Coordination properties of the 1,1′-bis[((6-methyl)-2-pyridyl)amido]ferrocene ligand towards group 11 complexes†

Javier E. Aguado,[a] Olga Crespo,[a] M. Concepción Gimeno,*[a] Peter G. Jones,[b] Antonio Laguna[a] and M. Dolores Villacampa[a]

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The coordination properties of the 1,1′-bis[((6-methyl)-2-pyridyl)amido]ferrocene ligand (**L**) towards group 11 and palladium complexes have been studied. **L** coordinates as the bridging ligand, through the pyridinic nitrogen atoms, when reacting with the gold(I) compounds [Au(OTf)(PPh$_3$)] and [Au(C$_6$F$_5$)(tht)] or with the gold(III) species [Au(C$_6$F$_5$)$_3$(tht)] leading to linear or square planar derivatives, respectively. The reaction of **L** with [O(AuPPh$_3$)$_3$]ClO$_4$ affords the tetranuclear compound [Au$_4$(L-H)$_2$(PPh$_3$)$_4$](ClO$_4$)$_2$ in which the amide groups have been deprotonated and the ligand acts as dianionic, N,N,N,N-tetradentate. The treatment of the ligand **L** with silver salts leads to mononuclear complexes with the ligand acting as N,N,O or N,N chelating in [AgL]OTf, or [AgL$_2$]OTf, or to dinuclear species with an N,N bridging ligand in [Ag$_2$(PPh$_3$)$_2$(μ-L)](OTf)$_2$. Tetracoordination around the copper atom is proposed for the copper complexes [CuL(PPh$_3$)$_2$]PF$_6$, [CuL]PF$_6$, or [CuL$_2$]PF$_6$ with the ligand coordinated in an NH,NH,N,N or an N,N chelating fashion. Finally the palladium compound [PtCl$_2$L] has been synthesized with a *trans*-chelating ligand. In the structures of some of these derivatives the presence of secondary interactions such as weak hydrogen bonds of the type C–H···O, C–H···N or C–H···X (X = F, Cl) or even M···O interactions leads to supramolecular networks.

Introduction

Ferrocene is a very versatile molecule with important properties such as high electron density, aromaticity and redox reversibility. These characteristics, together with the well established routes to mono and 1,1′-disubstituted ferrocene derivatives with a great variety of organic fragments containing donor atoms such as O, N, S, P, make ferrocene a very suitable building block in many fields of research.[1] Current areas of interest in ferrocene chemistry include the use in catalysis, materials and bioinorganic chemistry. These functionalized ferrocene derivatives and the study of their coordination to metal centres represent an important topic of research in many areas that seek special properties of such species, *e.g.* non-linear optical properties, charge transport, liquid crystals, electrochemical recognition, catalysis, nanoparticles, immunoassay reagents or biological applications.[1,2]

The introduction of a ferrocene group into supramolecular coordination systems not only incorporates a redox-active group but also leads to interesting assembled structures because of the conformational flexibility of the ferrocene moieties and the varying coordination numbers of metal ions. Several reports have dealt with the synthesis of ferrocene-based bidentate ligands that contain pyridine moieties, their interesting coordination properties and novel supramolecular structures.[3] These ferrocene-containing amidopyridyl compounds have been used in electrochemical molecular recognition as they are able to modify selectively their electrochemical properties upon coordination of the target species.[2e,4] More recently, ferrocene receptors for neutral molecules have been developed and been shown to bind biologically relevant molecules though complementary hydrogen-binding interactions.[5]

Our contributions to this field include several ferrocene ligands that show interesting coordination properties and in some cases give rise to supramolecular motifs through weak hydrogen bonds.[6] We report here on the coordination properties of the 1,1′-bis[((6-methyl)-2-pyridyl)amido]ferrocene ligand towards group 11 metals and palladium compounds. Several metallic complexes of Pd,[7] M^{2+} (M = Cu, Ni, Co)[8] have been reported with similar ligands. Here we describe the coordination behaviour of this ligand, which is thereby shown to act as a bidentate bridging, chelating or *trans*-chelating ligand and also as a tridentate or tetradentate neutral or dianionic chelating ligand.

