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Group 11 complexes with unsymmetrical P,S and P,Se disubstituted ferrocene ligands

Javier E. Aguado,^{*a*} Silvia Canales,^{*a*} M. Concepción Gimeno,^{*a*} Peter G. Jones,^{*b*} Antonio Laguna^{*a*} and M. Dolores Villacampa^{*a*}

^a Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, E-50009 Zaragoza, Spain

^b Institut für Anorganische und Analytische Chemie der Technischen Universität, Postfach 3329, D-38023 Braunschweig, Germany

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The reaction of the unsymmetrical ligands 1-diphenylphosphino-1'-(phenylsulfanyl)ferrocene and 1-diphenylphosphino-1'-(phenylselenyl)ferrocene, $Fc(EPh)PPh_2$ (E = S, Se), with several group 11 metal derivatives leads to the synthesis of complexes of the type $[MX{Fc(EPh)PPh_2}] (M = Au, X = Cl, C_6F_5; M = Ag, X = OTf)$, (OTf = trifluoromethanesulfonate), $[M{Fc(EPh)PPh_2}_2]X (M = Au, X = ClO_4; M = Ag, X = OTf)$, $[M(PPh_3){Fc(EPh)PPh_2}]OTf (M = Au, Ag), [Au_2{Fc(SPh)PPh_2}_2](ClO_4)_2, [Au(C_6F_5)_2{Fc(SePh)PPh_2}]ClO_4, [Au(C_6F_5)_3{Fc(EPh)PPh_2}], [Au_2(C_6F_5)_6{Fc(SePh)PPh_2}] or <math>[Cu{Fc(EPh)PPh_2}_2]PF_6$ (E = S, Se). In these complexes coordination depends upon the metal centre; with gold it takes place predominantly to the phosphorus atom and with silver and copper to both phosphorus and chalcogen atoms. The treatment of some of the gold complexes with other metal centres affords heterometallic derivatives that in some cases are in equilibrium with the homometallic derivatives. Several compounds have been characterized by X-ray diffraction, four pairs of homologous compounds, yet not a single pair is isotypic. In many of them a three dimensional network is formed through secondary bonds such as hydrogen bonds, Au ··· Cl or Au ··· Se interactions. The complex [Ag(OTf){Fc(SePh)PPh_2}] forms one-dimensional chains through trifluoromethanesulfonate bridging ligands.

Introduction

The chemistry of ferrocene-containing compounds has received considerable attention in recent years, associated with the utility of such products in many fields such as organic synthesis, catalysis or materials chemistry.¹⁻³ In these complexes the inherent properties of the ferrocene moiety such as its high stability and reversible redox character, have played an important role in coordination chemistry. The functionalization of the cyclopentadienyl rings with various donor groups and subsequent ligation to metal centres are an important topic of research in many fields that seek special properties of such species, for example non-linear optical properties, electrochemical sensors, molecular recognition, liquid crystals, catalysis or even nanoparticles.4-15 1,1'-Symmetrically substituted ferrocene species with several O, N, S or P donor centres are well-known, but species bearing different substituents in the cyclopentadienyl rings are much less common. Unsymmetrical ligands are important in view of their hemilability for catalysis.¹⁶ The first report of a P,S asymmetrically substituted ferrocene was made by Liu et al. who described the synthesis of the Fc(SPh)(PPh₂) derivative via selective transmetallation reactions of Fc(SnBu₃)₂, although no metal complexes were reported.^{17,18} An alternative fivestep synthesis was reported by Dong et al.¹⁹ The compound FcBr₂ was used as starting material to prepare the trisubstituted species $[Fe{1,2-(PPh_2)(SMe)(\eta^5-C_5H_3)}{(1'-(SMe)(\eta^5-C_5H_3))}$ C₅H₄)]²⁰ and a chiral phosphine-thioether ferrocene ligand has been used in the asymmetric addition of diethylzinc to alkylidine malonates.²¹ Also the reaction of aldehydes with isocyanoacetate has been reported by Hayashi et al. to be catalysed by a chiral ferrocenylphosphine-gold(I) complex.²² Long et al. have developed a new synthesis of several unsymmetrical P,S derivatives of the type $Fc(SR)(PPh_2)$ (R = H, Me, Mes), involving the reaction of FcLi₂(TMDA) with a mixture of ClPPh₂ and R_2S_2 . The coordination chemistry of these ligands towards several metals such as nickel, palladium or rhodium has been studied.23-25

As part of our studies of ferrocene derivatives as ligands,²⁶ we report here on the synthesis of the first unsymmetrical ferrocenyl ligand having both P and Se as donor atoms and on the reactivity of the $Fc(SPh)PPh_2$ and $Fc(SePh)PPh_2$ ligands with group 11 metal complexes. The reactivity of the three metals is different; gold predominantly coordinates through the phosphorus donor ligand, silver can coordinate either through the phosphorus only or through both donor atoms (phosphorus and chalcogen), and copper coordinates to both donor atoms. Some heteronuclear complexes have been prepared starting from the gold complexes. The crystal structure determinations of some of the gold and silver complexes provide experimental evidence for the importance of secondary bonds in the molecular architecture; in many of the complexes hydrogen bonding is present.

Results and discussion

The ligand 1-diphenylphosphino-1'-(phenylsulfanyl)ferrocene, Fc(SPh)PPh₂, has been synthesized by reaction of FcLi₂·TMDA with ClSnBu₃ and subsequent reactions with ClPPh₂ and Ph₂S₂. We have prepared the ligands Fc(SPh)PPh₂ and Fc(SePh)PPh₂ according to the published method described for the related ligand Fc(SMe)PPh2.23 The reaction of FcLi2(TMDA) with Cl₂PPh leads to the 1,1'-diphenylphosphinoferrocenophane ligand (FcPPh). This phosphine was then treated with PhLi to cleave one of the P-C bonds and give the 1-lithio-1diphenylphosphinoferrocene, which reacts in situ with S₂Ph₂ or Se₂Ph₂ to afford the unsymmetrical derivatives (Scheme 1). Compound 2 is an air- and moisture-stable orange solid. The ¹H NMR spectrum shows four different resonances for the α and β protons of each cyclopentadienyl ring and the ³¹P(¹H) NMR spectrum one resonance at -17.0 ppm, indicating the presence of a free phosphine ligand.



Synthesis of gold complexes

The reaction of $Fc(EPh)PPh_2$ with [AuX(tht)] (tht = tetrahydrothiophene) gives the complexes $[AuX{Fc(EPh)PPh_2}]$ (E = S, X = Cl (3), C_6F_5 (4)), (E = Se, X = Cl (5), C_6F_5 (6)) in good yield (see Scheme 2). The compounds are yellow-orange air- and moisture-stable solids that behave as non-conductors in acetone solutions. The IR spectra for complexes 3 and 5 show the absorptions arising from the vibrations v(Au-Cl) at 336 (m) and 335 (m) cm⁻¹, respectively. For complexes 4 and 6 the typical absorptions of a pentafluorophenyl unit bonded to gold(I) appear around 1500 (vs), 954 (s) and 800 (m) cm⁻¹. In the ¹H NMR spectra four resonances for the cyclopentadienyl protons are not observed because some of them are overlapped; thus for complexes 3, 4 and 6 three signals with a ratio 1 : 1:2 can be observed whereas for 5 only a broad resonance appears. The ³¹P NMR spectra indicate that the coordination of the gold(I) atoms takes place via phosphorus because a low-field displacement is observed; the position is very similar for the sulfur or the selenium derivatives, 28.1 (3) and 27.1 (5) ppm, or 37.7 (4), 38.1 (6) ppm. The ¹⁹F NMR spectra for 4 and 6 show the typical pattern for a pentafluorophenyl group with three resonances corresponding to the ortho, meta and para fluorine atoms. In the liquid secondary-ion mass spectra the molecular peaks appear at m/z = 710 (3, 70%), 842 (4, 100%), 882 (6, 25%); for compound 5 only the fragment arising from the loss of the chloro ligand at m/z = 723 (30%) can be observed.

The reaction of the ligands 1 or 2 with $[Au(tht)_2]ClO_4$ in a molar ratio 2 : 1 leads to the homoleptic complexes $[M{Fc(EPh)PPh_2}_2]ClO_4$ (E = S(7), Se (8)). Complexes 7 and 8 are air- and moisture-stable yellow (7) or orange (8) solids that behave as 1 : 1 electrolytes in acetone solutions. The ¹H NMR spectra show the presence of four multiplets or two multiplets for the cyclopentadienyl protons. In the ³¹P NMR spectra one resonance at 40.1 and 37.5 ppm, respectively, appears for the equivalent phosphorus atoms. In the mass spectra the cation molecular peaks at m/z = 1153 (7, 53%) and 1247 (8, 35%) can be observed. The reaction of 1 with [Au(tht)₂]ClO₄ in a molar ratio 1:1 was also carried out and gives a compound of stoichiometry $[Au_2{Fc(SPh)PPh_2}_2](ClO_4)_2$ (9). In the ³¹P NMR spectrum two different phosphorus environments are observed, one signal at 27.6 and other at 38.3 ppm; this could indicate the presence of two different isomers of complex 9, one would be the "head to head" and the other "head to tail" (Fig. 1). This would



Fig. 1 The two possible isomers of complex 9.



