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Synthesis, structure and redox behaviour of gold and silver complexes with 3-ferrocenylpyridine

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Abstract

3-Ferrocenylpyridine (Fcpy) reacts with gold(I) derivatives to afford neutral, [AuR(Fcpy)] (R = Cl, C_6F_5), or cationic complexes, [Au(Fcpy)(PPh_3)]OTf. Reaction with [Au(C_6F_5)$_2$(OEt_2)$_2$]ClO_4 or [Au(C_6F_5)$_3$(OEt_2)] gives the gold(III) complexes [Au(C_6F_5)$_2$(Fcpy)$_2$]ClO_4 or [Au(C_6F_5)$_3$(Fcpy)], respectively. The silver derivatives [Ag(Fcpy)(PPh_3)]OTf and [Ag(OTf)(Fcpy)$_2$] have also been synthesised. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Gold; Silver; Ferrocene; Ferrocenylpyridine; Redox behaviour

1. Introduction

In the last few years the chemistry of ferrocene and the design of new compounds containing the ferrocene unit has received much attention, associated with the utility of such compounds in many fields such as organic synthesis, homogeneous catalysis, material chemistry, and production of fine chemicals [1–4]. Numerous derivatives have been described in which the ferrocene unit is bound to a fragment containing one or more donor atoms. Studies of these ligands are important because the complexes thus obtained may have interesting redox properties or unusual structures.

The ferrocenylpyridines were synthesised some years ago [5,6] but their coordination properties have not been intensively studied. As far as we are aware, only some rhenium complexes with the 4-Fcpy [7] and one platinum derivative with the 3-Fcpy [6] ligand have been described. As part of our studies of ferrocene derivatives as ligands [8–15], we report here on the synthesis of several gold and silver complexes with the 3-ferrocenylpyridine ligand (henceforth abbreviated as Fcpy). Cyclic voltammetry studies have been performed and show one electron reversible oxidation based on the ferrocene moiety; the silver compounds show one further irreversible oxidation for the silver centre.

2. Results and discussion

2.1. Synthesis

Treatment of equimolecular amounts of [AuR(tht)] (R = Cl or C_6F_5, tht = tetrahydrothiophene) with 3-ferrocenylpyridine in dichloromethane affords the neutral complexes [AuR(Fcpy)] [R = Cl (**1**), C_6F_5 (**2**)] (Scheme 1). Compounds **1** and **2** are moisture- and air-stable red solids that behave as non-conductors in acetone solution. In the IR spectrum of **1** the bands arising from the ferrocene and pyridine moiety can be observed, and additionally a new band at 358 (s) cm^{-1} from the vibration ν(Au–Cl); the IR spectrum of complex **2** shows strong absorptions at 1505 (s), 955 (s) and 790 (s) cm^{-1} for the pentafluorophenyl unit. In the positive-ion liquid secondary ion mass spectrum (LSIMS) of **1** the molecular peak does not appear but the fragment arising from the loss of one chlorine is present at $m/z = 460$ (19%); the molecular peak of complex **2** appears at $m/z = 627$ (5%).

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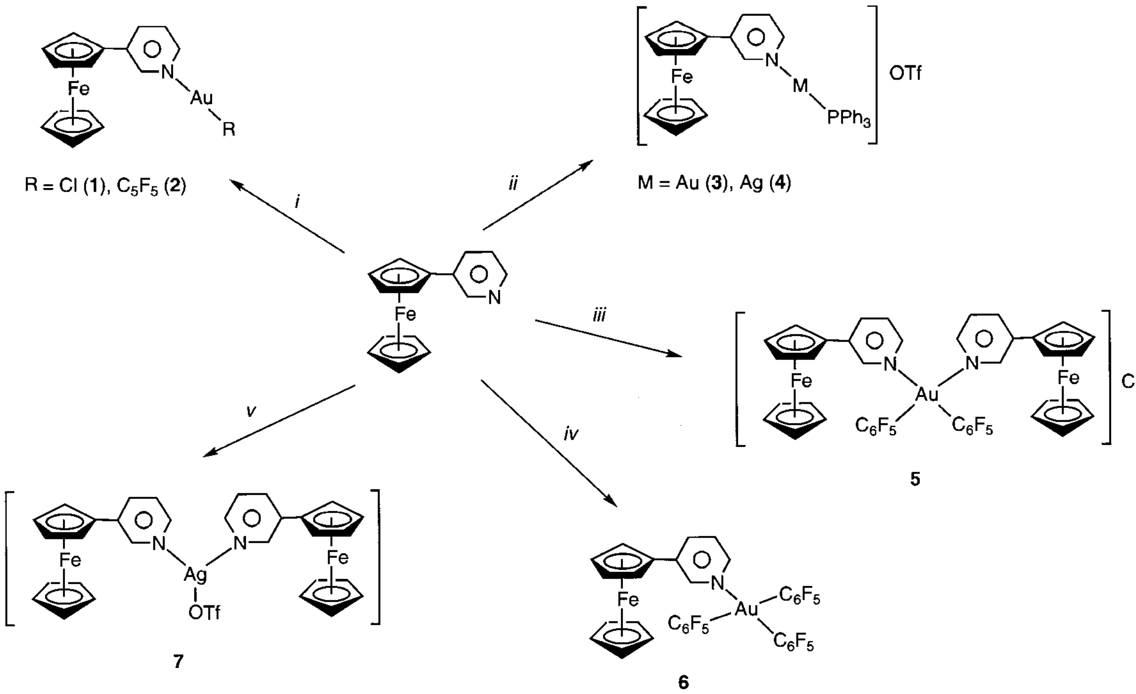
The ^{1}H-NMR spectra show the three resonances for the ferrocene protons in a ratio 2:2:5 for α- and β-protons of the substituted Cp ring and for the unsubstituted Cp ring, respectively. The pyridine protons appear as singlet (H_2), doublet (H_4), doublet of doublets (H_5) and doublet (H_6). The ^{19}F-NMR spectrum of **2** presents two multiplets for the *ortho* and *meta* and a triplet for the *para* fluorine.

