depth in spite of the potential that these species might have in biomedical applications[1–3] as well as their interesting structural coordination chemistry. A few complexes with these types of ligands are described in the literature and most are charge transfer or hypervalent T-shaped adducts with Br_2,[4] I_2[5] and IBr.[6] Recently new complexes with the chelating organodichalcogenone ligands Mbit/Mbis [1,1′-methylenebis(3-methylimidazoline-2-thione/selone)] or Ebit/Ebis [1,1′-(1,2-ethanediyl)bis(3-methylimidazoline-2-thione/selone)] with nickel(II), cobalt(II),[7] rhodium(III) and iridium(III)[8] have been reported. Complexes of Mbit with other metals have also been studied: Sb^{III}, Bi^{III},[9] Sn^{IV},[10] Pb^{II}[11] and Ag^{I}.[12] The most intensely studied ligand is Mbit and different coordination modes have been described in its metal complexes. A bidentate chelate fashion is predominant in most of the complexes that have been structurally characterised but other coordination modes such as bidentate bridging two metal centres have been found in cobalt(II)[7] and silver(I) polymeric complexes.[12]

Here we report the synthesis and characterization, both in solution and solid state, of new complexes with Bbit, Mbis, Ebis and Pbis with different metals: Au^{I}, Au^{III}, Ag^{I} and Cu^{I}. To the best of our knowledge no gold(I/III) or copper(I) complexes have been reported with this type of ligand and only one example is known with silver(I). Furthermore, few complexes with any selone ligands have been described for gold. In the complexes we describe, the ligands predominantly coordinate as bidentate bridging two metal centres; however, we also report a silver(I) complex with Mbis in which the ligand acts as tetradentate bridging-chelate organodichalcogenone system, which represents an unprecedented mode of coordination for this type of ligand.

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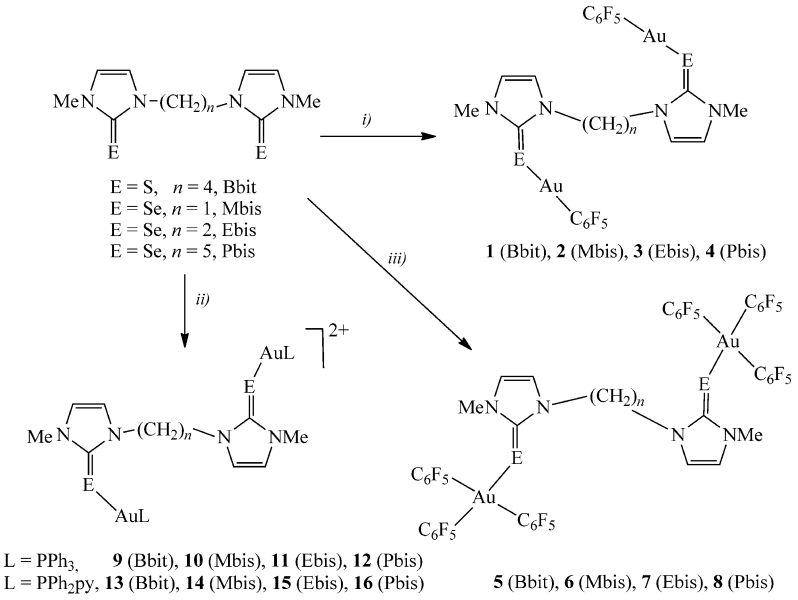
Results and Discussion

Synthesis

The syntheses of Bbit,[13] Mbis and Ebis[5] are known in the literature, and consist of two steps: the synthesis of the appropriate 3-methylimidazolium bis-cation salt and its reaction with elemental sulfur or selenium in methanol in the presence of a slight excess of K_2CO_3. We have improved the overall yield of this procedure by preparing quantitatively the 3-methylimidazolium bis-cation salts from the reaction of 1-methyl imidazole with an excess of the appropriate terminal dihalide under solvent-free and reflux conditions.[14] The use of solvent (AcOEt, THF) and stoichiometric quantities of the reactants in this step generally causes a significant decrease in yield of the 3-methylimidazolium bis-cation salt intermediate. We have also applied this synthetic procedure to the preparation of the new ligand Pbis (see Exp. Sect.).

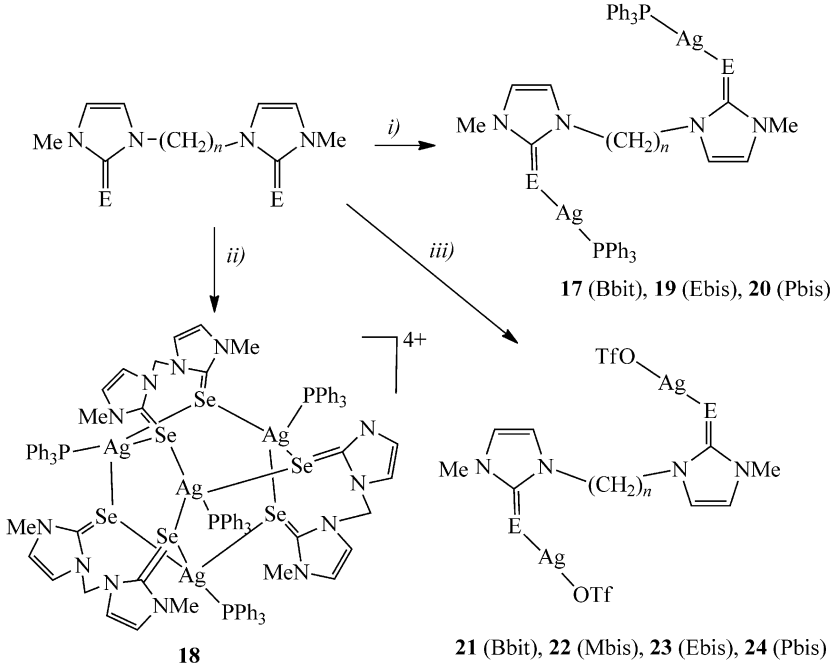
New gold(I/III) complexes were obtained by reacting the organodichalcogenone ligands with $[Au(C_6F_5)(tht)]$[15] (tht = tetrahydrothiophene), $[Au(C_6F_5)_3(tht)]$,[16] $[Au(OTf)(PPh_3)]$ (OTf = $CF_3SO_3^-$), or $[Au(OTf)(PPh_2py)]$ at room temperature, in a 1:2 molar ratio in dry organic solvents, i.e. THF (**1**, **2** and **4**), CH_2Cl_2 (**3**, **5**–**13**, **15** and **16**) and acetone (**14**) (Scheme 1). All of the complexes isolated have a 1:2 ligand to metal stoichiometry and those structurally characterised feature ligands bridging two metal fragments.



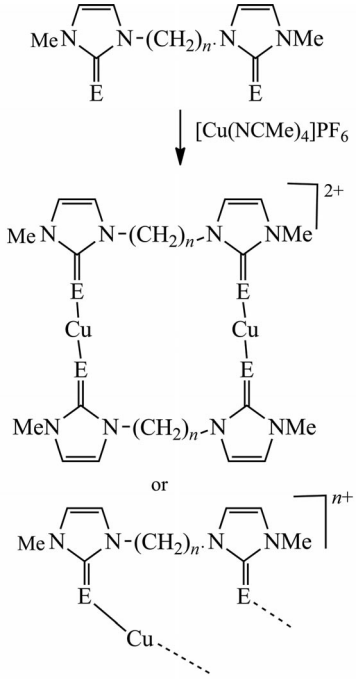
Scheme 1. i) 2 [Au(C_6F_5)(tht)], ii) 2 [Au(OTf)(PPh_3)] or 2 [Au(OTf)(PPh_2py)], iii) 2 [Au(C_6F_5)$_3$(tht)].

Silver(I) complexes were obtained after using a similar procedure as described above. The reactions have been carried out with [Ag(OTf)(PPh_3)] or Ag(OTf) in a molar ratio of 1:2 (Scheme 2). We propose that 1:2 complexes similar to those of gold are obtained, containing ligands bridging two metal centres with the exception of **18** with Mbis. In this case we have obtained [$Ag_4(PPh_3)_4(Mbis)_3$] featuring a unique adamantane-like Ag_4Se_6 central core. For this reason the synthesis of complex **18** was repeated in 3:4 ligand/[Ag(OTf)(PPh_3)] molar ratio obtaining the pure compound in high yield. For copper(I) the reactions were carried out using [$Cu(CH_3CN)_4$]PF_6 with the ligands in a molar ratio of 1:1. On the basis of microanalytical data, for the products we propose either a dinuclear structure with two ligand units bridging two metal centres or a polymeric structure (see Scheme 3); no coordinated acetonitrile molecules have been detected in the NMR spectra of the products.

All the isolated complexes form either stable white (**1**, **4**, **5**–**7**, **9**–**13**, **17**–**26** and **27**) or pale yellow (**2**, **3**, **8**, **9**, **14**–**16** and **28**) crystalline solids, which were characterized by elemental analysis, multinuclear NMR spectroscopy (^{1}H,



Scheme 2. i) 2 [Ag(OTf)(PPh_3)], ii) 4/3 [Ag(OTf)(PPh_3)], iii) 2 Ag(OTf).



Scheme 3. Proposed structures for the copper complexes.

^{19}F, $^{31}P\{^1H\}$, ^{77}Se and $^{13}C\{^1H\}$ in some of the complexes) in different deuterated solutions at room temperature. We were able to grow single crystals suitable for X-ray diffraction studies of **2**, **7**, **13** and **18**. The molecular structure of Pbis was also determined.

NMR Studies of Complexes

The NMR spectra for the gold(I/III) complexes were recorded in different deuterated solvents {$CDCl_3$ (**2**, **11**–**13**), [D_6]acetone (**5**, **7**) and [D_6]DMSO (**1**, **3**, **4**, **6**, **8**–**10**, **14**–**16**)}, at room temperature. Due to the low solubility of the silver(I) and copper(I) complexes in organic solvents, their NMR spectra were recorded in [D_6]DMSO. The ^{77}Se NMR spectra were recorded in [D_6]DMSO. The assignment of the ^1H and ^{13}C chemical shifts was made on the basis of 2D (COSY, HMQC and HMBC) NMR experiments. The ^{13}C NMR spectra have not been recorded for all the complexes because the low solubility, lack of information of the structure of many of them and, in the case of complexes with pentafluorophenyl units, because these carbon atoms are not usually observed in the ^{13}C NMR spectra.