Scheme 2 (i) [AuCl(tht)] or $[Au(C_6F_5)(tht)]$, (ii) $1/2 [Au(tht)_2]ClO_4$, (iii) $[Au(tht)_2]ClO_4$, (iv) $[Au(OTf)(PPh_3)]$, (v) $[Au(C_6F_5)_3(tht)]$, (vi) $2 [Au(C_6F_5)_3(tht)]$

also explain the different chemical shifts, the signal at 27.6 is in the typical region for a P–Au–S unit and that at 38.3 for a P–Au–P unit. The ¹H NMR spectrum is also in agreement with the presence of the two isomers.

The treatment of **1** with [Au(OTf)(PPh₃)] gives the mixed phosphine complex [Au(PPh₃){Fc(SPh)PPh₂}]OTf (**10**). As happens with other asymmetric gold(1) complexes, this derivative is in equilibria in solution with the homoleptic species, [Au(PPh₃)₂]OTf and [Au{Fc(SPh)PPh₂}₂]OTf, although the equilibria are strongly displaced in the direction of the heteroleptic compound. This can be easily seen in the ³¹P(¹H) NMR spectrum where complex **10** presents an AB system for the two different phosphorus, whereas the homoleptic species show only one signal for the equivalent phosphorus atoms. In the ¹H NMR spectrum compound **10** (most abundant) shows four resonances for the cyclopentadienyl protons. In the mass spectra all the fragments corresponding to all these cationic peaks are present, at m/z = 937 (**9**, 25%), 721 ([Au(PPh₃)₂]⁺, 20%), 1153 ([Au{Fc(SPh)PPh₂}₂]⁺, 10%).

Gold(III) derivatives of the type $[Au(C_6F_5)_3{Fc(EPh)PPh_2}]$ (E = S (11), Se (12)) or $[Au_2(C_6F_5)_6{Fc(EPh)PPh_2}]$ (E =Se (13)) have been obtained by reaction of the ligands with $[Au(C_6F_5)_3(OEt_2)]$ in 1 : 1 and 1 : 2 molar ratio. Complexes 11-13 are yellow (11) or orange (12, 13) air- and moisturestable solids that behave as non-conductors in acetone solution. The IR spectra show the typical absorptions arising from a tris(pentafluorophenyl)gold fragment around 970 (s), 803 (s) and 795 (s) cm⁻¹. In the ¹H NMR spectra the protons of the cyclopentadienyl rings appear as several multiplets. Although all of them should be inequivalent, the rapid exchange means that sometimes the resonances are overlapped; we thus observed 4 (11), 3 (12), or 5 (13) resonances with different integral ratios. Only one signal is observed in the ${}^{31}P({}^{1}H)$ NMR spectra for these complexes, as expected for one type of phosphorus atom. The ¹⁹F NMR spectra of complexes **11** and **12** shows the presence of two different pentafluorophenyl groups in the ratio 2 : 1, each group showing three resonances for the ortho, meta and para fluorine atoms, respectively. For compound 13 four different types of pentafluorophenyl units should appear, corresponding to twelve different resonances, but some of the positions are

overlapped. In the LSIMS+ the molecular peaks appear at m/z = 1176 (11, 34%), 1224 (12, 10%). For complex 13, which has two Au(C₆F₅)₃ units, the molecular peak is not present but the fragment arising from the loss of two pentafluorophenyl units appears at m/z = 1580 (13, 30%).

The complex $[Au(C_6F_5)_2{Fc(SePh)PPh_2}]ClO_4$ (14) has been prepared by reaction of 2 with $[Au(C_6F_5)_2(OEt_2)_2]ClO_4$. In this complex we suppose that the gold(III) centre is coordinated to the phosphorus and selenium atoms of the heterodifunctional ligand. Complex 14 is an orange-red air- and moisture-stable solid that behaves as a 1:1 electrolyte in acetone solution. In the IR spectrum the absorptions from the pentafluorophenyl groups and the perchlorate anion appear at 1100 (s, br) and 619 (m) cm⁻¹, respectively. In the ¹H NMR spectrum all the protons of the cyclopentadienyl rings are inequivalent and appear as seven multiplets because two of them are overlapped. The ${}^{31}P({}^{1}H)$ NMR spectrum shows only one resonance at 33.4 ppm for the phosphorus atom. In the ¹⁹F NMR spectrum six resonances for the two different pentafluorophenyl units can be observed. The LSIMS+ spectrum shows the cation molecular peak at m/z = 944 (20%).

Synthesis of silver and copper complexes

The reaction of 1 or 2 with AgOTf in a molar ratio 1 : 1 gives the complexes with stoichiometry $[Ag(OTf){Fc(EPh)PPh_2}] (E = S$ (15), Se (16)) (see Scheme 3). Complexes 15 and 16 are yellow or orange, respectively, air- and moisture-stable solids that are nonconductors in acetone solutions, which means that the triflate is coordinated to the silver centre. In the IR spectra the absorptions for a covalent trifluoromethanesulfonate anion are observed and appear around $v_{as}(SO_3) = 1320$ (vs) and 1307 (vs), $v_{svm}(CF_3) =$ 1229 (m), $v_{asym}(CF_3) = 1199$ (vs) and $v_{sym}(SO_3) = 1098$ (vs) cm⁻¹. In the ¹H NMR the signals for the cyclopentadienyl rings again appear overlapped and only three multiplets in a ratio 2 : 2 : 4 for compound 15 and two multiplets in a 4 : 4 ratio for complex 16 can be observed. Only one resonance appears in the ³¹P(¹H) NMR spectra, in agreement with the presence of only one type of phosphorus atom at room temperature. At -55 °C two doublets appear because of the coupling with the



E = S (20), Se (21)

Scheme 3 (i) [Ag(OTf)], (ii) 1/2 [Ag(OTf)], (iii) [Ag(OTf)(PPh₃)] (iv) [Cu(NCMe)₄]PF₆.

two silver nuclei, ¹⁰⁷Ag and ¹⁰⁹Ag. In the mass spectra, the cation molecular peaks appear at m/z = 585 (15, 100%) and 633 (16, 100%).

The reaction of 1 with AgOTf in a molar ratio 2 : 1 gives the complex $[Ag{Fc(SPh)PPh_2}_2]OTf(17)$, which is a yellow air- and moisture-stable solid that behaves as a 1 : 1 electrolyte in acetone solutions. In the IR spectrum the trifluoromethanesulfonate is only acting as the counterion, as can be seen from the absorptions at $v_{asym}(SO_3) = 1272$ (vs), $v_{sym}(CF_3) = 1237$ (m), $v_{asym}(CF_3) = 1156$ (vs) and $v_{sym}(SO_3) = 1025$ (vs) cm⁻¹. The ¹H NMR spectrum presents, apart from the multiplet due to the phenyl protons, four multiplets for the cyclopentadienyl protons. The ³¹P(¹H) NMR spectrum shows a broad singlet at room temperature that splits into two doublets at -55 °C because of the coupling with the silver nuclei. In the LSIMS+ the cation molecular peak appears at m/z = 1065 (10%) and also the fragment at m/z = 585 (50%) corresponding to $[Ag{Fc(SPh)PPh_2}]^+$ is present.

The treatment of 1 or 2 with $[Ag(OTf)(PPh_3)]$ in dichloromethane leads to the four-coordinated derivatives $[Ag(OTf)(PPh_3){Fc(EPh)PPh_2}]$ (E = S (18), Se (19)). Complexes 18 and 19 are vellow or orange, respectively, air- and moisture-stable solids. Their conductivities in acetone solutions are 10.1 and 15 Ω^{-1} cm² mol⁻¹, which means that the triflate ligand may dissociate to some extent. In the IR spectra the bands for a covalent triflate anion can be observed. In the ¹H NMR spectra three resonances for complex 18 and four resonances for compound 19 are associated with the cyclopentadienyl protons. The ³¹P(¹H) NMR spectra show broad signals at room temperature; at low temperature eight doublets are observed as a consequence of the presence of an AB system coupled to the two silver nuclei. In the mass spectra (LSIMS+) the cations molecular peaks appear at m/z = 847 (18, 15%) and 895 (19, 30%).

The reaction of **1** or **2** with the copper compound $[Cu(NCMe)_4]PF_6$ in a molar ratio 1 : 1 has also been carried out and gives the derivative $[Cu{Fc(EPh)PPh_2}_2]PF_6$ (E = S (**20**), Se (**21**)). In the same manner as for silver(1), and because of the high tendency of copper to adopt higher coordination numbers than gold(1), we propose a tetrahedral geometry for complexes **20** or **21**. These compounds are yellow or orange solids that behave as 1 : 1 electrolytes in acetone solutions. Their ¹H NMR spectra show signals from the cyclopentadienyl protons as four multiplets in the ratio 1 : 5 : 1 : 1 for complex **20** and four multiplets in a ratio 2 : 2 : 2 : 2 for **21**. In the ³¹P(¹H) NMR spectra only one resonance appears for the equivalent phosphorus atoms, at -8.9 and -7.6 ppm, respectively.