Results and discussion

The ligand 1,1′-bis[((6-methyl)-2-pyridyl)amido]ferrocene (**L**) has been prepared by reaction of di-chlorocarbonylferrocene with 2-amine-6-methylpyridine, molar ratio 1 : 2, in dichloromethane and in the presence of NEt$_3$ as has been previously reported.[9] The structure of the ligand has been reported at room temperature and 150 K in the Cambridge Database.[10]

The reactivity of **L** towards several gold compounds has been studied and thus the reaction of **L** with two equivalents of [Au(OTf)(PPh$_3$)] affords the complex [Au$_2$(μ-L)(PPh$_3$)$_2$](OTf)$_2$ (**1**) in which the gold atoms have coordinated to the ligand through the nitrogen atoms of the pyridine rings (see Scheme 1). The IR and NMR data agrees with the formulation proposed. The ^{1}H NMR

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[a] *Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-C.S.I.C., E-50009, Zaragoza, Spain*
[b] *Institut für Anorganische und Analytische Chemie der Technischen Universität, Postfach 3329, D-38023, Braunschweig, Germany*

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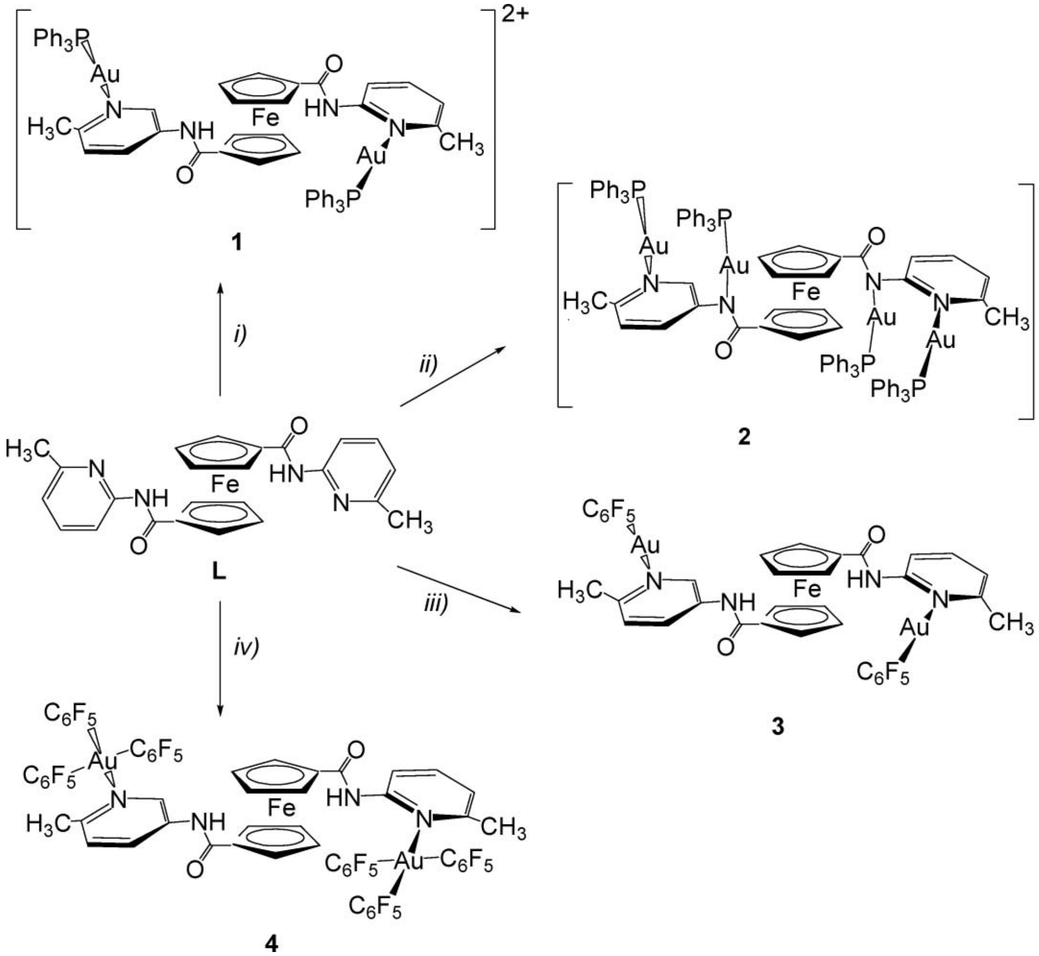