The aliphatic region of the ^1H NMR spectrum of the ligand Bbit in DMSO presents the resonance signals 1.64, 3.96 and 3.55 ppm for $–(CH_2)_4–$ and $–CH_3$. For the corresponding gold(I/III), silver(I) and copper(I) complexes the ranges of the values of these resonances are: 1.73–1.83 and 3.96–4.13 for $–(CH_2)_4–$ and 3.42–3.62 ppm for $–CH_3$. In the case of the Mbis ligand the ^1H NMR spectrum in DMSO exhibits in the aliphatic region singlet resonances for $–CH_3$ (3.56 ppm) and $–CH_2–$ (6.34 ppm) groups. For the corresponding metal complexes the resonances are found in the following ranges: 3.56–3.78 for $–CH_3$ and 6.54–6.80 ppm for $–CH_2–$. The ^1H NMR spectrum of Ebis ligand exhibits the following pattern in DMSO: 3.54 for $–CH_3$ and 4.44 ppm for $–(CH_2)_2–$. The ranges of the values for the corresponding complexes are: 3.40–3.81 for $–CH_3$ and 4.51–4.80 ppm for $–CH_2–$. For the Pbis ligand in DMSO, ^1H NMR signals are observed at 1.23, 1.72 and 4.01 for $–(CH_2)_5–$ and at 3.55 ppm for $–CH_3$; in the corresponding complexes the range of variability of these resonances is 1.19–1.36, 1.71–2.09, 4.07–4.42 and 3.64–3.99 ppm, respectively. The –CH–CH– protons of the imidazole rings appear in the range 7.12–7.76 ppm in the ligands and in the metal complexes a downfield shift is observed.

For the gold(I) derivatives **1**–**4** the ^{19}F NMR spectra show one set of resonances corresponding to the pentafluorophenyl group; two multiplets for the *ortho* and *meta* and a triplet for the *para* fluorine. In contrast, in the gold(III) derivitives **5**–**8** the ^{19}F NMR spectra exhibit a typical pattern for a square-planar geometry of the complex anion; two sets of resonances in a 2:1 intensity ratio for the *trans* and *cis* pentafluorophenyl groups, respectively. All the ^{19}F NMR spectra of the complexes containing the OTf group show a single signal corresponding to the anion.

The room temperature $^{31}P\{^1H\}$ and ^{77}Se NMR spectra for all of the complexes exhibit a singlet resonance. This behaviour is consistent with the equivalence, in solution and on the NMR time scale, of the phosphorus and selenium atoms, respectively, in the molecular unit of compounds containing phosphane ligands.

In the ^{77}Se NMR spectra a slight deshielding is observed for the gold complexes of the same ligand, e.g. with Ebis δ_{Se} = –23.4 in **3**, 8.2 in **11** and 18.5 ppm in **15**. This slight deshielding is due to the different AuL fragments: $Au(C_6F_5)$, $Au(PPh_3)^+$, $Au(PPh_2py)^+$, respectively. The deshielding increases with the increasing donor character of the AuL. A similar trend was observed for the silver complexes, e.g. with Ebis δ_{Se} = –73.9 in **19** and –160.6 ppm in **23** with $Ag(PPh_3)^+$ and Ag(OTf), respectively. The resonances for the selenium in the copper complexes were not observed after several hours because lack of solubility.

Crystal Structures

The crystal structure of the Pbis ligand and the complexes **2**, **7**, **13** and **18** have been determined by single-crystal X-ray diffraction studies and the crystallographic data are given in Table 1.

The ORTEP diagram for Pbis is shown in Figure 1. The Pbis ligand crystallized with a water molecule. The molecular structure shows that the imidazoline-2-selone rings are *cis* to each other and the bridging chain formed by the $–(CH_2)_5–$ alkyl moiety assumes a zigzag conformation. There are several secondary bonds that can be considered as hydrogen bonds, the shortest are O1···H4# 2.353(2) Å (# $x-1$, $y-1$, z) and Se2···H1# 2.680(45) Å with subtended angles of 156.2 and 167.1°, respectively. These bonds define a three dimensional supramolecular array (Figure 2).

Table 1. Crystalllographic data for Pbis·H_2O ligand and complexes **2**, **7**, **13** and **18**.

	Pbis·H_2O	**2**	**7**	**13**·2CH_2Cl_2	**18**·2Me_2CO·H_2O
Empirical formula	$C_{13}H_{22}N_4OSe_2$	$C_{10.50}H_6AuF_5N_2Se$	$C_{46}H_{14}Au_2F_{30}N_4Se_2$	$C_{52}H_{50}Au_2Cl_4F_6N_6O_6P_2S_4$	$C_{112}H_{118}Ag_4F_{12}N_{12}O_{17}P_4S_4Se_6$
M	408.27	531.10	1744.47	1694.89	3289.54
T [K]	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	orthorhombic	monoclinic	monoclinic	triclinic	orthorhombic
Space group	*Pbca*	*C*2/*c*	$P2_1/n$	$P\bar{1}$	*Pbca*
a [Å]	11.513(2)	10.897(2)	10.733(2)	11.530(2)	29.065(6)
b [Å]	8.7040(17)	15.871(3)	13.859(3)	11.875(2)	29.208(6)
c [Å]	33.124(7)	14.972(3)	17.730(4)	12.164(2)	29.912(6)
α [°]	90	90	90	98.90(3)	90
β [°]	90	91.10(3)	106.23(3)	95.97(3)°	90
γ [°]	90	90	90	116.05(3)	90
V [Å^3]	3319.3(11)	2589.1(9)	2532.2(9)	1450.2(5)	25394(9)
Z	8	8	2	1	8
μ(Mo-K_α) [mm^{-1}]	4.457	14.223	7.375	5.510	2.528
*R*1 [$I > 2\sigma(I)$]	0.0288	0.0165	0.0201	0.0499	0.0408
*wR*2	0.0530	0.0379	0.0452	0.1285	0.0882
GOF on F^2	1.185	1.161	1.162	1.053	1.072

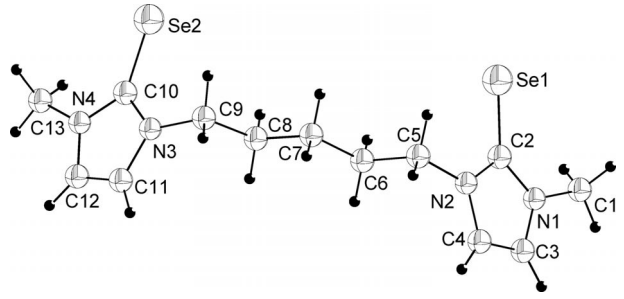


Figure 1. ORTEP representation at 50% probability and atom numbering scheme for Pbis in Pbis·H_2O. Selected bond lengths [Å] and angles (°): Se1–C2 1.854(3), Se2–C10 1.848(3), N2–C2–N1 105.6(2), N2–C2–Se1 127.27(18), N1–C2–Se1 127.09(19), N3–C10–N4 105.6(2), N3–C10–Se2 127.23(18), N4–C10–Se2 127.16(18).

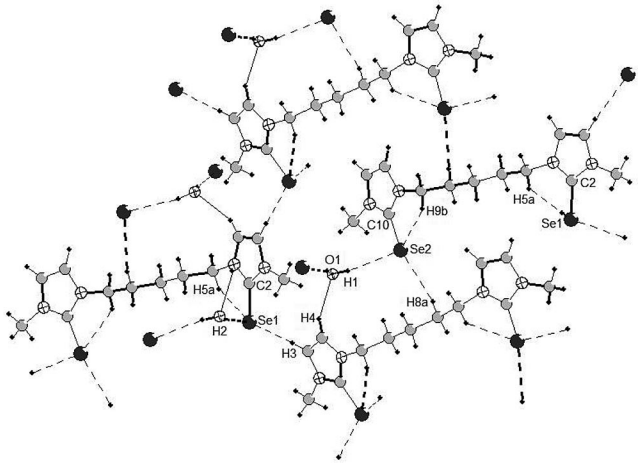


Figure 2. A layer network based on intermolecular hydrogen bonding in the crystal of Pbis·H_2O.

Figure 3 presents the ORTEP diagram for complex **2** with the imidazoline-2-selone rings *trans* to each other. In the molecular structure weak intramolecular interactions are formed between one fluorine atom of the C_6F_5 group and one hydrogen atom of the imidazoline ring [F1–H8 2.562(2) Å, cf. sum of the respective van der Waals radii $\sum r_{vdW}$(F,H) ≈ 2.70 Å].[17] Closer inspection of the crystal structure revealed the presence of intermolecular F···H_{methyl} hydrogen bonding interactions [F5···H11b# 2.287(2) Å (# $-x$, y, $-z + 1/2$)], which give rise to zigzag polymeric chains in the crystal lattice (Figure 4).

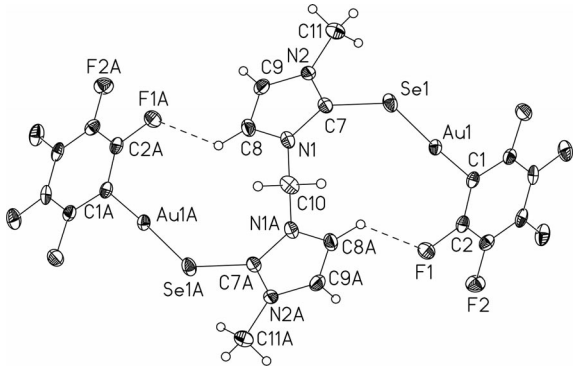


Figure 3. ORTEP representation at 50% probability and atom numbering scheme for **2**. Selected bond lengths [Å] and angles (°): Au1–C1 2.035(3), Au1–Se1 2.4263(5), Se1–C7 1.894(4), C1–Au1–Se1 177.49(10), C7–Se1–Au1 97.84(10), N1–C10–N1 109.6(4).

To date only one molecular structure containing the fragment –C–Au–Se=, [Au(C_6F_5)(SePPh$_3$)], has been reported.[18] The compound has hydrogen bonding interactions between two molecules forming dimers (F···H 2.51 Å). In the crystal there are interdimer F···H_{phenyl} contacts (F···H 2.56 Å), which result in a polymeric association of the dimers.