Synthesis of heteropolynuclear complexes

In the above-mentioned gold(I) complexes, it is noticeable that coordination, with the exception of 9, takes place only through the phosphorus atom. We therefore considered it interesting to study further coordination of some of these complexes to other metal centres in order to obtain heteropolynuclear derivatives. In this manner we attempted the reaction of [Au{Fc- $(SPh)PPh_2_2$ ClO₄ with AgClO₄, which gives the compound $[AuAg{Fc(SPh)PPh_2}_2](ClO_4)_2$ (22) in which the silver atom will be bonded to the sulfur centres. In the ³¹P(¹H) NMR spectrum one strong resonance at 39 ppm is observed and assigned to complex 22 and a weaker resonance at 30.1 also appears. We think that this signal could be attributable to some isomerization process to give the P-Au-S/P-Ag-S isomer (eqn. (2)), although the signal for the phosphorus atom bonded to silver is not observed, probably because of the small amount of this isomer and because Ag-P bonds usually give broad signals. We have tried other reactions of gold complexes with other silver salts, for example the reaction of $[Au(C_6F_5){Fc(SPh)PPh_2}]$ (4) with [Ag(OTf)(PPh₃)] with the idea that the silver atom will coordinate to the free sulfur donor atom in the starting compound. The

result is a mixture of complexes from which we have identified $[Au(C_6F_5)(PPh_3)], [Au\{Fc(SPh)PPh_2\}_2]^+$ (7) and starting material. Also the treatment of [Au(PPh₃){Fc(SPh)PPh₂}]OTf (10) with [Ag(OTf)(PPh₃)] gives complex 19 and [Au(PPh₃)₂]OTf. Therefore, all the reactions aimed at preparing mixed gold-silver complexes have led to a mixture of complexes in which both the homoleptic and heteroleptic species exist. Only in one case could we obtain a pure product and this came from the reaction of $[AuCl{Fc(SePh)PPh_2}]$ (5) with $[PdCl_2(NCPh)_2]$ in a molar ratio of 2: 1 from which the complex [{AuCl{Fc(SePh)PPh₂}}₂PdCl₂] (23) could be isolated. Complex 23 is an air- and moisture-stable red solid that is a non-conductor in acetone solutions. The ¹H NMR spectrum shows three multiplets in a ratio 2:3:3 for the cyclopentadienyl protons and the ³¹P(¹H) spectrum presents only one peak at 28.3 ppm for the two equivalent phosphorus atoms.



Electrochemistry

The electrochemical behaviour of some gold or silver complexes with the ligand Fc(SPh)PPh₂ have been studied by cyclic voltammetry at a platinum electrode in CH2Cl2. The free ligand undergoes a reversible one-electron oxidation process, based on the ferrocene unit, very close to that of ferrocene, 0.53 V. With respect to the ligand, the gold or silver complexes undergo anodic oxidations at higher potentials, as we have observed for other metal complexes. For example the complex $[Au(C_6F_5){Fc(SPh)PPh_2}]$ has a reversible oxidation process at 0.84 V. The silver complexes present a more complicated pattern because of the presence of one or two silver(I) atoms that can be oxidized to Ag^{2+} . Then the complex $[Ag(OTf){Fc(SPh)PPh_2}]$ presents a ferrocene-based reversible oxidation wave at 0.94 V and irreversible oxidation for the silver at 1.2 V. When a further ligand is bonded to silver such as triphenylphosphine as in $[Ag(OTf)(PPh_3){Fc(SPh)PPh_2}]$ there is an anodic displacement for the oxidation of the Ag(I) at 1.66 V, whereas the ferroceneferrocenium oxidation has a similar value, 0.91 V.

Crystal structures

The crystal structures of complexes $[AuCl{Fc(EPh)PPh_2}]$ (E = S (3), Se (5)) have been established by X-ray diffraction studies (Fig. 2 and 3). Selected bond lengths and angles are shown in Tables 1 and 2, respectively. It is noteworthy that the compounds

Table 1	Selected bor	nd lengths	[Å] and	angles [°] for	complex 3
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Au–P	2.2280(9)	P–C(21)	1.827(4)
Au–Cl	2.2939(10)	S–C(36)	1.753(4)
P–C(31)	1.796(4)	S–C(41)	1.767(4)
P-C(11) P-Au-Cl C(31)-P-C(11)	1.750(4) 1.813(4) 176.67(4) 108.31(16)	C(31)–P–Au C(11)–P–Au	110.18(12) 116.94(13)
C(31)–P–C(21)	106.64(17)	C(21)–P–Au	109.50(12)
C(11)–P–C(21)	104.69(17)	C(36)–S–C(41)	102.67(18)

Au–P	2.2220(15)	P-C(21)	1.823(6)
Au–Cl	2.2847(16)	Se-C(1)	1.893(7)
P-C(6)	1.778(6)	Se-C(11)	1.931(6)
P-C(31)	1.813(6)		
P-Au-Cl	176.81(6)	C(6)–P–Au	112.1(2)
C(6) - P - C(31)	106.5(3)	C(31)–P–Au	114.7(2)
C(6) - P - C(21)	104.1(3)	C(21)–P–Au	114.3(2)
C(31) - P - C(21)	104.1(3)	C(1)-Se-C(11)	98.0(3)

 Table 2
 Selected bond lengths [Å] and angles [°] for complex 5



Fig. 2 The structure of complex 3 in the crystal with the atom numbering scheme. Radii are arbitrary. The H atoms are omitted for clarity.



Fig. 3 Structure of complex 5. The H atoms are omitted for clarity.

are not isostructural, although neither compound is a solvate (cf. other homologous pairs below) and both have equivalent molecular structures. The reason could be the differences in the positions of the substituents in the Cp rings: for the sulfur derivative the cyclopentadienyl rings are almost eclipsed (torsion angle about the ring centroid 3.2°) with an angle between both substituents of approximately 72°, whereas for the selenium compound the cyclopentadienyl rings are also practically eclipsed (torsion angle about the ring centroid 5.5°) but the angle between both substituents is approximately 144°. In both complexes the gold atoms display the expected linear geometry with P-Au-Cl angles of 176.67(4) and 176.81(6)°. The Au-P and Au-Cl bond distances are very similar in both complexes, 2.2280(9), 2.2220(16) and 2.2939(10), 2.2847(16) Å and are typical for Cl-Au-P derivatives. There are no short intermolecular Au-Au contacts; the shortest are around 4.8 Å. In complex 5 there are intramolecular $Au \cdots Cl$ and $Au \cdots Se$ contacts around 3.7 Å that lead to the formation of a chain structure (Fig. 4).

The gold atoms are located relatively close to one C–C bond of the cyclopentadienyl group, the distances are 3.309 and 3.498 Å for the sulfur (to C31 and C32, respectively) and 3.327 and 3.623 Å for the selenium derivative (to C6 and C7, respectively). This could indicate the presence of a weak η^2 interaction with the Cp ring, as we have observed in other gold or silver complexes with ferrocene moieties.^{27,28} In the lattice there are several Cl···H or Au···H interactions involving the protons of the phenyl and cyclopentadienyl groups. These contacts range



Fig. 4 One-dimensional chain formed through $Au \cdots Cl$ and $Au \cdots Se$ interactions in complex 5.

from 2.7 to 2.9 Å and are mostly of acceptable linearity to be considered as hydrogen bonds.

The structures of complexes 4 and 6 (which again are not isostructural; 4 is a hexane solvate) have also been confirmed by X-ray diffraction studies and are shown in Figs. 5 and 6, with a selection of bond lengths and angles in Tables 3 and 4, respectively. For complex 6 there are two independent molecules in the asymmetric unit. The gold atoms are again in



Fig. 5 Perspective view of complex 4. The H atoms are omitted for clarity.



Fig. 6 The structure of complex 6 in the crystal, showing the two independent molecules.

Table 3 Selected bond lengths [Å] and angles [°] for complex 4

Au–C(11) Au–P P–C(1) P–C(31)	2.056(6) 2.2701(16) 1.800(6) 1.811(6)	P-C(41) S-C(10) S-C(21)	1.814(6) 1.761(6) 1.782(6)
C(11)-Au-P	177.13(17)	C(1)–P–Au	114.84(19)
C(1)-P-C(31)	105.3(3)	C(31)–P–Au	115.33(19)
C(1)-P-C(41)	103.6(3)	C(41)–P–Au	112.7(2)
C(31)-P-C(41)	103.7(3)	C(10)–S–C(21)	101.8(3)

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 Table 4
 Selected bond lengths [Å] and angles [°] for complex 6