The reaction of Fcpy with $[M(OTf)(PPh_3)]$ (M = Au, Ag) gives the cationic complexes $[M(Fcpy)(PPh_3)]OTf$ [M = Au (**3**), Ag (**4**)]. Acetone solutions of complexes **3** and **4** behave as 1:1 electrolytes. The solid IR spectra present bands at 1265 (vs, br), 1223 (s), 1150 (s) and 1023 (s) cm^{-1}, arising from the trifluoromethanesulfonate. In the LSIMS$^+$ spectra the cation molecular peaks appear at $m/z = 722$ (100%) and 633 (62%), respectively. The ^{1}H-NMR spectra show the three resonances for the ferrocene moiety and the four resonances for the pyridine protons. The ^{31}P-NMR spectrum of **3** consists of a singlet whereas that of **4** (at −55°C) consist of two doublets by coupling of the phosphorus atom with the two silver nuclei, ^{107}Ag and ^{109}Ag.

Gold(III) derivatives with the ferrocenylpyridine ligand can be achieved by reaction of Fcpy with $[Au(C_6F_5)_2(OEt_2)_2]ClO_4$ (molar ratio 2:1) leading to $[Au(C_6F_5)_2(FcPy)_2]ClO_4$ (**5**) or with $[Au(C_6F_5)_3(OEt_2)]$ (molar ratio 1:1) affording the complex $[Au(C_6F_5)_3(Fcpy)]$ (**6**). Complexes **5** and **6** are red air- and moisture-stable solids; **5** is a 1:1 electrolyte and **6** is non conducting in acetone solution. Their IR spectra show bands at 1512 (s), 1506 (s), 968 (s), 805 (m) and 786 (m) for the pentafluorophenyl groups, at 1100 (vs, br) and 619 (s) cm^{-1} for the perchlorate anion (complex **5**) and at 1507 (s), 969 (s), 820 (m) and 792 (m) (complex **6**) cm^{-1} also for the pentafluorophenyl groups. In the LSIMS$^+$ spectra the cation molecular peak appears for complex **5** at $m/z = 1057$ (20%) and the molecular peak at $m/z = 961$ (100%) is present for complex **6**.

The ^{1}H-NMR spectra for complexes **5** and **6** show one singlet for the unsubstituted Cp ring and two multiplets for the α- and β-protons of the substituted Cp rings; also the four resonances for the protons of the pyridine group appear. The ^{19}F-NMR spectra of **5** presents three resonances for the equivalent pentafluorophenyl rings; complex **6** presents six signals in a ratio 2:1 for the mutually *trans* pentafluorophenyl rings and for the *cis* pentafluorophenyl ring, respectively.

The treatment of AgOTf with two equivalents of ferrocenylpyridine in diethyl ether affords the complex $[Ag(OTf)(Fcpy)_2]$ (**7**) in high yield. Complex **7** is an air- and moisture-stable red solid that presents a low conductivity value in acetone for a 1:1 electrolyte, perhaps because of the weak coordination of the triflate anion. The IR spectrum shows the band for the trifluoromethanesulfonate ion coordinated to the silver centre at 1265 (vs, br), 1222 (s), 1150 (s) and 1104 (s) cm^{-1}. In the LSIMS$^+$ spectrum the cation appears at $m/z = 633$ as the most intense peak; the fragment arising from the loss of one Fcpy ligand is also present at $m/z = 370$ (76%).