The coordination geometry about the gold(I) atoms in **2** is linear [C1–Au1–Se1 177.49(10)°], whereas the bond connection about the selenium atom is V-shaped [C7–Se1–Au1 97.84(10)°]. These values are comparable to those found in [Au(C_6F_5)(SePPh$_3$)]: C–Au–Se 177.1(1)° and P–Se–Au 99.9(1)°. The Se1–Au1 bond length [2.4263(5) Å] in **2** is of the same magnitude as that found in [Au(C_6F_5)(SePPh$_3$)] [Se–Au 2.416(1) Å].[18]

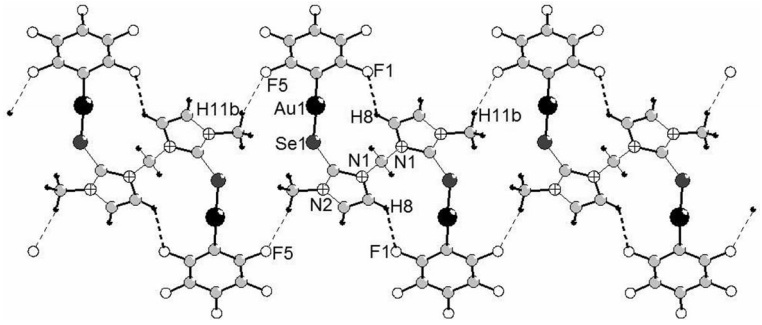


Figure 4. View along the *b* axis of the chain polymer in **2**.

A few structurally characterised metal complexes of Mbis have been reported: $[NiBr_2(Mbis)]$, $[CoCl_2(Mbis)]_n$, [Cp*Ir(Mbis)Cl]Cl and [Cp*Rh(Mbis)Cl][Cp*$RhCl_3$].[7,8] The complex $[CoCl_2(Mbis)]_n$ is different from the others in that polymeric chains are formed through the coordinative interactions established between the cobalt centres and the selenium atoms of Mbis which behaves as a bridging-chelate ligand. Also in this molecular structure, weak interactions are present between the hydrogen atoms of the CH_2 group and the imidazoline ring. The imidazoline-2-selone rings are *trans* to each other, as in **2**, and the coordination geometry around the selenium atoms in $[CoCl_2(Mbis)]_n$ is V-shaped, with a C–Se–Co angle of 93.6°. In the other three complexes of Mbis the ligand does not bridge two metal centres but behaves as a chelating bidentate ligand forming an eight-membered metallacycle with the metal centres.

Single crystals suitable for X-ray diffraction studies were obtained for **7** and the molecular structure is presented in the Figure 5. The molecular structures of **2** and **7** are very similar. In **7**, as in **2**, the imidazoline-2-selone rings are *trans* to each other and the ligand bridges two metal centres. Also similar to **2**, in **7** there are intramolecular F1···H4b contacts between one fluorine atom of the C_6F_5 group and one hydrogen atom from the alkyl chain bridging the imidazoline rings (Figure 5). Furthermore, the intermolecular F···H contacts (F···H 2.48 Å and 2.52 Å) involving the methyl groups leads to a layered structure in which a monomeric complex unit is connected to four neighboring molecules (Figure 6).

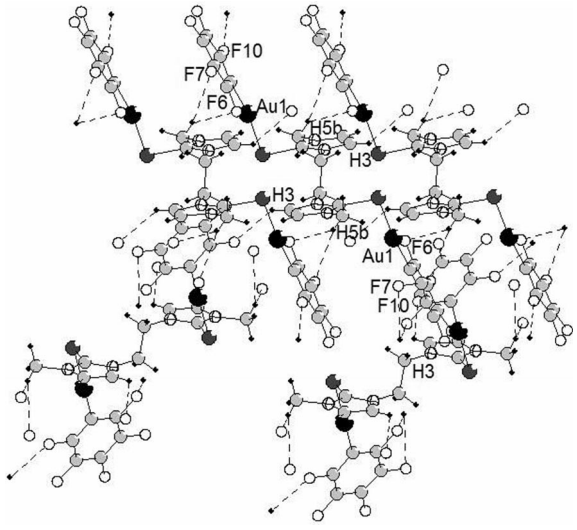


Figure 6. A layer network based on intermolecular hydrogen bonding in **7**.

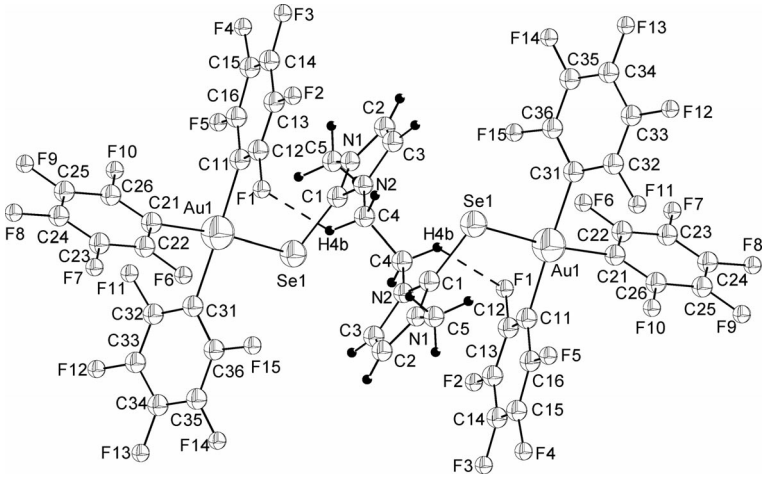


Figure 5. ORTEP representation at 50% probability and atom numbering scheme for **7**. Selected bond lengths [Å] and angles (°): Au1–C21 2.043(3), Au1–C11 2.052(3), Au1–C31 2.061(3), Au1–Se1 2.4607(6), Se1–C1 1.884(3), C21–Au1–Se1 173.43(9), C11–Au1–Se1 97.69(8), C31–Au1–Se1 85.09(8), C21–Au1–C11 88.83(12), C21–Au1–C31 88.40(12), C1–Se1–Au1 103.58(9).

The coordination geometry around the gold(III) atoms in **7** is square planar [C31–Au1–Se1 85.09(8)°, C11–Au1–Se1 97.69(8)°, C21–Au1–C31 88.40(12)°, C21–Au1–C11 88.83(12)°] and distorted V-shaped around the selenium atoms [C1–Se1–Au1 103.58(9)°]. The main reason for the distortion from ideal square planar and V-shaped geometries around the gold and selenium atoms could be due to the sterically demanding C_6F_5 groups. The selenium–gold distance [2.4607(6) Å] is comparable with those found in **2** [2.4263(5) Å] and [Au(C_6F_5)($SePPh_3$)] [2.416(1) Å].[18]

The structure of **13** was also confirmed by X-ray diffraction studies and is shown in Figure 7. The gold(I) atoms have a linear coordination geometry [P1–Au1–S1 173.77(7)°] and the sulfur atoms have a distorted V-shaped geometry [C1–S1–Au1 106.5(3)°]. These values are similar to those found in the other three complexes that contain an imidazoline thione group: [Au($PhTm^{Me}$)(PEt_3)][19] [Tm^{Me} = tris(2-mercapto-1-methylimidazolyl)borate] [P1–Au1–S1 171.55(7)° and C1–S1–Au1 101.0(2)°], [Au(Tm^{tBu})(PPh_3)][20] [Tm^{tBu} = tris(2-mercapto-1-*tert*-butylimidazolyl)borate] [P–Au–S1 97.21(4) and P–Au–S2 159.75(4)°] and [Au(Bm^{Me})-(PPh_3)][21] [Bm^{Me} = bis(2-mercapto-1-methylimidazolyl)-borate] [P–Au–S1 98.78(4)° and P–Au–S2 159.74(4)°], in which both sulfur atoms are coordinated to the gold centre.

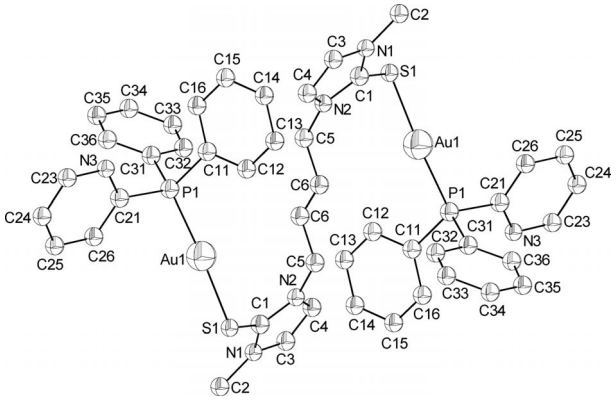


Figure 7. ORTEP representation at 50% probability and atom numbering scheme for the complex cation $[Au_2(PPh_2py)_2(Bbit)]^{2+}$ in **13**. All hydrogen atoms, counter anions and solvents (CH_2Cl_2) are omitted for clarity. Selected bond lengths [Å] and angles (°): Au1–S1 2.313(2), S1–C1 1.726(9), Au1–P1 2.264(2), P1–Au1–S1 173.77(7), C1–S1–Au1 106.5(3), N1–C1–S1 124.4(8), N2–C1–S1 128.1(8).

Furthermore, the values of the sulfur–gold distances are similar in all four complexes: 2.313(2) in **13**, 2.3335(17) in [Au($PhTm^{Me}$)(PEt_3)], 2.3511(12) in Au(Bm^{Me})(PPh_3) and 2.3488(11) Å in [Au(Tm^{tBu})(PPh_3)].

In **13**, several secondary hydrogen bonds between the fluorine atoms from the OTf groups and hydrogen atoms from the phenyl and pyridyl groups are also present to form a polymeric chain in the crystal lattice: [$F\cdots H_{pyridyl}$ {F2···H24# 2.617(7) Å, # $-x + 1, -y, -z$}] and $F\cdots H_{phenyl}$ [F1···H12 2.46(1) Å] (Figure 8).