Au(1)–C(21)	2.049(5)	Au(2)–C(71)	2.037(5)
Au(1) - P(1)	2.2773(14)	Au(2)-P(2)	2.2643(15)
Se(1)-C(1)	1.896(7)	Se(2) - C(51)	1.881(6)
Se(1)-C(11)	1.935(6)	Se(2) - C(61)	1.913(6)
P(1) - C(6)	1.797(6)	P(2)-C(56)	1.792(6)
P(1) - C(41)	1.808(6)	P(2)-C(81)	1.807(5)
P(1)–C(31)	1.813(6)	P(2)-C(91)	1.808(6)
C(21)-Au(1)-P(1)	171.17(16)	C(22)-C(21)-Au(1)	120.7(4)
C(1)-Se(1)-C(11)	98.7(3)	C(26)-C(21)-Au(1)	125.8(4)
C(6) - P(1) - Au(1)	112.93(18)	C(71)-Au(2)-P(2)	178.62(16)
C(41) - P(1) - Au(1)	117.99(19)	C(51)-Se(2)-C(61)	99.8(3)
C(31) - P(1) - Au(1)	109.40(18)	C(56) - P(2) - Au(2)	111.82(19)
C(5)-C(1)-Se(1)	126.7(5)	C(81)-P(2)-Au(2)	113.0(2)
C(2)-C(1)-Se(1)	125.3(5)	C(91)-P(2)-Au(2)	115.4(2)
Se(1)-C(1)-Fe(1)	124.6(3)	C(66)-C(61)-Se(2)	123.6(5)
P(1)-C(6)-Fe(1)	127.6(3)	C(62)-C(61)-Se(2)	116.4(5)
C(12)-C(11)-Se(1)	116.6(5)	C(76) - C(71) - Au(2)	121.6(4)
C(16)-C(11)-Se(1)	123.6(5)	C(72)–C(71)–Au(2)	122.8(4)

a linear geometry with C–Au–P angles of 177.13(17)° for the sulfur and 171.17(16)° (somewhat distorted) and 178.62(16)° for the selenium derivative. The Au–C bond distances are 2.056(6), 2.049(5) and 2.037(5) Å, respectively, and are typical for pentafluorophenyl(phosphine) gold(1) complexes. The Au–P bond lengths of 2.2701(16), 2.2773(14) and 2.2643(15) Å are longer than those corresponding to the chloro derivatives, indicating the higher *trans* influence of the pentafluorophenyl group. In the selenium derivative there is one intermolecular short Au–Se contact of 3.643 Å (Fig. 7); this contact is only present for one of the molecules. The cyclopentadienyl rings also display an almost eclipsed geometry in both complexes and the substituents subtend an angle of approximately 144°. In the lattice of both complexes there are several secondary bonds of the type F \cdots H (2.4–2.7 Å) and Au \cdots H (2.8–2.9 Å).



Fig. 7 Perspective view of the Au–Se interaction for one of the independent molecules of complex 6.

The structures of compounds 15 and 16 have been established by X-ray diffraction methods (Figs. 8 and 9, respectively). A selection of bond lengths and angles are shown in Tables 5 and 6, respectively. Yet again, the homologous pair is not isostructural. The structures of these complexes are indeed fundamentally different. First, complex 15 has a dimeric structure with a chelating heterodifunctional ligand and the triflate groups as bridging ligands, whereas compound 16 (for detailed discussion see below) consists of dimeric silver units with bridging heterodifunctional ligands that are further bonded to other dimeric units through bridging triflate ligands, thus leading to a chain structure. Secondly, complex 15 crystallizes as a dichloromethane solvate (ratio 15 : $CH_2Cl_2 = 1/4$).

Complex 15 crystallizes with two independent monomeric formula units, which associate to dimers by inversion symmetry;

Ag-O(1) ^a Ag-O(1) Ag-S(1) P-C(46) P-C(31) P-C(21)	2.4055(15) 2.4172(15) 2.7123(6) 1.801(2) 1.819(2) 1.821(2)	$\begin{array}{c} Ag'-O(1') \\ Ag'-O(1')^b \\ Ag'-S(1') \\ P'-C(146) \\ P'-C(121) \\ P'-C(131) \\ Q'(1) \\ Q'(1)$	2.3905(18) 2.4618(18) 2.7051(6) 1.807(2) 1.823(2) 1.828(2)
S(1) - C(11)	1.767(2) 1.787(2)	S(1') = C(1+1) S(1') = C(1+1)	1.733(2) 1.780(2)
$A_{\sigma}P$	2 3875(6)	$\Delta \sigma' P'$	23798(7)
115 1	2.5075(0)	115 1	2.3790(7)
$P-Ag-O(1)^a$	138.60(4)	P'-Ag'-O(1')	140.65(4)
P-Ag-O(1)	134.71(4)	$P' - Ag' - O(1')^b$	130.38(5)
$O(1)^{a}$ -Ag-O(1)	74.92(6)	$O(1') - Ag' - O(1')^{b}$	78.82(6)
P-Ag-S(1)	108.80(2)	P' - Ag' - S(1')	108.83(2)
$O(1)^a - Ag - S(1)$	88.95(5)	O(1') - Ag' - S(1')	92.61(5)
O(1)-Ag- $S(1)$	98.82(5)	$O(1')^{a}-Ag'-S(1')$	92.86(5)
C(46)–P–Ag	110.42(7)	C(146)–P'–Ag'	110.25(8)
C(31)–P–Ag	117.02(7)	C(121)–P'–Ag'	115.74(8)
C(21)–P–Ag	114.07(8)	C(131)–P'–Ag'	116.63(8)
C(41)-S(1)-Ag	101.43(8)	C(141)-S(1')-Ag'	99.66(8)
C(11)-S(1)-Ag	119.83(8)	C(111)-S(1')-Ag'	116.03(8)
$S(2)-O(1)-Ag^{a}$	122.88(9)	S(2')–O(1')–Ag'	135.99(11)
S(2)-O(1)-Ag	124.12(9)	$S(2')-O(1')-Ag'^{a}$	110.10(10)
$Ag^a - O(1) - Ag$	105.08(6)	$Ag'^{b}-O(1')-Ag'$	101.18(6)

Symmetry transformations used to generate equivalent atoms.^{*a*} -x + 1, -y + 1, -z. ^{*b*} -x + 2, -y, -z + 1.

Table 6	Selected bond	lengths [Å] and	l angles [°] for	complex 16
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$\begin{array}{c} \mathrm{Ag-O(3)^{a}}\\ \mathrm{Ag-P^{b}}\\ \mathrm{Ag-O(1)}\\ \mathrm{Ag-Se}\\ \mathrm{Se-C(1)} \end{array}$	2.414(4) 2.4264(17) 2.558(4) 2.6562(8) 1.902(6)	Se-C(11) P-C(6) P-C(31) P-C(21)	1.945(6) 1.806(6) 1.815(6) 1.830(6)
$O(3)^{a}-Ag-P^{b}$ $O(3)^{a}-Ag-O(1)$ $P^{b}-Ag-O(1)$ $O(3)^{a}-Ag-Se$ $P^{b}-Ag-Se$ O(1)-Ag-Se C(1)-Se-C(11) C(1)-Se-Ag C(6)-P-C(21) C(6)-P-C(21) $C(6)-P-Ag^{b}$ $C(31)-P-Ag^{b}$	118.21(11) 81.11(13) 115.38(10) 105.14(10) 127.11(5) 99.21(9) 100.5(3) 110.48(17) 99.3(2) 107.9(3) 100.7(3) 100.7(3) 105.5(3) 112.7(2) 112.4(2)	$\begin{array}{c} C(21)-P-Ag^b\\ C(5)-C(1)-Se\\ C(2)-C(1)-Se\\ C(10)-C(6)-P\\ C(7)-C(6)-P\\ C(16)-C(11)-Se\\ C(12)-C(11)-Se\\ C(26)-C(21)-P\\ C(22)-C(21)-P\\ C(32)-C(31)-P\\ C(36)-C(31)-P\\ S-O(1)-Ag\\ S-O(3)-Ag^a \end{array}$	116.72(19) 128.2(4) 123.9(5) 123.8(5) 130.0(4) 119.9(5) 120.5(5) 118.5(4) 122.6(5) 117.7(5) 123.1(5) 115.9(2) 133.1(2)

Symmetry transformations used to generate equivalent atoms.^{*a*} -x, -y + 1, $-z + 2^{b} - x + 1$, -y + 1, -z + 2.



Fig. 8 Structure of complex 15; one crystallographically independent dimer.

in both the overall bonding scheme is very similar (except for the orientation of the triflate ions, with Ag–O–S–C 142 or -98°) and consequently we will only discuss one of the molecules. The silver



Fig. 9 Molecular structure of complex 16.

centres display a distorted tetrahedral geometry, being bridged by the two oxygen atoms of the triflate ligands and chelated by the heterofunctional P,S ligand. The most regular angle is P– Ag–S(1) 108.80(2)°, with the angles O(1)–Ag–O(1)# (#: -x +1, -y + 1, -z) 74.92(6)° and P–Ag–O(1) 134.71(4)° furthest from ideal values.

The Ag–P distance of 2.3875(6) Å is slightly shorter than those found in other tetra-coordinated silver complexes such as $[Ag(dppe)_2]NO_3$ (dppe = bis(diphenylphosphino)ethane)²⁹ with distances in the range 2.488(3) to 2.527(3) Å. The Ag–S distance, 2.7123(6) Å, is considerably longer than those found in the silver compound $[Ag(OTf){Fc(SPh)_2}]_2$ (2.5037(8) and 2.5558(8) Å),^{26e} with a similar dimeric structure, and indicates a weaker bond. The Ag–O distances of 2.4055(15) and 2.4172(15) Å correspond to medium strength bonds.

The structure of complex 16 is a chain polymer consisting of linked rings. The asymmetric unit corresponds to the fragment $[Ag(OTf){Fc(SePh)PPh_2}]$, which gives rise to a dimer via an inversion centre, whereby the heterodifunctional ligands bridge both silver centres. The silver atom is bonded to one oxygen atom (O1) of the triflate anion within this first dimer, and also to a further oxygen (O3, generated via a second inversion centre). The triflates thus act as bridging ligands between silver centres, leading to eight-membered rings (Ag-O-S-O)2 and finally to the chain polymer (Fig. 10). The geometry around the silver centre is again distorted tetrahedral with angles P#2-Ag-Se 127.11(5)°, P#2-Ag-O(1) 115.38(10)°, O(1)-Ag-Se 99.21(9)° and O(3)#1-Ag–O(1) 81.11(13)° (#1 –x, –y + 1, –z + 2; #2 – x + 1, –y + 1, -z + 2). The Ag–Se distance is 2.6562(8) Å and is similar to those found in the complex [Ag(OTf){Fc(SePh)₂}] (2.5888(4) and 2.6339(3) Å), which has a dimeric structure with a bridging triflate ligand.26e The Ag-O distances are somewhat dissimilar, 2.414(4) and 2.558(4) Å, indicating a weaker bond to the triflate group within the asymmetric unit.