Scheme 1. (i) [AuCl(tht)] or $[Au(C_6F_5)(tht)]$, (ii) $[Au(OTf)(PPh_3)]$ or $[Ag(OTf)(PPh_3)]$, (iii) $[Au(C_6F_5)_2(OEt_2)_2]ClO_4$, (iv) $[Au(C_6F_5)_3(OEt_2)]$, (v) 1/2 Ag(OTf).

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

Au–C(31)	2.00(2)	C(1)–N	1.40(2)
Au–N	2.124(15)	C(5)–N	1.27(2)
Au–Au # 1	3.301(2)		
C(31)–Au–N	176.3(6)	C(5)–N–Au	122.6(13)
C(31)–Au–Au # 1	90.3(4)	C(1)–N–Au	117.2(12)
N–Au–Au # 1	93.4(4)	C(36)–C(31)–Au	123.8(10)

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

Table 2
Selected bond lengths (Å) and angles (°) for **3**

Au(1)–N(1)	2.070(9)	P(2)–C(71)	1.790(13)
Au(1)–P(1)	2.228(3)	P(2)–C(91)	1.795(12)
Au(2)–N(2)	2.065(10)	P(2)–C(81)	1.825(13)
Au(2)–P(2)	2.233(3)	C(14)–N(1)	1.343(15)
P(1)–C(41)	1.804(11)	N(1)–C(15)	1.370(15)
P(1)–C(61)	1.825(13)	C(29)–N(2)	1.35(2)
P(1)–C(51)	1.849(13)	N(2)–C(30)	1.294(14)
N(1)–Au(1)–P(1)	172.3(3)	C(51)–P(1)–Au(1)	115.8(4)
N(2)–Au(2)–P(2)	175.6(3)	C(71)–P(2)–Au(2)	109.8(4)
C(41)–P(1)–Au(1)	112.6(3)	C(91)–P(2)–Au(2)	115.9(4)
C(61)–P(1)–Au(1)	108.8(4)	C(81)–P(2)–Au(2)	112.0(4)

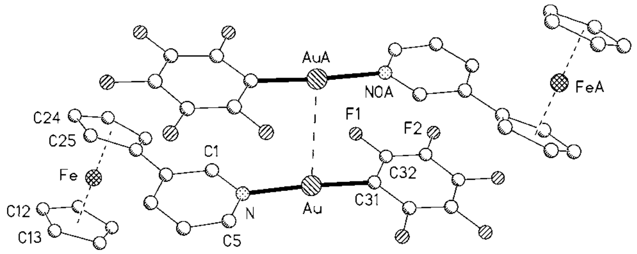


Fig. 1. The structure of complex **2** in the crystal showing the atom numbering scheme. Radii are arbitrary. H atoms are omitted for clarity.

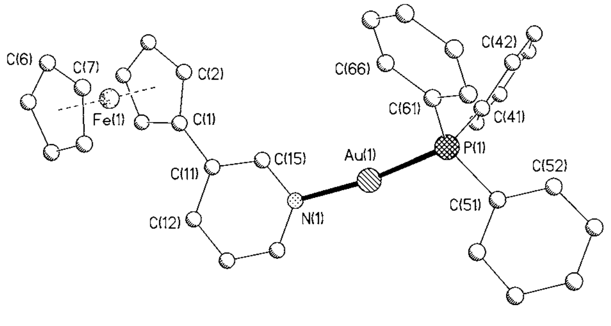


Fig. 2. The cation of one of the two independent formula units of complex **3** in the crystal. Radii are arbitrary. H atoms are omitted for clarity.

In the ^{1}H-NMR spectrum both ferrocenylpyridine groups are equivalent and the typical pattern for the ligand appears, with three resonances for the ferrocene moiety in a ratio 2:2:5 and four resonances for the pyridine unit in a 1:1:1:1 ratio.

2.2. Molecular structures

The structures of the following complexes have been established by X-ray diffraction: the gold(I) derivatives [Au(C_6F_5)(Fcpy)] (**2**) and [Au(Fcpy)(PPh_3)]OTf (**3**) and the gold(III) compounds [Au(C_6F_5)$_2$(Fcpy)$_2$]ClO_4 (**5**) and [Au(C_6F_5)$_3$(Fcpy)] (**6**).

Complex **2** crystallises in the monoclinic system and complex **3** in the orthorhombic system with four molecules of dichloromethane and two independent molecules in the asymmetric unit; these two molecules differ slightly in angles and bond distances. Selected bond lengths and angles of **2** and **3** are shown in Tables 1 and 2, respectively. In the lattice of compound **2** the molecules are associated into pairs across inversion centres via a weak intermolecular Au···Au interaction of 3.301(2) Å (Fig. 1). However, the cations of compound **3** (Fig. 2) are not associated in the crystal, presumably because steric effects of the bulky Ph_3P groups prevent the intimate approach required for metal–metal contacts.