Figure 9 presents the molecular structure of **18**, which crystallized with an acetone molecule. In the literature, the molecular structure of only one complex featuring the fragment Ag–Se=C, [{μ-$SeC(NH_2)_2$}Ag{$SeC(NH_2)_2$}$_2$]$_2Cl_2$·4DMF, has been established by single-crystal X-ray diffraction studies.[22]

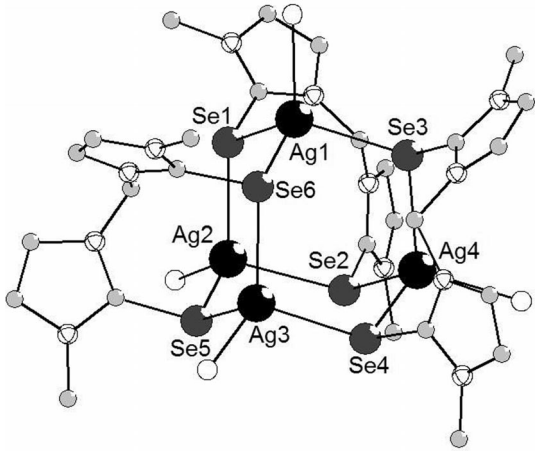


Figure 9. Molecular structure of the complex cation $[Ag_4(PPh_3)_4(Mbis)_3]^{4+}$ in **18**, all hydrogen atoms, phenyl gropus from PPh_3 and counter anions are omitted for clarity. Selected bond lengths [Å] and angles (°): Ag1–Se1 2.6603(7), Ag1–Se3 2.6693(7), Ag1–Se6 2.7251(7), Ag2–Se5 2.6818(7), Ag2–Se1 2.6885(7), Ag2–Se2 2.6937(7), Ag3–Se6 2.6440(7), Ag3–Se4 2.6819(7), Ag3–Se5 2.7151(7), Ag4–Se3 2.6377(7), Ag4–Se2 2.6747(7), Ag4–Se4 2.6815(7), Se1–Ag1–Se3 108.18(2), Se1–Ag1–Se6 111.637(19), Se3–Ag1–Se6 104.69(2), Se5–Ag2–Se1 104.29(2), Se5–Ag2–Se2 102.40(2), Se1–Ag2–Se2 106.40(2), Se6–Ag3–Se4 109.66(2), Se6–Ag3–Se5 108.58(2), Se4–Ag3–Se5 97.019(19), Se3–Ag4–Se2 108.23(2), Se3–Ag4–Se4 109.41(2), Se2–Ag4–Se4 101.75(2).

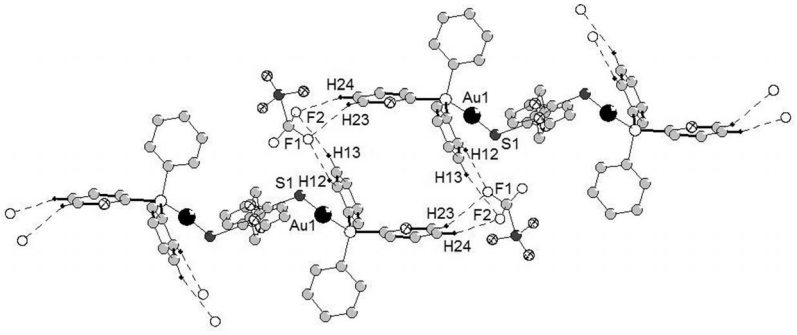


Figure 8. View along the *a* axis of the chain polymer in **13**.

In complex **18**, the tetracation $[Ag_4(PPh_3)_4(Mbis)_3]^{4+}$ features a rare adamantane-like Ag_4Se_6 central core with four $AgPPh_3^+$ fragments bridged by three Mbis units (Figure 9). In order to satisfy this topological disposition, each ligand acts as a tetradentate bridging-chelate system, which is an unprecedented coordination structural feature for organodiselone ligands. Each ligand is connected to three different metal centres, each Se donor in each ligand bridges two $AgPPh_3^+$ units and, at the same time, the two Se donor atoms from each ligand are bridged by one $AgPPh_3^+$ unit following the sequence Ag–Se–Ag–Se–Ag (the Se donors belong to the same ligand). Consequently, the coordination geometry around each silver centre is tetrahedral with each silver(I) atom bonded to three selenium atoms and one phosphorus atom. Interestingly, only one silver centre [Ag(1) in Figure 9] is bound to three selenium atoms each from a different ligand unit. The Ag–Se distances lie in the range 2.6603(7) to 2.7251(7) Å, and are, therefore, similar to those found in $[\{\mu\text{-}SeC(NH_2)_2\}Ag\{SeC(NH_2)_2\}_2]_2Cl_2\cdot 4DMF$ for the bridging selenourea units [2.706(2) and 2.750(2) Å]. In the Ag_4Se_6 core there are no interactions between the silver atoms. Adamantane-like Ag_4Se_6 discrete cluster arrangements have also been described in the complex ions $[Ag_4(SePh)_6]^{2-}$,[23] $[Ag_4(Se_4)_3]^{2-}$,[24] $[Ag_4\{(SePPh_2)_2N\}_3]^+$,[25] and $[Ag_4(fcSe_2)_3]^{2-}$ ($fcSe_2^{2-}$ = ferrocenyldiselenolate).[26] However, in all of these complex ions the adamantane-like Ag_4Se_6 arrangement is distorted so as to bring each silver(I) centre to assume a trigonal planar coordination of selenium atoms, and to establish Ag···Ag interactions of about 3.0 Å with the other three metal centres within a tetrahedral Ag_4 disposition. The tetrahedral geometry around each silver(I) centre in $[Ag_4(PPh_3)_4(Mbis)_3]^{4+}$ is determined by the presence of the coordinated PPh_3, which prevents the four metal centres from establishing argentophilic interactions with each other for steric reasons, thus preserving a regular adamantane-like arrangement for the Ag_4Se_6 cluster.

The cyclic voltamomgram of **18** in dichloromethane shows features very similar to those observed for the free ligand.[4]

Conclusions

New gold(I/III), silver(I) and copper(I) complexes with organodichalcogenone compounds featuring two 3-methylimidazoline-2-thione/selone groups have been prepared and characterized. These complexes are scarcely represented for these types of ligands. In the complexes reported we have found that coordination predominantly takes place with the ligands bridging two metal centres, but we have found one example for silver(I) with Mbis in which the ligand acts as tetradentate bridging-chelate ligand, which represents an unprecedented mode of coordination for this type of ligand. This coordination mode gives rise to a rare example of an Ag_4Se_6 cluster having a slightly distorted adamantane-like structure.

Experimental Section

General Procedures: Elemental (C, H, N and S) analyses were carried out with a Perkin–Elmer 2400 microanalyzer. Room-temperature NMR spectra were recorded with a Bruker ARX 400 spectrometer (^1H, 400 MHz, $^{13}C\{^1H\}$ 100.61 MHz, ^{19}F, 376.5 MHz and $^{31}P\{^1H\}$ NMR, 161.9 MHz). The chemical shifts are reported in ppm relative to the residual solvent peak [^1H $(CD_3)_2CO$: 2.05, $CHCl_3$: 7.26 and DMSO 2.50 ppm], $SiMe_4$, $CFCl_3$ and H_3PO_4 85%, respectively. ^{77}Se spectra were obtained at 76.4 MHz in $CDCl_3$ with a BRUKER ARX 400 spectrometer using dimethyl selenide as an external standard. Cyclic voltammetric experiments were performed by with an EG&G PARC Model 273 potentiostat. A three-electrode system was used, which consisted of a platinum disk working electrode, a platinum wire auxiliary electrode and a saturated calomel reference electrode. The measurements were carried out in CH_2Cl_2 with 0.1 M Bu_4NPF_6 as a supporting electrolyte. Under the present experimental conditions, the ferrocenium/ferrocene couple was located at 0.47 V vs. SCE.

Starting Materials: Solvents were dried and distilled prior to use. 1-methylimidazole, $Ag(O_3SCF_3)$ and terminal alkyl dihalides are commercially available. Other starting materials were prepared according to literature methods: Bbit,[13] Mbis,[5] Ebis,[5] $[Au(C_6F_5)(tht)]$,[15] $[Au(C_6F_5)_3(tht)]$,[16] $[AuCl(PPh_3)]$,[27] $[AuCl(PPh_2py)]$,[28] $[Ag(OTf)(PPh_3)]$[29] and $[Cu(NCMe)_4]PF_6$.[30]

Pbis: A mixture of 1,5-bis(3-methyl-imidazolium)pentane diiodide (obtained quantitatively by refluxing 1-methylimidazole in 1,5-diiodopentane for 2 h, followed by filtration and washing of the solid with diethyl ether) (9.70 g, 0.02 mol), K_2CO_3 (4.5 g, 0.03 mol), elemental Se (3.2 g, 0.04 mol) and ethanol (300 mL) was stirred under reflux for 24 h and filtered hot through a pad of celite. The solution was evaporated to dryness and the compound was obtained as an orange powder by crystallization from CH_2Cl_2/ethanol; yield 70%, 5.46 g. $C_{13}H_{20}N_4Se$ (312.085): calcd. C 40.01, H 5.17, N 14.36; found C 39.98, H 5.14, N 14.30. ^1H NMR (DMSO, 400 MHz): δ = 1.23 [q, $^3J_{HH}$ = 7.7 Hz, 2 H, –(CH_2)$_5$–], 1.72 [q, $^3J_{HH}$ = 7.4 Hz, 4 H, –(CH_2)$_5$–], 3.55 (s, 6 H, –CH_3), 4.01 [t, $^3J_{HH}$ = 7.3 Hz, 4 H, –(CH_2)$_5$–], 7.33 (d, $^3J_{HH}$ = 2.3 Hz, 4 H, –C*H*=C*H*–), 7.34 (m, $^3J_{HH}$ = 2.3 Hz, 4 H, –C*H*=C*H*–) ppm. ^{13}C NMR (DMSO, 100.6 MHz): δ = 22.57 and 27.93 [s, –(*C*H$_2$)$_5$–], 36.20 (s, –*C*H$_3$), 48.33 [s, –(*C*H$_2$)$_5$–], 119.34 and 120.42 (s, –*C*H=*C*H–), 154.15 (s, –*C*=Se), ^{77}Se NMR (DMSO, 76.4 MHz): δ 11.13 (s, 2 Se) ppm. Crystals suitable for X-ray diffraction analysis were grown from acetone/diethyl ether.

$[Au_2(C_6F_5)_2(Bbit)]$ (1): $[Au(C_6F_5)(tht)]$ (0.13 g, 0.28 mmol) and Bbit (0.042 g, 0.14 mmol) were stirred in THF (50 mL) for 1 h at room temperature. The white solution was concentrated under reduced pressure and solid was precipitated with hexane. The product was collected by filtration and recrystallized from acetone/*n*-hexane (1:5, v/v); yield 80%, 0.12 g. $C_{24}H_{18}Au_2F_{10}N_4S_2\cdot C_3H_6O$ (1068.056): calcd. C 30.34, H 2.26, N 5.24, S 5.99; found C 30.70, H 2.42, N 5.38, S 6.35. ^1H NMR (DMSO, 400 MHz): δ = 1.85 [br. s, 4 H, –(CH_2)$_4$–], 3.78 (s, 6 H, –CH_3), 4.31 [br. s, 4 H, –(CH_2)$_4$–], 7.53 (br. s, 4 H, –C*H*=C*H*–) ppm. ^{19}F NMR (DMSO, 376.48 MHz): δ = –162.4 (m, 4 F, –C$_6F_5$-*meta*), –160.3 (t, $^3J_{FF}$ = 21.2 Hz, 2 F, –C$_6F_5$-*para*), –115.3 (m, 4 F, –C$_6F_5$-*ortho*) ppm.