Scheme 1 i) 2 [Au(OTf)(PPh$_3$)], ii) 2 [O(AuPPh$_3$)$_3$]ClO$_4$, iii) 2 [Au(C$_6$F$_5$)(tht)], iv) 2 [Au(C$_6$F$_5$)$_3$(OEt$_2$)].

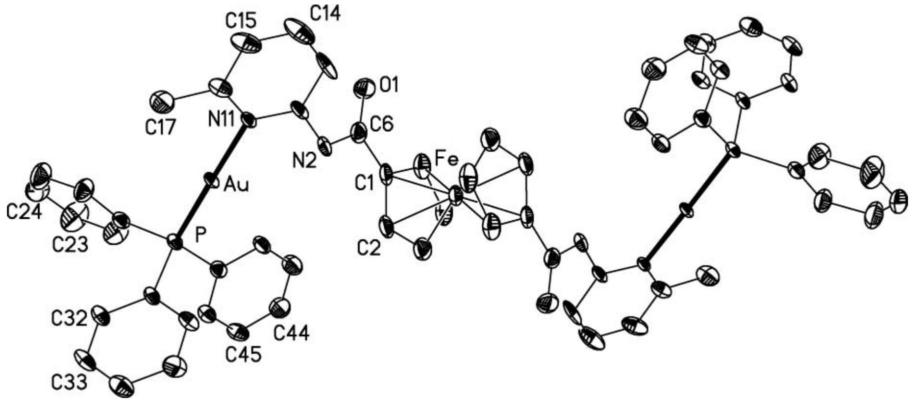


Fig. 1 Perspective view of the X-ray structure of complex **1** showing the atom labelling scheme. Hydrogen atoms have been omitted for clarity. Ellipsoids represent 50% probability levels.

spectrum shows the following resonances: two multiplets for the α and β protons of the ferrocenyl unit, in the aromatic region of the resonances for the phenyl and pyridine protons (overlapped), the amido protons and the methyl groups. The ^{31}P{^{1}H} NMR spectrum shows the equivalence of both phosphorus atoms as only one singlet appears.

The crystal structure of complex **1** has been established by X-ray diffraction and the molecule, which displays crystallographic inversion symmetry, can be seen in Fig. 1. A selection of bond lengths and angles are collected in Table 1. In the molecule the cyclopentadienyl units have an antiperiplanar disposition probably in order to minimize the steric hindrance of the bulky triphenylphosphine groups. The ferrocene ligand acts in a bridging mode. Each gold centre displays linear geometry [N11–Au–P = 179.31(14)°]. The Au–N and Au–P bond distances are 2.110(5) Å and 2.2353(17) Å, respectively (Table 1). The former are among the