The gold atoms, in both derivatives, have geometries slightly distorted from linearity with angles C(31)–Au–N 176.3(6)° for **2** and N(1)–Au(1)–P(1) 172.3(3) and N(2)–Au(2)–P(2) 175.6(3)° for **3**. Although the Au–N distance in **2**, 2.124(15) Å, is longer than the Au–N distances in **3**, 2.065(10) and 2.070(9) Å, the differences may not be highly significant. These values are in line with those found in related two-coordinated gold(I) compounds with an Au–N(pyridine) or similar bond, such as [Au(PPh_3)(dmpy)]ClO_4 (dmpy = 2,6-dimethylpyridine) [16] (2.091(13) Å) or [(AuPPh_3)py-{$SCH_2C(O)Ph$}-2]ClO_4 (two independent molecules with 2.082(4) and 2.092(4) Å) [17].

The Au–C distance in **2** (2.00(2) Å) is similar to that observed in the complex [Au(C_6F_5)(Ph_2C = N–N = CPh_2)] (1.992(9) Å) [18], in which an N–Au–C unit is present, or to those found in other pentafluorophenylgold(I) derivatives such as [Au_2(C_6F_5)$_2$(μ-dppm)] (2.058(12) and 2.063(12) Å) [19] (dppm = bis-(diphenylphosphino)methane). Au–P bond lengths in **3** (2.228(3) and 2.233(3) Å) are normal and compare well with those found in the above-mentioned related gold(I) complexes [Au(PPh_3)(dmpy)]ClO_4 (2.233(4) Å) [16] and [(AuPPh_3)py{$SCH_2C(O)Ph$}-2]ClO_4 (2.2359(13), 2.2388(13) Å) [17].

The expected square planar geometry for gold in complexes **5** and **6** was confirmed (Figs. 3 and 4, Tables 3 and 4). Mean deviations of the planes formed by the four donor atoms and the gold centre are 0.0034, N1, N2, C31, C41, Au (**5**) and 0.2899 Å, N11, C21, C31, C41, Au (**6**). These structures are, as far as we know, the first with gold(III) derivatives bonded both to pen-

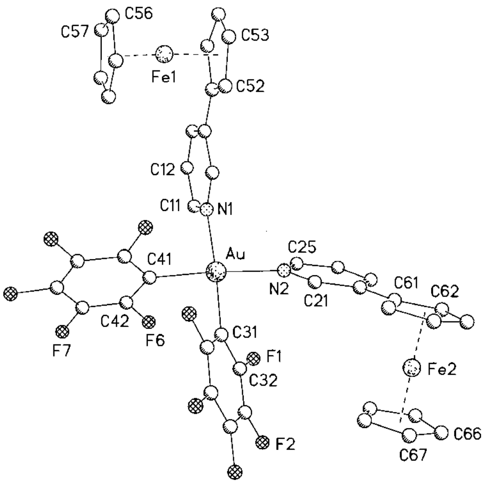


Fig. 3. Perspective view of the cation of complex **5** in the crystal. H atoms are omitted for clarity.

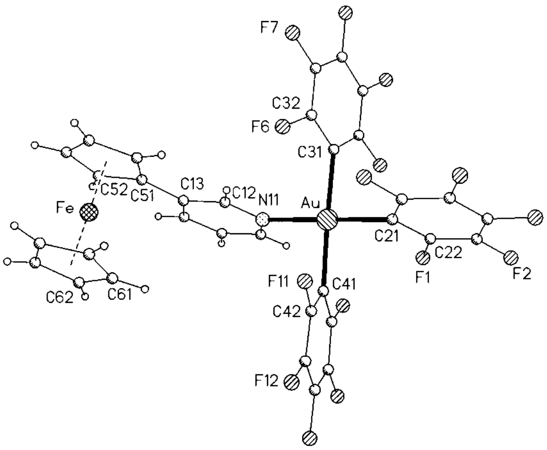


Fig. 4. Molecular structure of complex **6** in the crystal. H atoms are omitted for clarity.