Fig. 10 Structure of the chain polymer of complex 16.

We have also established the crystal structure of compounds **18** and **19**, which are shown in Figs. 11 and 12, respectively. A selection of bond lengths and angles can be seen in Tables 7 and 8.

Table 7 Selected bond lengths [Å] and angles [°] for complex 18

Ag-P(2)	2.4424(6)	Ag–S(1)	2.6741(6)
Ag-P(1)	2.4656(6)	S(1)–C(6)	1.761(2)
Ag-O(1)	2.506(2)	S(1)–C(11)	1.785(2)
P(2)-Ag-P(1)	128.09(2)	C(21)-P(1)-Ag	116.53(7)
P(2)-Ag-O(1)	121.72(6)	C(41)-P(2)-Ag	111.23(7)
P(1)-Ag-O(1)	86.98(6)	C(51)-P(2)-Ag	122.71(7)
P(2)-Ag-S(1)	115.760(19)	C(61)-P(2)-Ag	107.90(7)
P(1)-Ag-S(1)	105.447(18)	C(6)-S(1)-C(11)	103.43(11)
O(1)-Ag-S(1)	89.83(6)	C(6)-S(1)-Ag	107.69(7)
C(1)-P(1)-Ag	111.94(7)	C(11)-S(1)-Ag	106.29(7)
C(31)-P(1)-Ag	114.05(7)	S(2)-O(1)-Ag	139.15(17)

Table 8 Selected bond lengths [Å] and angles [°] for complex 19

Ag(1)–P(2) Ag(1)–P(1) Ag(1)–O(1)	2.4141(13) 2.4208(13) 2.541(4)	Ag(1)–Se(1) Se(1)–C(10) Se(1)–C(11)	2.8566(7) 1.895(5) 1.922(5)
$\begin{array}{l} P(2)-Ag(1)-P(1) \\ P(2)-Ag(1)-O(1) \\ P(1)-Ag(1)-O(1) \\ P(2)-Ag(1)-Se(1) \\ P(1)-Ag(1)-Se(1) \\ P(1)-Ag(1)-Se(1) \end{array}$	144.05(5) 112.44(12) 93.66(12) 103.25(4) 107.17(4)	O(1)-Ag(1)-Se(1) C(10)-Se(1)-C(11) C(10)-Se(1)-Ag(1) C(11)-Se(1)-Ag(1)	75.30(10) 100.2(2) 101.19(15) 114.17(15)



Fig. 11 Perspective view of complex 18 in the crystal.



Fig. 12 The structure of complex 19 in the crystal.

Both compounds are simple monomers. For complex **18** the triflate ligand is disordered over two positions, but the second position is only occupied to the extent of 15%. In both complexes the geometry around the silver centre is distorted tetrahedral.

The most regular angle is the bite angle of the heterofunctional ligand, P(1)–Ag–S(1) 105.447(18)° and P(1)–Ag–Se(1) 107.17(4) Å and the most irregular corresponds to the P–Ag–P angles of 128.09(2) and 144.09(4) Å, respectively.

The distance Ag-S is 2.6741(6) Å and Ag-Se is 2.8595(6) Å, which are rather long compared with other more regularly tetra-coordinated silver derivatives, indicating only a weak bond. The cyclopentadienyl rings are almost staggered and the substituents are located in opposite directions with an angle of approximately 72°.

Conclusions

The synthesis of the unsymmetrical ligands Fc(EPh)PPh₂ (E = S, Se) and coordination studies to group 11 metal compounds is described. These heterodifunctional ligands posses two donor atoms P,S or P,Se with different coordination capabilities. This can be seen in the complexes obtained with the three metals; gold predominantly coordinates through the phosphorus atom except when a weak ligand is displaced, as in the reaction with the gold(I) derivative $[Au(tht)_2]ClO_4$ (1 : 1) or with the gold(III) complex $[Au(C_6F_5)_2(OEt_2)_2]ClO_4$ to give $[Au_2{Fc(SPh)PPh_2}_2](ClO_4)_2$ and $[Au(C_6F_5)_2{Fc(SePh)PPh_2}]ClO_4$, respectively. The greater tendency of silver(I) and copper(I) to give complexes with high coordination numbers produces complexes with coordination to both phosphorus and chalcogen atoms. Four pairs of homologous compounds have been characterized by X-ray diffraction, but surprisingly not a single pair is isotypic. In many of the complexes a supramolecular structure is formed through secondary bonds such as $Au \cdots H$, $F \cdots H$ hydrogen bonds and $Au \cdots Cl$ or $Au \cdots Se$ interactions.

Although the gold(I) complexes are suitable precursors for the synthesis of heteropolynuclear compounds, the reaction with other metallic centers occurs but in most of the cases leads to a mixture of compounds, with the exception of the gold–silver derivative $[AuAg{Fc(SPh)PPh_2}_2](ClO_4)_2$ or the gold–palladium species complex $[{AuCl{Fc(SePh)PPh_2}}_2]_2PdCl_2]$.

Experimental

Instrumentation

Infrared spectra were recorded in the range 4000–200 cm⁻¹ on a Perkin-Elmer 883 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured in ca. 5 \times 10⁻⁴ mol dm⁻³ solutions with a Philips 9509 conductimeter. C, H and S analyses were carried out with a Perkin-Elmer 2400 microanalyzer. Mass spectra were recorded on a VG Autospec, with the liquid secondary-ion mass spectra (LSIMS) technique, using nitrobenzyl alcohol as matrix. NMR spectra were recorded on a Varian Unity 300 spectrometer, a Bruker ARX 300 spectrometer in CDCl₃ (otherwise stated). Chemical shifts are cited relative to SiMe₄ (¹H, external), 85% H₃PO₄ (³¹P, external) and CFCl₃ (¹⁹F, external). Cyclic voltammetric experiments were performed employing an EG & PARC model 273 potentiostat. A three-electrode system was used, which consists of a platinum disk working electrode. The measurements were carried out in CH_2Cl_2 solutions with 0.1 mol dm⁻³ Bu₄NPF₆ as a supporting electrolyte. Under the present experimental conditions, the ferrocenium-ferrocene couple was located at 0.47 V vs. SCE.

Materials

The starting materials FcPPh,³⁰ [AuCl(tht)],³¹ [Au(C₆F₅)(tht)],³¹ [Au(tht)₂]ClO₄,³² [Au(C₆F₅)₃(OEt₂)],³³ [Au(C₆F₅)₂(OEt₂)₂]ClO₄,³³ [Ag(OTf)(PPh₃)]³⁴ and [PdCl₂(NCPh)₂]³⁵ were prepared by published procedures. [Au(OTf)(PPh₃)] was prepared from [AuCl(PPh₃)]³⁶ by reaction with AgOTf in dichloromethane.

Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.

Synthesis

Synthesis of [Fc(EPh)PPh₂] (E = S (1), Se (2)). To a solution of FcPPh₂ (0.292 g, 1 mmol) in diethyl ether (20 mL) at 0 °C was added dropwise PhLi (0.55 ml, 1 mmol). After 1 h of reaction, PhSSPh (0.218 g, 1 mmol) or PhSeSePh (0.312 g, 1 mmol) was added and the mixture was stirred for 24 h at room temperature. The solutions were washed with water and the organic phase dried over Na₂SO₄. Evaporation of the solvent gave a residue that was chromatographed over alumina using hexane : diethyl ether (4 : 1) as eluent. The first band corresponds to compounds 1 or **2**, respectively. Compound 1: Yield 56%. Compound **2**: Yield: 51%. $\Lambda_{\rm M}$ 1.3 Ω^{-1} cm² mol⁻¹. Elemental analysis (%), Found: C, 63.54; H, 4.03. Calc. for C₂₈H₂₃FeO₃PSe: C, 64.00; H, 4.38. NMR data. ¹H, δ : 4.03 (m, 2H, C₅H₄), 4.14 (m, 2H, C₅H₄), 4.28 (m, 2H, C₅H₄), 4.40 (m, 2H, C₅H₄), 7.06–7.45 (m, 15H, Ph). ³¹P(¹H), δ : -17.0 (s, 1P, PPh₂) ppm.