Table 1 Selected bond lengths (Å) and angles (°) for **1**

Au–N(11)	2.110(5)	Au–P	2.2353(17)
N(11)–Au–P	179.31(14)	C(31)–P–Au	110.4(2)
C(21)–P–Au	114.1(2)	C(12)–N(11)–Au	117.6(4)
C(41)–P–Au	113.4(2)	C(16)–N(11)–Au	121.7(4)

longest Au–N bonds in gold(I) complexes in which the gold centre displays linear coordination, *cf.* $[Au(Fcpy)(PPh_3)]OTf$ (FcPy = 3-ferrocenylpyridine), two independent molecules, Au–P 2.233(3), 2.228(3) Å, Au–N 2.065(10), 2.070(9) Å;[11] $[Au(dmpy)(PPh_3)]ClO_4$ (dmpy = 2,6-dimethylpyridine), Au–P 2.233(4) Å, Au–N 2.091(3) Å;[12] $[Au(pbzim)(PPh_3)]ClO_4$ (pbzim = 2,6-di-*tert*-butylpyridine), Au–P 2.233(4) Å, Au–N 2.091(3) Å];[12] $[Au(C_6F_5)(FcPy)]$ (Au–N 2.114(15) Å)[11] or $[\{Au(PPh_3)\}_2\{Fc(SPy)_2\}](OTf)_2$ [$Fc(Spy)_2$ = 1,1′-bispyridylthioferrocene)], Au–P 2.2420(17) Å, Au–N 2.083(6) Å.[6g]

Several hydrogen bonds of the type C–H···O, N–H···O and C–H···F contribute to the final packing (see ESI Table S1†). Hydrogen bonds that involve the triflate oxygen atoms must be interpreted with care, as the anion is disordered over two positions with occupation factors 0.54, 0.46. The cations are connected to form chains parallel to the x axis by the weak hydrogen bond C42–H42···O1 [*d*(C–H···O) 3.414(8) Å, *d*(H···O) 2.62 Å] combined with the contact Au···O1 3.09 Å (Fig. 2).

The ligand **L** possesses, apart from the nitrogen atoms of the pyridine groups, two amido NH groups that can also coordinate to metallic centres. The gold compound $[O(AuPPh_3)_3]ClO_4$ is an excellent aurating agent that can deprotonate twice, forming H_2O, and thus incorporate up to three gold atoms into another compound. In the case of **L** the amido protons can be deprotonated and then there are four coordination sites that are the two pyridine nitrogens and the amide groups. The reaction of **L** with two equivalents of the oxonium complex at room temperature gives a mixture of complex **1** and another complex that according to its NMR spectrum is the tetragold species $[Au_4(L\text{-}2H)(PPh_3)_4](ClO_4)_2$ (**2**). If we carry out the same reaction under reflux conditions for 24 h the expected complex $[Au_4(L\text{-}2H)(PPh_3)_4](ClO_4)_2$ (**2**), in which the ligand is acting as tetradentate by coordination to gold through the deprotonated NH groups and the pyridine atoms, is isolated. The rest of the gold atoms coming from the oxonium compound are lost possibly in the form of $[Au(PPh_3)_2]OTf$, $[Au(OTf)(PPh_3)]$ or other unidentified by-products. The $^{31}P\{^1H\}$ NMR spectrum shows two resonances at 30.2 and 27.8 ppm, arising at the two different types of phosphorus atoms, and with a chemical shift characteristic of P–Au–py and P–Au–amide environments. In the IR spectra the absorption due to the NH is no longer observed. The ^1H NMR spectrum presents the resonances for the ferrocenyl unit as three multiplets in a ratio of 4 : 2 : 2, a singlet for the methyl protons and the resonances of the pyridine ring and phenyl rings; the signal corresponding to the NH proton has disappeared.