$[Au_2(C_6F_5)_2(Mbis)]$ (2): Compound **2** was synthesised by the same procedure described for **1** using $[Au(C_6F_5)(tht)]$ (0.127 g, 0.28 mmol) and Mbis (0.047 g, 0.14 mmol); yield 80%, 0.12 g. $C_{21}H_{12}Au_2F_{10}N_4Se_2$ (1063.856): calcd. C 23.69, H 1.14, N 5.26; found C 23.47, H 1.28, N 4.86. ^1H NMR ($CDCl_3$, 400 MHz): δ = 3.79 (s, 6 H, –CH_3), 6.70 (s, 2 H, –CH_2–), 6.89 (d, $^3J_{HH}$ = 2.1 Hz,

2 H, –CH=C*H*–), 8.14 (s, 2 H,br, –C*H*=CH–) ppm. ^{19}F NMR ($CDCl_3$, 376.48 MHz): δ = –162.4 (m, 4 F, –C_6F_5-*meta*), –159.5 (t, $^3J_{FF}$ = 20.1 Hz, 2 F, –C_6F_5-*para*), –116.6 (m, 4 F, –C_6F_5-*ortho*) ppm. ^{77}Se NMR (DMSO, 76.4 MHz): δ –17.5 (s, 2 Se) ppm.

[$Au_2(C_6F_5)_2$(Ebis)] (3): Compound **3** was synthesised by the same procedure described for **1** using [$Au(C_6F_5)$(tht)] (0.045 g, 0.10 mmol) and Ebis (0.017 g, 0.05 mmol) in CH_2Cl_2 (20 mL); yield 46%, 0.04 g. $C_{22}H_{14}Au_2F_{10}N_4Se_2$ (1077.872): calcd. C 24.49, H 1.31, N 5.21; found C 24.69, H 1.36, N 5.43. ^{1}H NMR [DMSO, 400 MHz]: δ = 3.82 (s, 6 H, –C*H*$_3$), 4.80 (s, 4 H, –C*H*$_2$–C*H*$_2$–), 7.49 and 7.65 (s, 4 H, –C*H*=C*H*–) ppm. ^{19}F NMR [DMSO, 376.48 MHz]: δ = –162.8 (m, 4 F, –C_6F_5-*meta*), –161.5 (t, $^3J_{FF}$ = 21.2 Hz, 2 F, –C_6F_5-*para*), –114.5 (m, 4 F, –C_6F_5-*ortho*), ^{77}Se NMR (DMSO, 76.4 MHz): δ –23.4 (s, 2 Se) ppm.

[$Au_2(C_6F_5)_2$(Pbis)] (4): Compound **4** was synthesised by the same procedure described for **1** using [$Au(C_6F_5)$(tht)] (0.121 g, 0.26 mmol) and Pbis (0.052 g, 0.13 mmol); yield 86%, 0.13 g. $C_{25}H_{20}Au_2F_{10}N_4Se_2$ (1119.919): calcd. C 26.79, H 1.80, N 5.00; found C 26.97, H 1.72, N 5.18. ^{1}H NMR [DMSO, 400 MHz]: δ = 1.19 [m, 2 H, –(C*H*$_2$)$_5$–], 2.09 [m, 4 H, –(C*H*$_2$)$_5$–], 3.99 (s, 6 H, –C*H*$_3$), 4.42 [m, 4 H, –(C*H*$_2$)$_5$–], 7.66 (m, 4 H, –C*H*=C*H*–) ppm. ^{19}F NMR [DMSO, 376.48 MHz]: δ = –162.8 (m, 4 F, –C_6F_5-*meta*), –161.6 (t, $^3J_{FF}$ = 21.2 Hz, 2 F, –C_6F_5-*para*), –114.6 (m, 4 F, –C_6F_5-*ortho*), ^{77}Se NMR (DMSO, 76.4 MHz): δ –24.9 (s, 2 Se) ppm.

[$Au_2(C_6F_5)_6$(Bbit)] (5): To a solution of [$Au(C_6F_5)_3$(tht)] (0.167 g, 0.21 mmol) in CH_2Cl_2 (20 mL) was added Bbit (0.03 g, 0.10 mmol) and the mixture was stirred for 1 h at room temperature. The white solution was concentrated under reduced pressure and precipitated with hexane. The product was collected by filtration and recrystallized from acetone/n-hexane (1:5, v/v); yield 60%, 0.1 g. $C_{48}H_{18}Au_2F_{30}N_4S_2$ (1677.982): calcd. C 34.33, H 1.08, N 3.34, S 3.81; found C 34.25, H 1.30, N 3.29, S 3.85. ^{1}H NMR [$(CD_3)_2CO$, 400 MHz]: δ = 1.90 [br. s, 4 H, –(C*H*$_2$)$_4$–], 3.88 (s, 6 H, –C*H*$_3$), 4.31 [br. s, 4 H, –(C*H*$_2$)$_4$–], 7.54 (d, $^3J_{HH}$ = 2.2 Hz, 2 H, –CH=CH–), 7.55 (d, $^3J_{HH}$ = 2.2 Hz, 2 H, –CH=CH–) ppm. ^{19}F NMR [$(CD_3)_2$-CO, 376.48 MHz]: δ = –122.7 (m, 8 F, –C_6F_5-*ortho*), –124.0 (m, 4 F, –C_6F_5-*ortho*), –160.5 (t, $^3J_{FF}$ = 19.4 Hz, 4 F, –C_6F_5-*para*), –161.1 (t, $^3J_{FF}$ = 19.5 Hz, 2 F, –C_6F_5-*para*), –162.0 (m, 8 F, –C_6F_5-*meta*), –165.0 (m, 4 F, –C_6F_5-*meta*) ppm.

[$Au_2(C_6F_5)_6$(Mbis)] (6): Compound **6** was synthesised by the same procedure described for **5** using [$Au(C_6F_5)_3$(tht)] (0.211 g, 0.26 mmol) and Mbis (0.045 g, 0.13 mmol); yield 64%, 0.16 g. $C_{45}H_{12}Au_2F_{30}N_4Se_2$ (1731.824): calcd. C 31.18, H 0.70, N 3.23; found C 31.33, H 0.53, N 3.39. ^{1}H NMR [DMSO, 400 MHz]: δ = 3.68 (s, 6 H, –C*H*$_3$), 6.45 (s, 2 H, –C*H*$_2$–), 7.78 (s, 2 H, br, –CH=C*H*–), 7.89 (s, 2 H, br, –C*H*=CH–) ppm. ^{19}F NMR [DMSO, 376.48 MHz]: δ = –161.5 (m, 4 F, –C_6F_5-*meta*), –160.7 (m, 8 F, –C_6F_5-*meta*), –157.1 (t, $^3J_{FF}$ = 21.1 Hz, 2 F, –C_6F_5-*para*), –156.8 (t, $^3J_{FF}$ = 20.5 Hz, 4 F, –C_6F_5-*para*), –122.1 (m, 4 F, –C_6F_5-*ortho*), –120.2 (m, 8 F, –C_6F_5-*ortho*), ^{77}Se NMR (DMSO, 76.4 MHz): δ 75.8 (s, 2 Se) ppm.

[$Au_2(C_6F_5)_6$(Ebis)] (7): Compound **7** was synthesised by the same procedure described for **5** using [$Au(C_6F_5)_3$(tht)] (0.157 g, 0.20 mmol) and Ebis (0.035 g, 0.10 mmol); yield 64%, 0.16 g. $C_{46}H_{14}Au_2F_{30}N_4Se_2$ (1745.840): calcd. C 31.61, H 0.81, N 3.21; found C 31.34, H 0.58, N 3.28. ^{1}H NMR [DMSO, 400 MHz]: δ = 3.58 (s, 6 H, –C*H*$_3$), 4.51 (s, 4 H, –C*H*$_2$–C*H*$_2$–), 7.48 (d, $^3J_{HH}$ = 1.8 Hz, 4 H, –C*H*=C*H*–), 7.63 (d, $^3J_{HH}$ = 2.1 Hz, 4 H, –C*H*=C*H*–) ppm. ^{19}F NMR [$(CD_3)_2CO$, 376.48 MHz]: δ = –164.9 (m, 4 F, –C_6F_5-*meta*), –164.0 (m, 8 F, –C_6F_5-*meta*), –161.1 (t, $^3J_{FF}$ = 19.5 Hz, 2 F, –C_6F_5-*para*), –160.5 (t, $^3J_{FF}$ = 19.4 Hz, 4 F, –C_6F_5-*para*), –124.2 (m, 4 F, –C_6F_5-*ortho*), –121.8 (m, 8 F, –C_6F_5-*para*) ppm. ^{77}Se NMR (DMSO, 76.4 MHz): δ 43.9 (s, 2 Se) ppm.

[$Au_2(C_6F_5)_6$(Pbis)] (8): Compound **8** was synthesised by the same procedure described for **5** using [$Au(C_6F_5)_3$(tht)] (0.181 g, 0.23 mmol) and Pbis (0.045 g, 0.115 mmol); yield 87%, 0.18 g. $C_{49}H_{20}Au_2F_{30}N_4Se_2$ (1787.887): calcd. C 32.89, H 1.13, N 3.13; found C 32.83, H 1.20, N 3.22,. ^{1}H NMR (DMSO, 400 MHz): δ = 1.16 [m, 2 H, –(C*H*$_2$)$_5$–], 1.71 [t, $^3J_{HH}$ = 6.8 Hz, 4 H, –(C*H*$_2$)$_5$–], 3.70 (s, 6 H, –C*H*$_3$), 4.07 [t, $^3J_{HH}$ = 6.2 Hz, 4 H, –(C*H*$_2$)$_5$–], 7.68 (d, $^3J_{HH}$ = 1.9 Hz, 2 H, –CH=C*H*–), 7.69 (d, $^3J_{HH}$ = 1.9 Hz, 2 H, –C*H*=CH–) ppm. ^{19}F NMR (DMSO, 376.48 MHz): δ = –161.7 (m, 4 F, –C_6F_5-*meta*), –161.0 (m, 8 F, –C_6F_5-*meta*), –157.4 (m, 6 F, –C_6F_5-*para*), –122.3 (m, 4 F, –C_6F_5-*ortho*), –119.9 (m, 8 F, –C_6F_5-*ortho*), ^{77}Se NMR (DMSO, 76.4 MHz): δ 49.6 (s, 2 Se) ppm.