Synthesis of $[AuX{Fc(EPh)PPh_2}]$ (E = S, X = Cl (3), C_6F_5 (4);), (E = Se, X = Cl (5), C_6F_5 (6). To a solution of [Fc(SPh)PPh₂] (0.048 g, 0.1 mmol) or [Fc(SePh)PPh₂] (0.053 g, 0.1 mmol) in 20 mL of dichloromethane was added to the corresponding amount of [AuCl(tht)] (0.032 g, 0.1 mmol) or $[Au(C_6F_5)(tht)]$ (0.045 g, 0.1 mmol) and the mixture stirred for 15 min. The solution was concentrated to ca. 5 mL and addition of hexane (10 mL) gave complexes 3, 4, 5 or 6 as yelloworange solids. Complex 3: yield 89%. Λ_M 3.1 Ω^{-1} cm² mol⁻¹. Elemental analysis (%), Found: C, 47.20; H, 3.40; S, 4.68. Calc. for C₂₈H₂₃AuClFePS: C, 47.31; H, 3.26; S, 4.51. NMR data. ¹H, *δ*: 4.39 (m, 2H, C₅H₄), 4.45 (m, 4H, C₅H₄), 4.67 (m, 2H, C₅H₄), 7.10–7.68 (m, 15H, Ph). ³¹P(¹H), δ : 28.1 (s, 1P, PPh₂) ppm. Complex 4: yield 87%. Λ_M 1.5 Ω^{-1} cm² mol⁻¹. Elemental analysis (%), Found: C, 48.84; H, 2.75; S, 3.95. Calc. for C₃₄H₂₃AuF₅FePS: C, 48.47; H, 2.75; S, 3.80. NMR data. ¹H, δ : 4.46 (m, 4H, C₅H₄), 4.54 (m, 2H, C₅H₄), 4.65 (m, 2H, C₅H₄), 6.95–7.77 (m, 15H, Ph). ³¹P(¹H), δ: 37.7 (s, 1P, PPh₂) ppm. ¹⁹F, δ: -116.4 (m, 2F, o-F), -158.8 (t, 1F, p-F, ³J(FF) 19.6 Hz), -162.6 (m, 2F, m-F). Complex 5: yield 89%. Λ_M 3.8 Ω^{-1} cm² mol⁻¹. Elemental analysis (%), Found: C, 43.96; H, 3.03. Calc. for C₂₈H₂₃AuClFePSe: C, 44.38; H, 3.05. NMR data. ¹H, δ : 4.03 (m, 8H, C₅H₄), 7.05–7.58 (m, 15H, Ph). ³¹P(¹H), δ : 27.2 (s, 1P, PPh₂) ppm. Complex 6: yield 68%. $\Lambda_M 0.8 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. Elemental analysis (%), Found: C, 45.51; H, 2.50. Calc. for $C_{34}H_{23}AuF_5FePSe: C, 45.92; H, 2.60. NMR data. {}^{1}H, \delta: 4.38$ (m, 4H, C₅H₄), 4.43 (m, 2H, C₅H₄), 4.56 (m, 2H, C₅H₄), 7.08-7.62 (m, 15H, Ph). ${}^{31}P({}^{1}H)$, δ : 27.2 (s, 1P, PPh₂) ppm. ${}^{19}F$, δ : -117.0 (m, 2F, o-F), -159.5 (t, 1F, p-F, ³J(FF) 20 Hz, -163.4 (m, 2F, *m*-F).

Synthesis of $[Au{Fc(EPh)PPh_2}_2]cIO_4$ (E = S (7), Se(8)). To a solution of $[Fc(SPh)PPh_2]$ (0.096 g, 0.2 mmol) or $[Fc(SePh)PPh_2]$ (0.106 g, 0.2 mmol) in 20 mL of dichloromethane was added $[Au(tht)_2]CIO_4$ (0.047 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 7 or 8 as yellow or orange solids, respectively. Complex 7: yield 80%. Λ_M 101.4 Ω^{-1} cm² mol⁻¹. Elemental analysis (%), Found: C, 53.48; H, 3.54; S, 4.95. Calc. for $C_{56}H_{46}AuCIFe_2O_4P_2S_2$: C, 53.67; H, 3.70; S, 5.11. NMR data. ¹H, δ : 4.23 (m, 2H, C_5H_4), 4.36 (m, 2H, C_5H_4), 4.47 (m, 2H, C_5H_4), 5.79 (m, 2H, C_5H_4), 6.65– 7.81 (m, 30H, Ph). ³¹P(¹H), δ : 40.1 (s, 2P, PPh₂) ppm. Complex 8: yield 82%. Λ_M 97.1 Ω^{-1} cm² mol⁻¹. Elemental analysis (%), Found: C, 49.49; H, 3.63. Calc. for $C_{56}H_{46}AuCIFe_2O_4P_2Se_2$: C, 49.93; H, 3.44. NMR data. ¹H, δ : 4.84 (m, 8H, C_5H_4), 5.12 (m, 8H, C₅H₄), 6.71–7.58 (m, 30H, Ph). ³¹P(¹H), δ : 37.5 (s, 2P, PPh₂) ppm.

Synthesis of $[Au_2{Fc(SPh)PPh_2}](ClO_4)_2$ (9). To a solution of $[Fc(SPh)PPh_2]$ (0.096 g, 0.2 mmol) in 20 mL of dichloromethane was added $[Au(tht)_2]ClO_4$ (0.094 g, 0.2 mmol) and the mixture was stirred for 15 min. Concentration of the solution to *ca*. 5 mL and addition of diethyl ether (10 mL) gave complex **9** as a yellow solid. Yield 76%. Λ_M 187.2 Ω^{-1} cm² mol⁻¹. Elemental analysis (%), Found: C, 43.65; H, 3.05; S, 4.34. Calc. for $C_{56}H_{46}Au_2Cl_2Fe_2O_8P_2S_2$: C, 43.40; H, 2.99; S, 4.13. NMR data. ¹H, δ : 4.2–4.8 (m, br, 16H, C_5H_4), 7.1–7.8 (m, 30H, Ph). ³¹P(¹H), δ : 38.3 (s, 2P, PPh₂, head to head isomer), 27.6 (s, 2P, PPh₂, head-to-tail isomer) ppm.

Synthesis of $[Au(PPh_3){Fc(SPh)PPh_2}]OTf (10)$. To a solution of $[Fc(SPh)PPh_2]$ (0.048 g, 0.1 mmol) in 20 mL of dichloromethane was added $[Au(OTf)(PPh_3)]$ (0.061 g, 0.1 mmol) and the mixture was stirred for 15 min. Concentration of the solution to *ca*. 5 mL and addition of diethyl ether (10 mL) gave complex **10** as a yellow solid. Yield 83%. NMR data. ¹H, δ : 4.25 (m, 2H, C₅H₄), 4.39 (m, 2H, C₅H₄), 4.43 (m, 2H, C₅H₄), 4.82 (m, 2H, C₅H₄), 7.1–7.8 (m, 30H, Ph). ³¹P(¹H), δ : 42.7 (AB system, 2P, PPh₂ + PPh₃, *J*(AB) 334) ppm.

Synthesis of $[Au(C_6F_5)_3{Fc(EPh)PPh_2}]$ (E = S (11), Se(12)). To a solution of [Fc(SPh)PPh₂] (0.048 g, 0.1 mmol) or [Fc(SePh)PPh₂] (0.053 g, 0.1 mmol) in 20 mL of dichloromethane was added [Au(C_6F_5)₃(tht)] (0.078 g, 0.1 mmol) and the mixture was stirred for 30 min. Concentration of the solution to ca. 5 mL and addition of hexane (10 mL) gave complexes 11 or 12 as yellow or orange solids, respectively. Complex 11: yield 75%. Λ_M 1.4 Ω^{-1} cm² mol⁻¹. Elemental analysis (%), Found: C, 46.61; H, 1.99; S, 2.79. Calc. for $C_{46}H_{23}AuF_{15}FePS: C, 46.96; H, 1.97; S, 2.72. NMR data. {}^{1}H, \delta:$ 4.04 (m, 2H, C5H4), 4.07 (m, 2H, C5H4), 4.19 (m, 2H, C5H4), 4.47 (m, 2H, C₅H₄), 6.96–7.80 (m, 15H, Ph). ${}^{31}P({}^{1}H)$, δ : 15.8 (s, 1P, PPh₂) ppm. ¹⁹F NMR, δ: -122.0 (m, 2F, o-F), -120.1 (m, 4F, o-F), -158.2 [t, 2F, p-F, ³J(FF) 19.8 Hz], -157.8 [t, 1F, p-F, ³J(FF) 19.9 Hz], -161.7 (m, 2F, m-F), -161.4 (m, 4F, m-F). Complex 12: yield 65%. Λ_M 4.5 Ω^{-1} cm² mol⁻¹. Elemental analysis (%), Found: C, 44.94; H, 1.81. Calc. for C₄₆H₂₃AuF₁₅FePSe: C, 45.16; H, 1.89. NMR data. ¹H, δ : 4.01 (m, 4H, C₅H₄), 4.20 (m, 2H, C_5H_4), 4.43 (m, 2H, C_5H_4), 7.50–7.80 (m, 15H, Ph). ³¹P(¹H), δ : 15.9 (s, 1P, PPh₂) ppm. ¹⁹F NMR, δ : -122.5 (m, 2F, o-F), -120.7 (m, 4F, o-F), -158.8 [t, 2F, p-F, ³J(FF) 19 Hz], -158.5 [t, 1F, p-F, ³J(FF) 20 Hz], -162.4 (m, 2F, m-F), -162.1 (m, 4F, *m*-F).