Table 3
Selected bond lengths (Å) and angles (°) for **5**

Au–C(31)	2.011(9)	N(1)–C(15)	1.335(11)
Au–C(41)	2.015(9)	N(1)–C(11)	1.373(11)
Au–N(1)	2.076(7)	N(2)–C(21)	1.334(11)
Au–N(2)	2.089(7)	N(2)–C(25)	1.340(11)
C(31)–Au–C(41)	87.5(3)	C(31)–Au–N(2)	90.1(3)
C(31)–Au–N(1)	176.4(3)	C(41)–Au–N(2)	175.3(3)
C(41)–Au–N(1)	88.9(3)	N(1)–Au–N(2)	93.5(3)

Table 4
Selected bond lengths (Å) and angles (°) for **6**

Au–C(21)	2.017(3)	Au–N(11)	2.101(3)
Au–C(41)	2.067(3)	N(11)–C(12)	1.336(5)
Au–C(31)	2.068(3)	N(11)–C(16)	1.348(4)
C(21)–Au–C(41)	88.67(13)	C(21)–Au–N(11)	179.85(14)
C(21)–Au–C(31)	89.51(13)	C(41)–Au–N(11)	91.42(12)
C(41)–Au–C(31)	178.08(14)	C(31)–Au–N(11)	90.41(12)

tafluorophenyl rings and a nitrogen donor atom. The Au–C distances to mutually *trans* pentafluorophenyl groups in compound **6** are 2.067(3), 2.068(3) Å. These distances lie in the same range as those found in other tris(pentafluorophenyl)gold(III) derivatives such as [Au$(C_6F_5)_3(S_2S{-}PEt_3)$] (2.067(4), 2.076(4) Å) [20]. The *trans* influence of the pentafluorophenyl ligand is reflected in the different Au–C distances found for carbon atoms *trans* to the nitrogen atom of the ferrocenyl ligand: C(21)–Au in **6** (2.017(3) Å) or C(31)–Au, C(41)–Au in **5** (2.011(9), 2.015(9) Å, respectively). Au–N distances in both complexes (2.076(7), 2.089(7) Å, **5**; 2.101(3) Å, **6**) are longer than those found in other gold(III) complexes in which an Au–N(pyridine) or related bond is present, e.g. [Au{dpk-$(OH)_2$}-Cl_2]Cl (dpk = di-2-pyridylmethanediol-*N*,*N′*) (2.039(5), 2.042(5) Å) [21], or in [Au$Cl_3(C_6H_7{-}NO)$] (2.021(9) Å) [22], corresponding to a higher *trans* influence of the pentafluorophenyl ligand than of the chlorine ligand. The only other reported compound containing this ligand, [Pt(Fcpy)$_2$Cl$_2$], displays a similar geometry [6] to that of complex **5**, with the platinum centre showing a square-planar stereochemistry, bonded to two carbon and two nitrogen atoms.

Compounds **3** and **5** display several short and reasonably linear C–H···O contacts that might be interpreted as hydrogen bonds. For **3** the shortest (H···O < 2.5 Å) are C104–H10E···O3 [H···O 2.11 Å, C–H···O 151°]; C102–H10B···O6 [2.34 Å, 152°]; C56–H56···O2 [2.41 Å, 150°] and C29–H29···O1 [2.46 Å, 174°] (H10E and H10B are hydrogens of dichloromethane), and for **5** C15–H15···O1 [2.20 Å, 151°]; C25–H25···O5 [2.42 Å, 163°]; C65–H65···O2 [2.42 Å, 159°]; C11–H11···O5 [2.43 Å, 124°]; C23–H23···O3 [2.46 Å, 136°] and C13–H13···O2 [2.49 Å, 134°] (O5 is the ether oxygen).

2.3. Electrochemistry

The electrochemical behaviour of the gold and silver complexes with the 3-ferrocenylpyridine ligand has been studied by cyclic voltammetry at a platinum electrode in CH_2Cl_2. The free ligand undergoes a reversible one electron oxidation process, based on the ferrocene unit, at a potential very close to that of free ferrocene. The coordination of a gold(I) fragment produces a shift to slightly higher potentials for the oxidation–reduction of the ferrocene moiety. The silver(I) compounds, show, in addition of the wave due to the ferrocene oxidation, a more anodic irreversible wave that can be assigned to the one electron oxidation of Ag^+ to Ag^{2+}. Complexes **5** and **7**, which possess two ferrocenylpyridine units, show a simultaneous oxidation of these units rather than a two-step process, as was observed for the platinum complex cis-[PtCl$_2$(Fcpy)$_2$] [7]. Table 5 summarises the electrochemical data for these compounds.