[$Au_2(OTf)_2(PPh_3)_2$(Bbit)] (9): To a solution of [Au(OTf)(PPh_3)] (0.172 g, 0.28 mmol), which has been obtained by reaction of [AuCl(PPh_3)] with Ag(OTf) in CH_2Cl_2 (20 mL) and used in situ, was added Bbit (0.04 g, 0.14 mmol) and stirred for 1 h at room temperature. The white solution was concentrated under reduced pressure and precipitated with hexane. The product was collected by filtration and recrystallized from acetone/n-hexane (1:5, v/v); yield 74%, 0.15 g. $C_{50}H_{48}Au_2F_6N_4O_6P_2S_4$ (1498.1167): calcd. C 40.06, H 3.23, N 3.74, S 8.54; found C 40.60, H 3.43, N 3.80, S 8.65. ^{1}H NMR (DMSO, 400 MHz): δ = 1.78 [br. s, 4 H, –(C*H*$_2$)$_4$–], 3.72 (s, 6 H, –C*H*$_3$), 4.21 [br. s, 4 H, –(C*H*$_2$)$_4$–], 7.58 (m, 30 H, P–C_6H_5, 4 H, –C*H*=C*H*–) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 26.07 [s, –(*C*H$_2$)$_4$–], 36.31 (s, –*C*H$_3$), 48.20 [s, –(*C*H$_2$)$_4$–], 121.12 and 122.12 (s, –*C*H=*C*H–), 127.90 (d, $^1J_{PC}$ = 60.5 Hz, P–C_6H_5-*ipso*), 129.67 (d, $^3J_{PC}$ = 11.7 Hz, P–C_6H_5-*meta*), 132.40 (s, P–C_6H_5-*para*), 134.01 (d, $^2J_{PC}$ = 13.5 Hz, P–C_6H_5-*ortho*) ppm. ^{19}F NMR (DMSO, 376.48 MHz): δ = –77.7 (s, 6 F, C$F_3SO_3^-$) ppm. ^{31}P NMR (DMSO, 161.9 MHz): δ = 35.7 (s, 2 P, *P*Ph_3) ppm.

[$Au_2(OTf)_2(PPh_3)_2$(Mbis)]·2C_3H_6O (10): Compound **10** was synthesised by the same procedure described for **9** using [Au(OTf)-(PPh_3)] (0.146 g, 0.24 mmol) and Mbis (0.04 g, 0.12 mmol); yield 76%, 0.14 g. $C_{47}H_{42}Au_2F_6N_4O_6P_2S_2Se_2$·2$C_3H_6O$ (1668.042): calcd. C 38.13, H 3.26, N 3.36, S 3.83; found C 38.38, H 2.96, N 2.86, S 3.71. ^{1}H NMR (DMSO, 400 MHz): δ = 3.79 (s, 6 H, –C*H*$_3$), 6.77 (s, 2 H, –C*H*$_2$–), 7.63 (m, 30 H, P–C_6H_5, 4 H, –C*H*=C*H*–) ppm. ^{13}C NMR NMR (DMSO, 100.6 MHz): δ = 37.64 (s, –*C*H$_3$), 61.20 [s, –*C*H$_2$–], 122.89 and 124.82 (s, –*C*H=*C*H–), 127.95 (d, $^1J_{PC}$ = 58.8 Hz, P–C_6H_5-*ipso*), 129.63 (d, $^3J_{PC}$ = 11.4 Hz, P–C_6H_5-*meta*), 132.32 (s, P–C_6H_5-*para*), 133.63 (d, $^2J_{PC}$ = 13.7 Hz, P–C_6H_5-*ortho*) ppm. ^{19}F NMR (DMSO, 376.48 MHz): δ = –77.7 (s, 6 F, C$F_3SO_3^-$) ppm. ^{31}P NMR (DMSO, 161.9 MHz): δ = 36.0 (s, 2 P, *P*Ph_3), ^{77}Se NMR (DMSO, 76.4 MHz): δ 4.6 (s, 2 Se) ppm.

[$Au_2(OTf)_2(PPh_3)_2$(Ebis)]·(0.5)C_6H_{14} (11): Compound **11** was synthesised by the same procedure described for **9** using [Au(OTf)-(PPh_3)] (0.122 g, 0.20 mmol) and Ebis (0.035 g, 0.10 mmol); yield 44%, 0.07 g. $C_{48}H_{44}Au_2F_6N_4O_6P_2S_2Se_2$·0.5$C_6H_{14}$ (1609.029): calcd. C 38.03, H 3.19, N 3.48, S 3.97; found C 37.49, H 2.88, N 3.36, S 3.46. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.87 (s, 6 H, –C*H*$_3$), 4.94 (s, 4 H, –C*H*$_2$–C*H*$_2$–), 7.48 (m, 30 H, P–C_6H_5, 4 H, –C*H*=C*H*–) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 38.21 (s, –*C*H$_3$), 49.61 [s, –(*C*H$_2$)$_2$–], 123.11 and 124.98 (s, –*C*H=*C*H–), 129.66 (d, $^3J_{PC}$ = 8.7 Hz, P–C_6H_5-*meta*), 132.47 (s, P–C_6H_5-*para*), 133.84 (d, $^2J_{PC}$ = 11.1 Hz, P–C_6H_5-*ortho*), 140.59 (s, –*C*=Se) ppm. ^{19}F NMR ($CDCl_3$, 376.48 MHz): δ = –78.1 (s, 6 F, C$F_3SO_3^-$) ppm. ^{31}P NMR {^{1}H} ($CDCl_3$, 161.9 MHz): δ = 37.8 (s, 2 P, *P*Ph_3) ppm. ^{77}Se NMR (DMSO, 76.4 MHz): δ = 8.2 (1s, 2 Se) ppm.

[$Au_2(OTf)_2(PPh_3)_2$(Pbis)] (12): Compound **12** was synthesised by the same procedure described for **9** using [Au(OTf)(PPh_3)] (0.118 g,

0.20 mmol) and Pbis (0.038 g, 0.10 mmol); yield 71%, 0.11 g. $C_{51}H_{50}Au_2F_6N_4O_6P_2S_2Se_2$ (1606.89): calcd. C 38.06, H 3.13, N 3.48, S 3.98; found C 38.42, H 3.17, N 3.44, S 4.15. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.33 [m, 2 H, –(CH_2)$_5$–], 1.85 [m, 4 H, –(CH_2)$_5$–], 3.87 (s, 6 H, –CH_3), 4.27 [t, $^3J_{HH}$ = 7.0 Hz, 4 H, –(CH_2)$_5$–], 7.57 (m, 30 H, P–C_6H_5, 4 H, –CH=CH–) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 22.62 and 28.85 [s, –(CH_2)$_5$–], 37.84 (s, –CH_3), 50.00 [s, –(CH_2)$_5$–], 122.64 and 123.72 (s, –CH=CH–), 128.17 (d, $^1J_{PC}$ = 58.9 Hz, P–C_6H_5-*ipso*), 129.54 (d, $^3J_{PC}$ = 11.7 Hz, P–C_6H_5-*meta*), 132.30 (s, P–C_6H_5-*para*), 133.91 (d, $^2J_{PC}$ = 13.6 Hz, P–C_6H_5-*ortho*) ppm. ^{19}F NMR ($CDCl_3$, 376.48 MHz): δ = –78.1 (s, 6 F, C$F_3SO_3^-$) ppm. ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ = 37.2 (s, 2 P, PPh$_3$) ppm. ^{77}Se NMR ($CDCl_3$, 76.4 MHz): δ = –1.7 (s, 2 Se) ppm.

[Au$_2$(OTf)$_2$(PPh$_2$py)$_2$(Bbit)] (13): To a solution of [Au(OTf)(PPh$_2$py)] (0.086 g, 0.14 mmol), which was obtained by reaction of [AuCl(PPh$_2$py)] with Ag(OTf) in CH_2Cl_2 (20 mL) and used in situ, was added Bbit (0.02 g, 0.07 mmol) and stirred for 1 h at room temperature. The solution was concentrated under reduced pressure and precipitated with hexane. The product was collected by filtration and recrystallized from acetone/n-hexane (1:5, v/v); yield 75%, 0.08 g. $C_{48}H_{46}Au_2F_6N_6O_6P_2S_4$ (1500.107): calcd. C 38.40, H 3.09, N 5.60, S 8.52; found C 38.63, H 3.07, N 5.55, S 8.41. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.90 [m, 4 H, –(CH_2)$_4$–], 3.87 (s, 6 H, –CH_3), 4.32 [s, 4 H, –(CH_2)$_4$–], 7.27 (d, $^3J_{HH}$ = 2.0 Hz, 4 H, –CH=CH–), 7.49 (m, 20 H, P–C_6H_5, 4H py), 7.86 [dd, $^3J_{PH}$ = 7.6, $^3J_{HH}$ = 7.4 Hz, 2 H, H_3(py)], 8.81 [d, $^3J_{HH}$ = 4.0 Hz, 2 H, H_6(py)] ppm. ^{19}F NMR ($CDCl_3$, 376.48 MHz): δ = –78.1 (s, 6 F, C$F_3SO_3^-$) ppm. ^{31}P NMR {^{1}H} ($CDCl_3$, 161.9 MHz): δ = 36.3 (s, 2 P, PPh$_2$py) ppm.

[Au$_2$(OTf)$_2$(PPh$_2$py)$_2$(Mbis)] (14): Compound **14** was synthesised by the same procedure described for **13** using [Au(OTf)(PPh$_2$py)] (0.061 g, 0.10 mmol) and Mbis (0.017 g, 0.05 mmol) in acetone (20 mL); yield 51%, 0.04 g. $C_{45}H_{40}Au_2F_6N_6O_6P_2S_2Se_2$ (1553.949): calcd. C 34.81, H 2.60, N 5.41, S 4.11; found C 35.30, H 2.93, N 5.43, S 3.54. ^{1}H NMR (DMSO, 400 MHz): δ = 3.76 (s, 6 H, –CH_3), 6.76 (s, 2 H, –CH_2–), 7.66 (m, 20 H, P–C_6H_5, 4H py + 4 H, –CH=CH–), 7.95 [dd, $^3J_{PH}$ = 7.2, $^3J_{HH}$ = 7.1 Hz, 2 H, H_3(py)], 8.79 [d, $^3J_{HH}$ = 4.0 Hz, 1 H, H_6(py)] ppm. ^{19}F NMR (DMSO, 376.48 MHz): δ = –77.7 (s, 6 F, C$F_3SO_3^-$) ppm. ^{31}P NMR (DMSO, 161.9 MHz): δ = 35.3 (s, 2 P, PPh$_2$py) ppm. ^{77}Se NMR (DMSO, 76.4 MHz): δ = 30.6 (s, 2 Se) ppm.