Synthesis of $[Au_2(C_6F_5)_6{Fc(SePh)PPh_2}]$ (13). To a solution of [Fc(SePh)PPh₂] (0.053 g, 0.1 mmol) in 20 mL of dichloromethane was added [Au(C₆F₅)₃(OEt₂)] (0.154 g, 0.2 mmol) and the mixture was stirred for 30 min. Concentration of the solution to ca. 5 mL and addition of hexane (10 mL) gave complexes 13 as an orange solid. Yield 71%. Λ_M 2.1 Ω^{-1} cm² mol⁻¹. Elemental analysis (%), Found: C, 40.38; H, 1.32. Calc. for $C_{64}H_{23}Au_2F_{30}$ FePSe: C, 40.0; H, 1.20. NMR data. ¹H, δ : 3.71 (m, 1H, C₅H₄), 3.93 (m, 1H, C₅H₄), 4.01 (m, 2H, C₅H₄), 4.05 (m, 2H, C₅H₄), 4.11 (m, 2H, C₅H₄), 7.1–7.77 (m, 15H, Ph). ³¹P(¹H), δ: 14.6 (s, 1P, PPh₂) ppm. ¹⁹F NMR, δ: -122.5 (m, 1F, o-F), -122.2 (m, 1F, o-F), -121.5 (m, 2F, o-F), -120.1 (m, 2F, o-F), -157.5 [t, 2F, p-F, ³J(FF) 19.0 Hz], -157.4 [t, 1F, p-F, ³*J*(FF) 20.0 Hz], -155.9 [t, 1F, *p*-F, ³*J*(FF) 19.1 Hz], -155.6 [t, 2F, p-F, ³J(FF) 19.0 Hz], -161.4 (m, 1F, m-F), -161.1 (m, 2F, *m*-F), -160.8 (m, 1F, *m*-F), -160.2 (m, 2F, *m*-F).

Synthesis of $[Au(C_6F_5)_2{Fc(SePh)PPh_2}]ClO_4$ (14). To a solution of $[Fc(SePh)PPh_2]$ (0.053 g, 0.1 mmol) in 20 mL of dichloromethane was added a solution of $[Au(C_6F_5)_2(OEt_2)_2]ClO_4$ (0.077 g, 0.1 mmol) in diethyl ether and the mixture was stirred for 30 min. Concentration of the solution to *ca.* 5 mL and addition of hexane (10 mL) gave complex **14** as an orange solid. Yield 62%. $\Lambda_{\rm M}$ 136 Ω⁻¹ cm² mol⁻¹. Elemental analysis (%), Found: C, 41.90; H, 2.15. Calc. for C₄₀H₂₃AuClF₁₀FeO₄PSe: C, 41.56; H, 2.00. NMR data. ¹H, δ : 4.63 (m, 1H, C₅H₄), 4.95 (m, 1H, C₅H₄), 5.01 (m, 1H, C₅H₄), 5.07 (m, 1H, C₅H₄), 5.13 (m, 1H, C₅H₄), 5.25 (m, 2H, C₅H₄), 5.33 (m, 1H, C₅H₄), 7.1–7.87 (m, 15H, Ph). ³¹P(¹H), δ : 33.4 (s, 1P, PPh₂) ppm. ¹⁹F NMR, δ : –124.3 (m, 1F, *o*-F), –123.0 (m, 1F, *o*-F), –122.3 (m, 1F, *o*-F), –121.1 (m, 1F, *o*-F), –154.7 [t, 1F, *p*-F, ³*J*(FF) 19.0 Hz], –157.9 (m, 1F, *m*-F), –158.3 (m, 1F, *m*-F), –158.7 (m, 1F, *m*-F).

Synthesis of $[Ag(OTf){Fc(EPh)PPh_2}]$ (E = S (15), Se(16)). To a solution of [Fc(SPh)PPh2] (0.096 g, 0.2 mmol) or [Fc(SePh)PPh₂] (0.106 g, 0.2 mmol) in 20 mL of dichloromethane was added [Ag(OTf)] (0.052 g, 0.2 mmol) and the mixture was stirred for 30 min. Concentration of the solution to ca. 5 mL and addition of diethyl ether (10 mL) gave complexes 15 or 16 as yellow or orange solids, respectively. Complex 15: yield 71%. Λ_M 4.5 Ω^{-1} cm² mol⁻¹. Elemental analysis (%), Found: C, 46.88; H, 3.46; S, 7.97. Calc. for C₂₉H₂₃AgF₃FeO₃PS₂: C, 47.37; H, 3.15; S, 8.72. NMR data. ¹H, δ: 4.33 (m, 4H, C₅H₄), 4.53 (m, 2H, C₅H₄), 4.64 (m, 2H, C₅H₄), 7.0–7.8 (m, 15H, Ph). ³¹P(¹H), -55 °C, δ: 5.2 (2d, 1P, PPh₂, J(¹⁰⁹AgP) 755, J(¹⁰⁷AgP) 657 Hz) ppm. Complex 16: yield 83%. Λ_{M} 1.6 Ω^{-1} cm² mol⁻¹. Elemental analysis (%), Found: C, 44.18; H, 3.02; S, 4.22. Calc. for C₂₉H₂₃AgF₃FeO₃PSSe: C, 44.53; H, 2.96; S, 4.09. NMR data. 1 H, δ : 4.51 (m, 4H, C₅H₄), 4.77 (m, 4H, C₅H₄), 7.4–7.6 (m, 15H, Ph). ³¹P(¹H), -55 °C, δ: 4.1 (2d, 1P, PPh₂, J(¹⁰⁹AgP) 695, J(¹⁰⁷AgP) 608 Hz) ppm.

Synthesis of [Ag{Fc(SPh)PPh₂}₂]OTf (17). To a solution of [Fc(SPh)PPh₂] (0.096 g, 0.2 mmol) in 20 mL of dichloromethane was added [Ag(OTf)] (0.026 g, 0.1 mmol) and the mixture was stirred for 30 min. Concentration of the solution to *ca*. 5 mL and addition of diethyl ether (10 mL) gave complexes 17 as a yellow solid. Yield 81%. $\Lambda_{\rm M}$ 101 Ω^{-1} cm² mol⁻¹. Elemental analysis (%), Found: C, 56.26; H, 3.51; S, 7.60. Calc. for C₅₇H₄₆AgF₃Fe₂O₃P₂S₃: C, 56.40; H, 3.82; S, 7.92. NMR data. ¹H, δ : 4.20 (m, 2H, C₅H₄), 4.23 (m, 2H, C₅H₄), 4.28 (m, 2H, C₅H₄), 4.50 (m, 2H, C₅H₄), 7.0–7.5 (m, 30H, Ph). ³¹P(¹H), -55 °C, δ : 0.94 (2d, 1P, PPh₂, $J(^{109}\text{AgP})$ 471.3, $J(^{107}\text{AgP})$ 410.4 Hz) ppm.

Synthesis of $[Ag(OTf)(PPh_3){Fc(EPh)PPh_2}]$ (E = S (18), Se(19)). To a solution of $[Fc(SPh)PPh_2]$ (0.048 g, 0.1 mmol) or [Fc(SePh)PPh₂] (0.053 g, 0.1 mmol) in 20 mL of dichloromethane was added the corresponding amount of [Ag(OTf)(PPh₃)] (0.052 g, 0.1 mmol) and the mixture was stirred for 30 min. Concentration of the solution to ca. 5 mL and addition of diethyl ether (10 mL) gave complexes 18, or 19 as yellow-orange solids. Complex 18: yield 83%. $\Lambda_{\rm M}$ 15.2 Ω^{-1} cm² mol⁻¹. Elemental analysis (%), Found: C, 56.88; H, 4.21; S, 6.12. Calc. for C₄₇H₃₈AgF₃FeO₃P₂S₂: C, 56.58; H, 3.83; S, 6.21. NMR data. ¹H, δ : 4.26 (m, 4H, C₅H₄), 4.3 3 (m, 2H, C₅H₄), 4.52 (m, 2H, C₅H₄), 6.9–7.5 (m, 30H, Ph). ³¹P(¹H), AB system, broad, δ_A , 7.9, δ_B , 3.0 ppm, J_{AB} 127, $J^{109}AgP \sim 522$, $J^{107}AgP$ ~ 453 Hz. Complex 19: yield 72%. Λ_M 10.5 Ω^{-1} cm² mol⁻¹. Elemental analysis (%), Found: C, 53.64; H, 3.66; S, 2.68. Calc. for C₄₇H₃₈AgF₃FeO₃P₂SSe: C, 54.04; H, 3.66; S, 3.07. NMR data. ¹H, *δ*: 4.45 (m, 2H, C₅H₄), 4.60 (m, 2H, C₅H₄), 4.80 (m, 2H, C_5H_4), 4.86 (m, 2H, C_5H_4), 6.9–7.8 (m, 30H, Ph). ³¹P(¹H), AB system, δ_A , 11.5, δ_B , 5.2 ppm, J_{AB} 109, J^{109} AgP 500, J^{107} AgP 435 Hz.

Synthesis of $[Cu{Fc(EPh)PPh_2]_2]PF_6$ (E = S (20), Se(21)). To a solution of $[Fc(SPh)PPh_2]$ (0.096 g, 0.2 mmol) or $[Fc(SePh)PPh_2]$ (0.106 g, 0.2 mmol) in 20 mL of dichloromethane was added $[Cu(NCMe)_4]PF_6$ (0.037 g, 0.1 mmol) and the mixture was stirred for 30 min. Concentration of the solution to *ca*. 5 mL and addition of diethyl ether (10 mL) gave complexes **20**, or **21** as yellow–orange solids. Complex **20**: yield 80%. Λ_{M} 98 Ω^{-1} cm² mol⁻¹. Elemental analysis (%), Found: C, 57.63; H, 4.21; S, 5.62. Calc. for $C_{56}H_{46}CuF_6Fe_2P_3S_2$: C, 57.72; H, 3.98; S, 5.50. NMR data. ¹H, δ : 3.70 (m, 1H, C_5H_4), 4.00 (m, 1H, C_5H_4), 4.43 (m, 5H, C_5H_4), 4.65 (m, 1H, C_3H_4), 7.1–7.5 (m, 30H, Ph). ³¹P(¹H), δ : –8.9 (s, 2P, PPh₂) ppm. Complex **21**: yield 83%. Λ_M 106 Ω^{-1} cm² mol⁻¹. Elemental analysis (%), Found: C, 53.42; H, 3.65. Calc. for $C_{56}H_{46}CuF_6Fe_2P_3Se_2$: C, 53.42; H, 3.68. NMR data. ¹H, δ : 3.79 (m, 2H, C_5H_4), 4.26 (m, 2H, C_5H_4), 4.33 (m, 2, C_5H_4), 4.46 (m, 1H, C_5H_4), 7.1–7.5 (m, 30H, Ph). ³¹P(¹H), δ : –7.6 (s, 2P, PPh₂) ppm.