Table 5
Electrochemical data for complexes **1**–**7**

Compound	E_1 (V)	E_2 (V)
L Fcpy	0.48	
1 [AuCl(Fcpy)]	0.52	
2 [Au(C_6F_5)(Fcpy)]	0.62	
3 [Au(Fcpy)PPh_3]TfO	0.53	
4 [Ag(Fcpy)PPh_3]TfO	0.76	1.03
5 [Au(C_6F_5)$_2$(Fcpy)$_2$]ClO_4	0.56	
6 [Au(C_6F_5)$_3$(Fcpy)]	0.69	
7 [Ag(OTf)(Fcpy)$_2$]	0.51	0.99

3. Experimental

IR 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. 5×10^{-4} mol dm^{-3} solutions with a Philips 9509 conductimeter. C, H, N and S analyses were carried out with a Perkin–Elmer 2400 microanalyzer. Mass spectra were recorded on a VG Autospec, with the LSIMS technique, using nitrobenzyl alcohol as matrix. NMR spectra were recorded on a Varian Unity 300 spectrometer and a Bruker ARX 300 spectrometer in $CDCl_3$. Chemical shifts are cited relative to $SiMe_4$ (^1H, external), $CFCl_3$ (^{19}F, external) and 85% H_3PO_4 (^{31}P, external). Cyclic voltammetric experiments were performed by employing an EG&G PARC Model 273 potentiostat. A three-electrode system was used, which consists 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 solutions 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 versus SCE. The starting materials Fcpy [7], [AuCl(tht)] [23], [Au(C_6F_5)(tht)] [23], [Au(C_6F_5)$_2$(OEt_2)$_2$]ClO_4 [24] and [Au(C_6F_5)$_3$(OEt_2)] [25] were prepared by published procedures. [Au($OClO_3$)(PPh_3)] was prepared from [AuCl(PPh_3)] [26] and $AgClO_4$. [Au(OTf)(PPh_3)] was prepared from [AuCl(PPh_3)] by reaction with AgOTf in dichloromethane and [Ag(OTf)(PPh_3)] by reaction of AgOTf and PPh_3 in diethyl ether.

3.1. Syntheses

3.1.1. [AuR(Fcpy)] [R = Cl (**1**), C_6F_5 (**2**)]

To a solution of Fcpy (0.026 g, 0.1 mmol) in dichloromethane (20 cm^3) was added [AuCl(tht)] (0.032 g, 0.1 mmol) or [Au(C_6F_5)(tht)] (0.045 g, 0.1 mmol) and the mixture was stirred for 2 h. The solution was concentrated to ca. 5 cm^3 and addition of diethyl ether (15 cm^3) gave complex **1** or addition of hexane (15 cm^3) gave complex **2** as red solids. Complex **1**: Yield 59%. Anal. Calc. for $C_{15}H_{13}AuClFeN$: C, 36.36; H, 2.64; N, 2.73. Found: C, 35.90; H, 2.31; N, 2.73%. Λ_M 36 Ω^{-1} cm^2 mol^{-1}. ^1H-NMR, δ: 4.09 (s, 5H, C_5H_5), 4.48 (m, 2H, C_5H_4), 4.65 (m, 2H, C_5H_4), 7.39 (m, 1H, py), 7.93 (m, 1H, py), 8.31 (m, 1H, py), 8.61 (s, 1H, py). Complex **2**: Yield 68%. Anal. Calc. for $C_{21}H_{13}AuF_5FeN$: C, 40.22; H, 2.09; N, 2.23. Found: C, 39.75; H, 1.76; N, 2.14%. Λ_M 4 Ω^{-1} cm^2 mol^{-1}. ^1H-NMR, δ: 4.20 (s, 5H, C_5H_5), 4.53 (m, 2H, C_5H_4), 4.87 (m, 2H, C_5H_4), 7.45 (dd, 1H, py, H5, J(HH) 5.37 and 8.06 Hz), 7.97 (d, 1H, py, H4, J(HH) 8.06 Hz), 8.39 (d, 1H, py, H6, J(HH) 5.37 Hz), 8.62 (s, 1H, py, H2). ^{19}F-NMR, δ: −116.5 (m, 2F, *o*-F), −159.7 (t, 1F, *p*-F, J(FF) 20.0 Hz), −163.3 (m, 2F, *m*-F).

3.1.2. [M(Fcpy)(PPh_3)]OTf [M = Au (**3**), Ag (**4**)]