[Au$_2$(OTf)$_2$(PPh$_2$py)$_2$(Ebis)] (15): Compound **15** was synthesised by the same procedure described for **13** using [Au(OTf)(PPh$_2$Py)] (0.122 g, 0.20 mmol) and Ebis (0.035 g, 0.10 mmol); yield 57%, 0.09 g. $C_{46}H_{42}Au_2F_6N_6O_6P_2S_2Se_2$ (1567.965): calcd. C 35.20, H 2.70, N 5.36, S 4.08; found C 35.13, H 2.79, N 5.48, S 3.55. ^{1}H NMR (DMSO, 400 MHz): δ = 3.77 (s, 6 H, –CH_3), 4.82 (s, 4 H, –CH_2–CH_2–), 7.61 (m, 20 H, P–C_6H_5, 2H py + 4 H, –CH=CH–), 7.95 [dd, $^3J_{PH}$ = 7.4, $^3J_{HH}$ = 7.1 Hz, 2 H, H_3(py)], 8.79 [d, $^3J_{HH}$ = 3.5 Hz, 1 H, H_6(py)] ppm. ^{19}F NMR (DMSO, 376.48 MHz): δ = –77.7 (s, 6 F, C$F_3SO_3^-$) ppm. ^{31}P NMR {^{1}H} (DMSO, 161.9 MHz): δ = 36.0 (s, 2 P, PPh$_2$py) ppm. ^{77}Se NMR (DMSO, 76.4 MHz): δ = 18.5 (s, 2 Se) ppm.

[Au$_2$(OTf)$_2$(PPh$_2$py)$_2$(Pbis)] (16): Compound **16** was synthesised by the same procedure described for **13** using [Au(OTf)(PPh$_2$py)] (0.086 g, 0.14 mmol) and Pbis (0.027 g, 0.07 mmol); yield 78%, 0.086 g. $C_{49}H_{48}Au_2F_6N_6O_6P_2S_2Se_2$ (1610.011): calcd. C 36.58, H 3.00, N 5.22, S 3.97; found C 37.04, H 3.26, N 5.44, S 3.75. ^{1}H NMR (DMSO, 400 MHz): δ = 1.23 [m, 2 H, –(CH_2)$_5$–], 1.78 [m, 4 H, –(CH_2)$_5$–], 3.71 (s, 6 H, –CH_3), 4.10 [t, $^3J_{HH}$ = 7.1 Hz, 4 H, –(CH_2)$_5$–], 7.58 (m, 20 H, P–C_6H_5, 2 H py + 4 H, –CH=CH–), 7.95 [m, 2 H, H_3(py)], 8.79 [d, $^3J_{HH}$ = 4.3 Hz, 1 H, H_6(py)] ppm. ^{19}F NMR (DMSO, 376.48 MHz): δ = –77.7 (s, 6 F, C$F_3SO_3^-$) ppm. ^{31}P NMR (DMSO, 161.9 MHz): δ = 36.6 (s, 2 P, PPh$_3$), ^{77}Se NMR (DMSO, 76.4 MHz): δ 2.1 (s, 2 Se) ppm.

[Ag$_2$(OTf)$_2$(PPh$_3$)$_2$(Bbit)] (17): Compound **17** was synthesised by the same procedure described for **5** using [Ag(OTf)(PPh$_3$)] (0.147 g, 0.28 mmol) and Bbit (0.04 g, 0.14 mmol); yield 54% 0.10 g. $C_{50}H_{48}Ag_2F_6N_4O_6P_2S_4$ (1317.994): calcd. C 45.47, H 3.67, N 4.24, S 9.70; found C 44.60, H 3.43, N 3.80, S 9.65. ^{1}H NMR (DMSO, 400 MHz): δ = 1.73 [br. s, 4 H, –(CH_2)$_4$–], 3.42 (s, 6 H, –CH_3), 3.96 [br. s, 4 H, –(CH_2)$_4$–], 7.31 (m, 12 H, P–C_6H_5-*ortho*, 4 H, –CH=CH–), 7.44 (dd, J_{HH} = 7.0 Hz, 12 H, P–C_6H_5-*meta*), 7.52 (dd, $^3J_{HH}$ = 7.0 Hz, 6 H, P–C_6H_5-*para*) ppm. ^{13}C NMR (DMSO, 100.6 MHz): δ = 24.24 [s, –(CH_2)$_4$–], 34.80 (s, –CH_3), 46.09 [s, –(CH_2)$_4$–], 118.36 and 120.38 (s, –CH=CH–), 129.10 (d, $^3J_{PC}$ = 9.5 Hz, P–C_6H_5-*meta*), 130.66 (s, P–C_6H_5-*para*), 131.49 (d, $^1J_{PC}$ = 26.6 Hz, P–C_6H_5-*ipso*), 133.23 (d, $^2J_{PC}$ = 16.2 Hz, P–C_6H_5-*ortho*), 155.77 (s, –C=S) ppm. ^{19}F NMR (DMSO, 376.48 MHz): δ = –77.7 (s, 6 F, C$F_3SO_3^-$) ppm. ^{31}P NMR (DMSO, 161.9 MHz): δ = 8.6 (s, 2 P, PPh$_3$) ppm.

[Ag$_4$(OTf)$_4$(PPh$_3$)$_4$(Mbis)$_3$] (18): Compound **18** was synthesised by the same procedure described for **5** using [Ag(OTf)(PPh$_3$)] (0.088 g, 0.17 mmol) and Mbis (0.042 g, 0.125 mmol) in acetone; yield 85%, 0.11 g. $C_{103}H_{96}Ag_4F_{12}N_{12}O_{12}P_4S_4Se_6{\cdot}2C_6H_{12}$ (3247.798): calcd. C 42.49, H 3.72, N 5.17, S 3.94; found C 42.59, H 3.35, N 5.62, S 3.40. ^{1}H NMR [DMSO, 400 MHz]: δ = 3.56 (s, 18 H, –CH_3), 6.54 (s, 6 H, –CH_2–), 7.52 (m, 60 H, P–C_6H_5, 12 H, –CH=CH–) ppm. ^{13}C NMR (DMSO, 100.6 MHz): δ = 37.07 (s, –CH_3), 59.88 [s, –CH_2–], 121.01 and 123.25 (s, –CH=CH–), 129.14 (d, $^3J_{PC}$ = 9.5 Hz, P–C_6H_5-*meta*), 130.68 (s, P–C_6H_5-*para*), 131.57 (d, $^1J_{PC}$ = 27.6 Hz, P–C_6H_5-*ipso*), 133.26 (d, $^2J_{PC}$ = 16.4 Hz, P–C_6H_5-*ortho*), 148.61 (s, –C=Se) ppm. ^{31}P NMR (DMSO, 161.9 MHz): δ 8.2 (4P, s, PPh$_3$). ^{77}Se NMR (DMSO, 76.4 MHz): δ –48.9 (s, 2 Se).

Synthesis [Ag$_2$(OTf)$_2$(PPh$_3$)$_2$(Ebis)] (19): Compound **19** was synthesised by the same procedure described for **5** using [Ag(OTf)(PPh$_3$)] (0.104 g, 0.20 mmol) and Ebis (0.035 g, 0.10 mmol) in acetone (20 mL); yield 61%, 0.08 g. $C_{48}H_{44}Ag_2F_6N_4O_6P_2S_2Se_2{\cdot}C_3H_6O$ (1443.893): calcd. C 42.38, H 3.48, N 3.88, S 4.43; found C 42.43, H 3.00, N 3.98, S 3.74. ^{1}H NMR (DMSO, 300 MHz): δ = 3.40 (s, 6 H, –CH_3), 4.66 (s, 4 H, –CH_2–CH_2–), 7.30 (dd, $^3J_{HH}$ = 7.8 Hz, 12 H, P–C_6H_5-*meta*), 7.41 (dd, $^3J_{HH}$ = 7.8 Hz, 12 H, P–C_6H_5-*ortho*), 7.49 (m, 6 H, P–C_6H_5-*para*, 4 H, –CH=CH–) ppm. ^{13}C NMR (DMSO, 100.6 MHz): δ = 36.61 (s, –CH_3), 46.70 [s, –(CH_2)$_2$–], 121.06 and 122.50 (s, –CH=CH–), 129.06 (d, J_{PC} = 9.4 Hz, P–C_6H_5-*meta*), 130.57 (s, P–C_6H_5-*para*), 131.71 (d, $^1J_{PC}$ = 25.7 Hz, P–C_6H_5-*ipso*), 133.24 (d, $^2J_{PC}$ = 16.4 Hz, P–C_6H_5-*ortho*), 147.57 (s, –C=Se) ppm. ^{19}F NMR (DMSO, 376.48 MHz): δ = –77.7 (s, 6 F, C$F_3SO_3^-$) ppm. ^{31}P NMR {^{1}H} (DMSO, 161.9 MHz): δ = 7.1 (s, 2 P, PPh$_3$) ppm. ^{77}Se NMR (DMSO, 76.4 MHz): δ –73.9 (s, 2 Se).

[Ag$_2$(OTf)$_2$(PPh$_3$)$_2$(Pbis)] (20): Compound **20** was synthesised by the same procedure described for **5** using [Ag(OTf)(PPh$_3$)] (0.106 g, 0.20 mmol) and Pbis (0.04 g, 0.10 mmol); yield 34%, 0.05 g. $C_{51}H_{50}Ag_2F_6N_4O_6P_2S_2Se_2$ (1427.898): calcd. C 42.86, H 3.53, N 3.92, S 4.48; found C 43.32, H 3.50, N 3.67, S 4.24. ^{1}H NMR [$(CD_3)_2CO$, 400 MHz]: δ = 1.36 [q, $^3J_{HH}$ = 7.2 Hz, 2 H, –(CH_2)$_5$–], 1.89 [m, 4 H, –(CH_2)$_5$–], 3.64 (s, 6 H, –CH_3), 4.21 [t, $^3J_{HH}$ = 7.1 Hz, 4 H, –(CH_2)$_5$–], 7.22 (m, 24 H, P–C_6H_5-*ortho*, *meta*), 7.50 (m, 4 H, –CH=CH–; 6 H, P–C_6H_5-*para*) ppm. ^{13}C NMR [$CO(CD_3)_2$, 100.6 MHz]: δ = 24.01 [s, –(CH_2)$_5$–], 38.91 (s, –CH_3), 51.05 and 55.96 [s, –(CH_2)$_5$–], 123.07 and 124.69 (s, –CH=CH–), 131.09 (d, $^3J_{PC}$ = 9.6 Hz, P–C_6H_5-*meta*), 132.72 (s, P–

C_6H_5-*para*), 133.28 (d, $^1J_{PC}$ = 27.8 Hz, P–C_6H_5-*ipso*), 135.44 (d, $^2J_{PC}$ = 16.0 Hz, P–C_6H_5-*ortho*), 147.93 (s, –*C*=Se) ppm. ^{19}F NMR [$(CD_3)_2CO$, 376.48 MHz]: δ = –80.1 (s, 6 F, $CF_3SO_3^-$) ppm. ^{31}P NMR [$(CD_3)_2CO$, 161.9 MHz]: δ = 10.3 (s, 2 P, PPh_3) ppm. ^{77}Se NMR [DMSO, 76.4 MHz]: δ –98.6 (s, 2 Se) ppm.