Synthesis of [AuAg{Fc(SPh)PPh₂}₂](ClO₄)₂ (22). To a solution of [Au{Fc(SPh)PPh₂}₂]ClO₄ (0.125 g, 0.1 mmol) in 20 mL of dichloromethane was added AgClO₄ (0.021 g, 0.1 mmol) and the mixture was stirred for 30 min. Concentration of the solution to *ca*. 5 mL and addition of diethyl ether (10 mL) gave complexes 22 as a yellow solid. Yield 81%.%. $\Lambda_{\rm M}$ 153 Ω^{-1} cm² mol⁻¹. Elemental analysis (%), Found: C, 46.45; H, 3.36; S, 4.48. Calc. for C₅₆H₄₆AuAgCl₂Fe₂O₄P₂S₂: C, 46.05; H, 3.17; 4.39. NMR data. ¹H, δ : 5.04 (br, m, 4H, C₅H₄), 5.26 (br, m, 4H, C₅H₄), 6.7–7.5 (m, 30H, Ph). ³¹P(¹H), δ : 39.09 (s, 2P, PPh₂, head to head isomer, 97%), 30 (s, 2P, PPh₂, head to tail isomer, 3%) ppm.

Synthesis of $[Au_2PdCl_4{Fc(EPh)PPh_2}_2]$ (23). To a solution of $[Fc(SePh)PPh_2]$ (0.106 g, 0.2 mmol) in 20 mL of dichloromethane was added a solution of $[PdCl_2(NCPh)_2]$ (0.038 g, 0.1 mmol) and the mixture was stirred for 30 min. Concentration of the solution to *ca*. 5 mL and addition of hexane (10 mL) gave complex **23** as an orange solid. Yield 87%. $\Lambda_M 1.8 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. Elemental analysis (%), Found: C, 39.49; H, 2.60. Calc. for $C_{56}H_{46}Au_2Cl_4Fe_2P_2PdSe_2$: C, 39.73; H, 2.74. NMR data. ¹H, δ : 4.46 (m, 3H, C₅H₄), 4.52 (m, 3H, C₃H₄), 4.81

(m, 2H, C₅H₄), 7.4–7.7 (m, 30H, Ph). ${}^{31}P({}^{1}H)$, δ : 28.3 (s, 2P, PPh₂) ppm.

Crystal structure determinations

Data were registered on a Siemens STOE AED-2 (4), Bruker SMART 1000 CCD (3, 15, 18) or Bruker SMART APEX (5, 6, 16, 19) diffractometer. The crystals were mounted in inert oil on glass fibres and transferred to the cold gas stream of the corresponding diffractometer. Data were collected using monochromated MoK α radiation ($\lambda = 0.71073$ Å) in ω -scan mode or ω and ϕ -scans (3, 15, 18). An absorption correction was applied on the basis of ϕ -scans for 4 and of indexed faces for 3, 15 and 18; otherwise the program SADABS, based on multiple scans, was used. The structures were solved by direct methods and refined on F^2 using the program SHELXL-97.³⁷ All non-hydrogen atoms were refined anisotropically (with the exception of solvent of 4). Hydrogen atoms were included using a riding model.

Special features of refinement. For **3** the Flack parameter was refined to -0.015(4). For complex **4** extensive regions of badly resolved residual electron density could not be clearly identified as disordered solvent molecules, so the main peaks were refined as partially occupied carbons. For the calculation of composition, *etc.*, the solvent content was estimated as half a hexane molecule per asymmetric unit. For **15** and **18** the asymmetric unit contains a dichloromethane molecule disordered over an inversion centre. In **18** the triflate group is disordered over two sites in the ratio 85 : 15. Suitable similarity restraints were used to ensure stability of refinement. Further crystal data are given in Tables 9 and 10.

CCDC reference numbers 272428–272435.

See http://dx.doi.org/10.1039/b507058a for crystallographic data in CIF or other electronic format.

Table 9 X-Ray data for complexes 3, 4, 5 and 6

Compound	3	$4 \cdot 1/2C_6H_{14}$	5	6
Formula	C28H23AuClFePS	C37H30AuF5FePS	C28H23AuClFePSe	C ₃₄ H ₂₃ AuF ₅ FePSe
$M_{ m r}$	710.76	885.46	757.66	889.27
Habit	Yellow plate	Yellow prism	Orange plate	Orange prism
Crystal size (mm)	$0.18 \times 0.13 \times 0.08$	$0.49 \times 0.27 \times 0.23$	$0.28 \times 0.12 \times 0.04$	$0.32 \times 0.26 \times 0.15$
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_{1}2_{1}2_{1}$	C2/c	$P2_{1}/c$	P(-1)
Cell constants:				
a/Å	9.1540(8)	31.212(6)	10.0410(7)	11.7891(5)
b/Å	10.6559(8)	12.970(3)	22.0090(15)	14.7442(6)
c/Å	25.390(2)	22.518(5)	11.8345(8)	18.4764(8)
a/°	90	90	90	73.385(1)
β/°	90	132.70(3)	106.220(1)	84.788(1)
y/°	90	90	90	76.932(1)
$V/Å^3$	2476.6(3)	6699(3)	2511.2(3)	2996.6(2)
Z	4	8	4	4
$D_{\rm x}/{ m Mg}~{ m m}^{-3}$	1.906	1.756	2.004	1.971
μ/mm^{-1}	6.7	4.97	8.04	6.7
F(000)	1376	3464	1448	1704
T∕°C	-130	-100	-173	-173
$2 heta_{ m max}$	57	50	57.1	57.4
No. of refl.:				
measured	45484	7063	16363	20097
independent	6147	5916	5936	13522
Transmissions	0.34 - 0.73	0.69-0.76	0.21-0.73	0.22-0.43
$R_{ m int}$	0.081	0.026	0.066	0.039
Parameters	298	413	298	775
Restraints	92	85	0	0
$wR(F^2, \text{ all Refl.})$	0.043	0.082	0.076	0.096
$R(F, >4\sigma(F))$	0.023	0.034	0.040	0.042
S	0.980	1.007	0.824	0.933
Max. $\Delta \rho$ (e Å ⁻³)	0.74	1.01	1.8	2.1

Compound	$15 \cdot 1/4 CH_2 Cl_2$	16	$18 \cdot 1/2 CH_2 Cl_2$	19
Formula	Course Hays AgClos Fr FeOr PS	C ₂₀ H ₂₂ AgF ₂ FeO ₂ PSSe	C475H20A9CIF2FeO2P2S2	C47H20A9F2FeO2P2SSe
М.	756.52	728.18	1040.02	1044.45
Habit	Yellow plate	Orange prism	Yellow plate	Orange prism
Crystal size (mm)	$0.48 \times 0.24 \times 0.04$	$0.12 \times 0.10 \times 0.08$	$0.33 \times 0.23 \times 0.07$	$0.18 \times 0.18 \times 0.10$
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	P(-1)	P(-1)	$P2_1/n$	$P2_{1}/c$
Cell constants:			1.	1.
a/Å	11.5500(10)	9.7756(9)	10.7313(8)	12.9511(14)
b/Å	12.6343(10)	12.0232(11)	18.2674(14)	16.8249(19)
c/Å	19.8830(16)	12.7493(12)	22.6389(16)	20.548(2)
a/°	87.345(3)	66.890(1)	90	90
β/°	87.028(3)	86.717(2)	97.837(3)	106.689(3)
v/°	80.112(3)	84.285(2)	90	90
$V/Å^3$	2852.4(4)	1371.1(2)	4396.5(6)	4288.8(8)
Ζ	4	2	4	4
$D_{\rm x}/{\rm Mg}~{\rm m}^{-3}$	1.762	1.895	1.571	1.618
μ/mm^{-1}	1.5	2.7	1.06	1.82
F(000)	1514	772	2108	2096
T/°C	-130	-173	-130	-173
$2\theta_{\rm max}$	60.06	57.5	56.6	56.7
No. of refl.:				
measured	36536	9061	84636	28043
independent	16266	6158	10919	10106
Transmissions	0.58-0.91	0.73-0.81	0.70-0.94	0.82-1.0
$R_{ m int}$	0.047	0.062	0.069	0.076
Parameters	743	361	583	532
Restraints	13	0	190	0
$wR(F^2, \text{ all Refl.})$	0.081	0.111	0.080	0.128
$R(F, >4\sigma(F))$	0.032	0.053	0.031	0.059
S	0.991	0.807	1.013	0.966
Max. $\Delta \rho$ (e Å ⁻³)	1.02	1.08	0.66	0.73

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