The reaction of **L** with two equivalents of $[Au(C_6F_5)(tht)]$ (tht = tetrahydrothiophene) gives the complex $[Au_2(C_6F_5)_2(\mu\text{-}L)]$ (**3**) in which the ligand bridges both gold fragments. The ^1H NMR spectrum contains two multiplets for the α and β protons of the cyclopentadienyl units, a singlet for the methyl group, two doublets and a triplet for the pyridine moiety and a singlet for the amide protons. The ^{19}F NMR spectrum however shows inequivalent pentafluorophenyl rings, probably because of the restricted rotational freedom of the pentafluorophenyl group around the $Au\text{–}C_{ipso}$ bond, and thus six resonances in a ratio 2 : 2 : 1 : 1 : 2 : 2 for the *meta*, *para* and *ortho* fluorine, respectively, can be observed. This restricted rotation of pentafluorophenyl rings has been previously observed by us and others in many gold, palladium and platinum complexes with pentafluorophenyl rings.[13] A rapid exchange between the pyridine and NH coordination sites is ruled out because of the low tendency of gold(I) centers to bond the nitrogen atom of an amide CO-NH- group. The LSIMS mass spectrum presents the molecular peak at m/z = 1182 (15%).

The gold(III) derivative $[Au_2(C_6F_5)_6(\mu\text{-}L)]$ (**4**) has also been synthesized by reaction of the ligand with $[Au(C_6F_5)_3(OEt_2)]$ in a molar ratio 1 : 2. The spectroscopic data corroborates the coordination of the tris(pentafluorophenyl) fragments to both pyridine nitrogen atoms giving a dinuclear derivative with the ligand bridging both gold centres. The ^1H NMR spectrum presents multiplets for the α and β protons of the cyclopentadienyl groups, singlets for the methyl and NH protons, and the pyridine protons appear as a doublet (5,5′), a triplet (4,4′) and a doublet (3,3′). The ^{19}F NMR spectrum shows two types of pentafluorophenyl units in a ratio 2 : 1, the mutually *trans* fluorines are equivalent, and each one presents three different resonances for the *ortho*, *meta* and *para* fluorine. The mass spectrum presents the molecular peak at m/z = 1850 (7%) and the fragment at m/z = 1152 (7%) originating from the loss of one "$Au(C_6F_5)_3$" unit.

The reactivity of the ligand **L** towards silver(I) complexes has been tested; thus the treatment with one equivalent of Ag(OTf)