[$Ag_2(OTf)_2$(Bbit)] (21): To a solution of Ag(OTf) (0.065 g, 0.25 mmol) in acetone (20 mL) was added Bbit (0.035 g, 0.125 mmol) and the mixture stirred for 1 h at room temperature. The white solution was concentrated under reduced pressure and precipitated with hexane; yield 85%, 0.085 g. $C_{14}H_{18}Ag_2F_6N_4O_6S_4$ (793.811): calcd. C 21.16, H 2.28, N 7.06, S 16.11; found C 21.03, H 2.16, N 7.00, S 15.91. ^{1}H NMR (DMSO, 400 MHz): δ = 1.83 [m, 4 H, –(CH_2)$_4$–], 3.62 (s, 6 H, –CH_3), 4.13 [m, 4 H, –(CH_2)$_4$–], 7.46 (m, 4 H, –C*H*=C*H*–) ppm. ^{19}F NMR (DMSO, 376.48 MHz): δ = –77.7 (s, 6 F, $CF_3SO_3^-$) ppm.

[$Ag_2(OTf)_2$(Mbis)] (22): Compound **22** was synthesised by the same procedure described for **21** using Ag(OTf) (0.061 g, 0.23 mmol) and Mbis (0.04 g, 0.12 mmol); yield 85%, 0.09 g. $C_{11}H_{12}Ag_2F_6N_4O_6S_2Se_2$ (847.653): calcd. C 15.57, H 1.43, N 6.61, S 7.54; found C 15.36, H 1.31, N 6.15, S 7.42. ^{1}H NMR (DMSO, 400 MHz): δ = 3.78 (s, 6 H, –CH_3), 6.73 (s, 2 H, –CH_2–), 7.84 (s, 4 H, br, –CH=C*H*–) ppm. ^{19}F NMR (DMSO, 376.48 MHz): δ = –77.7 (s, 6 F, $CF_3SO_3^-$), ^{77}Se NMR (DMSO, 76.4 MHz): δ –131.2 (s, 2 Se) ppm.

[$Ag_2(OTf)_2$(Ebis)] (23): Compound **23** was synthesised by the same procedure described for **21** using Ag(OTf) (0.051 g, 0.20 mmol) and Ebis (0.035 g, 0.10 mmol); yield 65%, 0.05 g. $C_{12}H_{14}Ag_2F_6N_4O_6S_2Se_2$ (861.669): calcd. C 16.72, H 1.64, N 6.50, S 7.42; found C 17.36, H 1.50, N 6.74, S 7.68. ^{1}H NMR (DMSO, 400 MHz): δ = 3.76 (s, 6 H, –CH_3), 4.63 (s, 4 H, –CH_2–CH_2–), 7.68 (d, $^3J_{HH}$ = 1.9 Hz, 2 H, –C*H*=CH–), 7.74 (d, $^3J_{HH}$ = 1.9 Hz, 2 H, –CH=C*H*–) ppm. ^{19}F NMR (DMSO, 376.48 MHz): δ = –77.7 (s, 6 F, $CF_3SO_3^-$), ^{77}Se NMR (DMSO, 76.4 MHz): δ –160.6 (s, 2 Se) ppm.

[$Ag_2(OTf)_2$(Pbis)]·(0.5)C_3H_6O (24): Compound **24** was synthesised by the same procedure described for **21** using Ag(OTf) (0.039 g, 0.15 mmol) and Pbis (0.03 g, 0.076 mmol); yield 72%, 0.05 g. $C_{15}H_{20}Ag_2F_6N_4O_6S_2Se_2$ (903.716): calcd. C 19.92, H 2.23, N 6.19, S 7.07; found C 20.35, H 2.13, N 6.66, S 6.68. ^{1}H NMR (DMSO, 400 MHz): δ = 1.22 [q, $^3J_{HH}$ = 6.7 Hz, 2 H, –(CH_2)$_5$–], 1.87 [m, 4 H, –(CH_2)$_5$–], 3.73 (s, 6 H, –CH_3), 4.20 [t, $^3J_{HH}$ = 6.7 Hz, 4 H, –(CH_2)$_5$–], 7.67 (m, 4 H, –C*H*=C*H*–) ppm. ^{19}F NMR (DMSO, 376.48 MHz): δ = –77.7 (s, 6 F, $CF_3SO_3^-$), ^{77}Se NMR (DMSO, 76.4 MHz): δ –154.6 (s, 2 Se) ppm.

[Cu_2(Bbit)$_2$](PF_6)$_2$ (25): To a solution $[Cu(CH_3CN)_4]PF_6$ (0.03 g, 0.08 mmol) in acetone (20 mL) was added Bbit (0.023 g, 0.08 mmol) and the mixture stirred for 30 min at room temperature. The solution was concentrated under reduced pressure and precipitated with hexane; yield 84%, 0.04 g. $C_{12}H_{18}CuF_6N_4PS_2$·C_3H_6O (548.033): calcd. C 32.84, H 4.41, N 10.22, S 11.66; found C 32.76, H 4.11, N 10.44, S 11.01. ^{1}H NMR (DMSO, 400 MHz): δ = 1.75 [m, 4 H, –(CH_2)$_4$–], 3.57 (s, 6 H, –CH_3), 4.09 [m, 4 H, –(CH_2)$_4$–], 7.34 (m, 4 H, –C*H*=C*H*–) ppm. ^{19}F NMR (DMSO, 376.48 MHz): δ = –70.1 (d, $^1J_{PF}$ = 711.3 Hz, 12 F, PF_6^-) ppm.

[Cu_2(Mbis)$_2$](PF_6)$_2$ (26): Compound **26** was synthesised by the same procedure described for **25** using $[Cu(CH_3CN)_4]PF_6$ (0.012 g, 0.03 mmol) and Mbis (0.011 g, 0.03 mmol); yield 83%, 0.015 g. $C_9H_{12}CuF_6N_4PSe_2$ (543.833): calcd. C 19.86, H 2.22, N 10.30; found C 19.43, H 2.20, N 9.92. ^{1}H NMR (DMSO, 400 MHz): δ = 3.61 (s, 6 H, –CH_3), 6.80 (s, 2 H, –CH_2–), 7.64 (d, $^3J_{HH}$ = 2.1 Hz, 2 H, –C*H*=CH–), 7.78 (d, $^3J_{HH}$ = 2.1 Hz, 2 H, –CH=C*H*–) ppm. ^{19}F NMR (DMSO, 376.48 MHz): δ = –70.1 (d, $^1J_{PF}$ = 711.3 Hz, 12 F, PF_6^-) ppm.

[Cu_2(Ebis)$_2$](PF_6)$_2$ (27): Compound **27** was synthesised by the same procedure described for **25** using $[Cu(CH_3CN)_4]PF_6$ (0.037 g, 0.10 mmol) and Ebis (0.035 g, 0.10 mmol) in CH_2Cl_2 (20 mL); yield 38%, 0.04 g. $C_{10}H_{14}CuF_6N_4PSe_2$ (557.848): calcd. C 21.51, H 2.53, N 10.04; found C 21.19, H 2.29, N 9.82. ^{1}H NMR (DMSO, 400 MHz): δ = 3.59 (s, 6 H, –CH_3), 4.73 (s, 4 H, –CH_2–CH_2–), 7.35 (d, $^3J_{HH}$ = 1.6 Hz, 2 H, –C*H*=CH–), 7.48 (d, $^3J_{HH}$ = 1.6 Hz, 2 H, –CH=C*H*–) ppm. ^{31}P NMR {^{1}H} (DMSO, 161.9 MHz): δ = –143.7 ppm. ^{19}F NMR (DMSO, 376.48 MHz): δ = –70.6 (d, $^1J_{PF}$ = 711.2 Hz) ppm.

[Cu_2(Pbis)$_2$](PF_6)$_2$ (28): Compound **28** was synthesised by the same procedure described for **25** using $[Cu(CH_3CN)_4]PF_6$ (0.02 g, 0.05 mmol) and Pbis (0.019 g, 0.05 mmol); yield 83%, 0.025 g. $C_{13}H_{20}CuF_6N_4PSe_2$ (599.895): calcd. C 26.00, H 3.36, N 9.34; found C 25.49, H 3.02, N 9.02. ^{1}H NMR (DMSO, 400 MHz): δ = 1.22 [q, $^3J_{HH}$ = 7.1 Hz, 2 H, –(CH_2)$_5$–], 1.87 [m, 4 H, –(CH_2)$_5$–], 3.73 (s, 6 H, –CH_3), 4.20 [t, $^3J_{HH}$ = 7.0 Hz, 4 H, –(CH_2)$_5$–], 7.67 (m, 4 H, –C*H*=C*H*–) ppm. ^{19}F NMR (DMSO, 376.48 MHz): δ = –70.6 (d, $^1J_{PF}$ = 711.2 Hz) ppm.

Crystal Structures: Cell refinement gave cell constants corresponding to monoclinic or orthorhombic cells whose dimensions are given in Table 1 along with other experimental parameters. Crystals of Pbis, **2**, **7**, **13** and **18** were mounted in inert oil on a glass fibre and transferred to the cold gas stream of an Xcalibur Oxford Diffraction diffractometer equipped with a low-temperature attachment. Data were collected using monochromated Mo-K_α radiation (λ = 0.71073 Å). Scan type ω. Absorption correction based on multiple scans were applied with the program SADABS.[31] The structures were refined on F^2 using the program SHELXL-97.[32] All of the non-hydrogen atoms were treated anisotropically. Hydrogen atoms were included in idealized positions with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they were attached. The drawings were created with the DIAMOND program.[33]

CCDC-799270 (for Pbis), -799271 (for **2**), -799272 (for **7**), -799273 (for **13**), -799274 (for **18**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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