To a solution of Fcpy (0.026 g, 0.1 mmol) in dichloromethane (20 cm^3) was added [Au(OTf)PPh_3] (0.061 g, 0.1 mmol) or [Ag(OTf)PPh_3] (0.052 g, 0.1 mmol) and the mixture was stirred for 1 h. The solution was concentrated to ca. 5 cm^3 and addition of diethyl ether (15 cm^3) gave complexes **3** or **4** as red solids. Complex **3**: Yield 63%. Anal. Calc. for $C_{34}H_{28}AuF_3FeNO_3SP$: C, 43.96; H, 3.16; N, 1.46; S, 3.32. Found: C, 44.09; H, 3.31; N, 1.32; S, 3.45%. Λ_M 122 Ω^{-1} cm^2 mol^{-1}. ^1H-NMR, δ: 4.20 (s, 5H, C_5H_5), 4.45 (m, 2H, C_5H_4), 4.90 (m, 2H, C_5H_4), 7.3–7.8 (m, 2H, py + 15H, Ph), 7.99 (d, 1H, py, H6, J(HH) 6.68 Hz), 8.58 (s, 1H, py, H2). $^{31}P\{^1H\}$-NMR, 29.3 (s, 1P, PPh_3). Complex **4**: Yield 70%. Anal. Calc. for $C_{34}H_{28}AgF_3FeNO_3SP$: C, 52.20; H, 3.60; N, 1.79; S, 4.09. Found: C, 52.62; H, 3.59; N, 1.66; S, 3.88%. Λ_M 110 Ω^{-1} cm^2 mol^{-1}. ^1H-NMR, δ: 4.20 (s, 5H, C_5H_5), 4.53 (m, 2H, C_5H_4), 4.87 (m, 2H, C_5H_4), 7.27 (dd, 1H, py, H5, J(HH) 6.96 and 4.88 Hz), 7.3–7.6 (m, 15H, Ph), 7.66 (d, 1H, py, H4, J(HH) 6.96 Hz), 8.35 (d, 1H, py, H6, J(HH) 4.88 Hz), 8.75 (s, 1H, py, H2). $^{31}P\{^1H\}$-NMR, −55°C, 14.9 (2d, 1P, PPh_3, $J(^{109}AgP)$ 753.9, $J(^{107}AgP)$ 653.9 Hz).

3.1.3. [Au(C_6F_5)$_2$(Fcpy)$_2$]ClO_4 (**5**)

To a diethyl ether solution (20 cm^3) of [Au(C_6F_5)$_2$(OEt_2)$_2$]ClO_4 (0.071 g, 0.1 mmol) was added Fcpy (0.052 g, 0.2 mmol). The mixture was stirred for 30 min, during which time an orange precipitate appeared. The solid was filtered off to give an orange solid of complex **5**. Yield 44%. Anal. Calc. for $C_{42}H_{26}AuClF_{10}Fe_2N_2O_4$: C, 43.61; H, 2.26; N, 2.42. Found: C, 43.05; H, 2.31; N, 2.30%. Λ_M 110 Ω^{-1} cm^2 mol^{-1}. ^1H-NMR, δ: 4.08 (s, 10H, C_5H_5), 4.60 (m, 4H, C_5H_4), 4.95 (m, 4H, C_5H_4), 7.52 (m, 2H, py, H5), 7.87 (d, 2H, py, H4, J(HH) 3.27 Hz), 8.35 (d, 2H, py, H6, J(HH) 2.06 Hz), 8.65 (s, 2H, py, H2). ^{19}F-NMR, δ: −122.4 (m, 4F, *o*-F), −152.2 (t, 2F, *p*-F, J(FF) 20.0 Hz), −158.8 (m, 4F, *m*-F).

3.1.4. *[Au(C_6F_5)$_3$(Fcpy)]* (**6**)

To a diethyl ether solution (20 cm^3) of [Au(C_6F_5)$_3$(OEt_2)] (0.077 g, 0.1 mmol) was added Fcpy (0.026 g, 0.1 mmol). The mixture was stirred for 30 min and then the solution was evaporated to ca. 1 cm^3; addition of hexane afforded an orange solid of complex **6**. Yield 80%. Anal. Calc. for $C_{33}H_{13}AuF_{15}FeN$: C, 41.23; H, 1.36; N, 1.45. Found: C, 40.79; H, 1.02; N, 1.26%. Λ_M 3 Ω^{-1} cm^2 mol^{-1}. ^{1}H-NMR, δ: 4.00 (s, 5H, C_5H_5), 4.54 (m, 2H, C_5H_4), 4.67 (m, 2H, C_5H_4), 7.48 (m, 1H, py, H5), 7.92 (m, 1H, py, H4), 8.32 (m, 1H, py, H6), 8.63 (s, 1H, py, H2). ^{19}F-NMR, δ: −122.7 (m, 2F, *o*-F), −125.0 (m, 4F, *o*-F), −156.5 (t, 2F, *p*-F, *J*(FF) 19.9 Hz), −157.4 (t, 1F, *p*-F, *J*(FF) 20.0 Hz) −161.2 (m, 4F, *m*-F), −162.3 (m, 2F, *m*-F).

3.1.5. *[Ag(OTf)(Fcpy)$_2$]* (**7**)

To a diethyl ether solution (20 cm^3) of Ag(OTf) (0.021 g, 0.1 mmol) was added Fcpy (0.052 g, 0.2 mmol). The mixture was stirred for 30 min, during which time a red precipitate appeared. The solid was filtered off to give a red solid of complex **7**. Yield 85%. Anal. Calc. for $C_{31}H_{26}AgF_3Fe_2N_2O_3S$: C, 47.64; H, 3.35; N, 3.58; S, 4.10. Found: C, 47.49; H, 3.43; N, 3.61; S, 4.10/%. Λ_M 76 Ω^{-1} cm^2 mol^{-1}. ^{1}H-NMR, δ: 4.28 (s, 10H, C_5H_5), 4.64 (m, 4H, C_5H_4), 4.98 (m, 4H, C_5H_4), 7.25 (m, 2H, py, H5), 7.72 (m, 2H, py, 4H), 8.41 (m, 2H, py, H6), 8.65 (s, 2H, py, H2).

3.2. *Crystal structure determinations*

The crystals were mounted in inert oil on glass fibres and transferred to the cold gas stream of a Siemens P4 diffractometer equipped with an LT-2 low temperature attachment. Data were collected using monochromated Mo–K$_\alpha$ radiation (λ = 0.71073 Å). Scan type ω. Absorption corrections were based on Ψ-scans. The structures were solved by the heavy-atom method, and refined on F^2 using the programs SHELXL-93 (**2**, **3**, **5**) or SHELXL-97 (**6**) [27]. Most non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included using a riding model. Further details are given in Table

Table 6
Details of data collection and structure refinement for complexes **2**, **3**, **5** and **6**

Compound	**2**	**3** $2CH_2Cl_2$	**5** $1.5CH_2Cl_2\cdot(CH_3CH_2)_2O$	**6**
Chemical formula	$C_{21}H_{13}AuF_5FeN$	$C_{36}H_{32}AuCl_4F_3FeNO_3PS$	$C_{47}H_{37}AuCl_3F_{10}Fe_2N_2O_5$	$C_{33}H_{13}AuF_{15}FeN$
Crystal habit	Orange plate	Orange lath	Red tablet	Orange lath
Crystal size (mm)	0.40 × 0.15 × 0.01	0.80 × 0.20 × 0.10	0.60 × 0.40 × 0.15	0.55 × 0.20 × 0.10
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Triclinic
Space group	$P2_1/n$	$Pca2_1$	$C2/c$	$P\bar{1}$
a (Å)	10.582(4)	33.520(4)	37.726(5)	10.1227(12)
b (Å)	7.395(2)	9.6011(14)	13.916(3)	12.8984(12)
c (Å)	23.233(8)	23.811(2)	19.591(3)	13.2744(16)
α (°)	–	–	–	66.351(8)
β (°)	93.35(2)	–	104.97(2)	71.746(10)
γ (°)	–	–	–	88.884(8)
U (Å^3)	1814.9(10)	7663(2)	9936(3)	1496.5(3)
Z	4	8	8	2
D_{calc} (g cm^{-3})	2.295	1.805	1.758	2.133
M	627.14	1041.27	1314.80	961.26
F(000)	1184	4080	5160	916
T (°C)	−100	−100	−100	−100
$2\theta_{max}$ (°)	50	50	50	50
μ(Mo–K$_\alpha$) (cm^{-1})	0.893	0.463	0.376	0.550
Transmission	1–0.705	1–0.562	1–0.677	0.986–0.632
No. of reflections measured	3217	11 374	8793	5149
No. of unique reflections	3185	11 363	8659	5061
R_{int}	0.1097	0.1977	0.0419	0.0180
R [a] [$F>4\sigma(F)$]	0.0653	0.0494	0.0515	0.0197
wR [b](F^2, all reflections)	0.1582	0.1146	0.1357	0.0432
No. of reflections used	3185	11 363	8649	5061
No. of parameters	152	519	630	472
No. of restraints	35	101	541	133
S [c]	0.881	0.945	0.865	0.971
Max. $\Delta\rho$ (e Å^{-3})	2.608	1.681	1.524	0.411

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

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

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

6. Special details of refinement: a system of restraints to light-atom displacement-factor components and local ring symmetry was used. Compound **2**: C and N atoms were refined isotropically. Compound **3**: C atoms and the second triflate ion, which is not well-resolved, were refined isotropically. The high merging *R* value is not meaningful, because very few equivalent reflections were present, and these were at high 2θ values. The absolute structure (polar axis direction) was determined by the method of Flack [28]; the *x* parameter refined to $-0.016(7)$. Compound **6**: The Cp-ring C_{61}–C_{65} is disordered over two positions with occupation factors 0.711, 0.289. The minor component was refined isotropically with idealised geometry.

4. Supplementary material

Complete crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre under the numbers CCDC-133385–133388. Copies can be obtained free of charge from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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