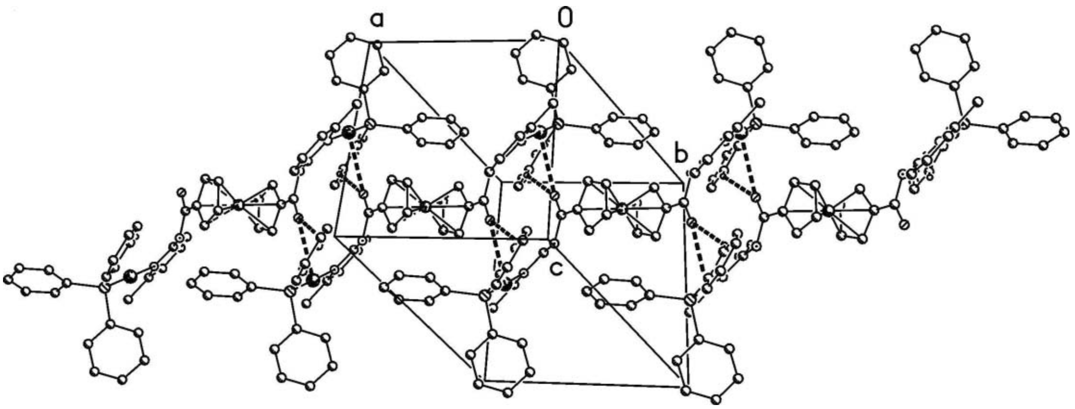
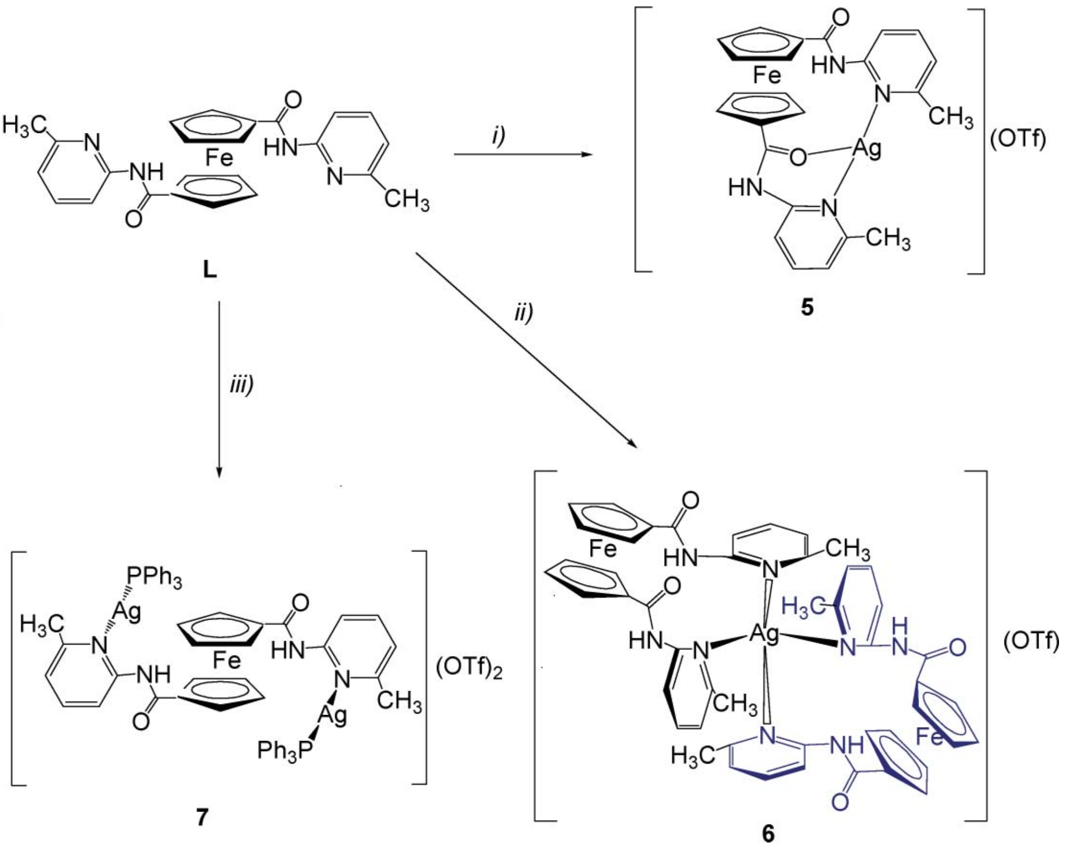


Fig. 2 Formation of chains through hydrogen bonds and Au···O interactions in compound **1**.



Scheme 2 i) Ag(OTf) ii) $\frac{1}{2}$ Ag(OTf), iii) 2 [Ag(OTf)(PPh$_3$)]

Table 2 Selected bond lengths (Å) and angles (°) for **5**

Ag–N(21)	2.1768(19)	Ag–O(2)	2.5605(16)
Ag–N(31)	2.1998(19)	Ag–O(2)#1	2.7178(17)
N(21)–Ag–N(31)	179.23(7)	N(21)–Ag–O(2)#1	91.01(6)
N(21)–Ag–O(2)	103.79(6)	N(31)–Ag–O(2)#1	88.92(6)
N(31)–Ag–O(2)	75.56(6)	O(2)–Ag–O(2)#1	115.00(4)

affords the complex [Ag(L)]OTf (**5**) in high yield (see Scheme 2). The ^{1}H NMR spectrum of the compound shows the typical resonances for the ligand protons but with a different chemical shift in agreement with the coordination to a metallic center. The mass spectrum presents the molecular peak [Ag(OTf)(L)]$^+$ at $m/z = 712$ (5%), although the most intense peak corresponds to the cation molecular peak, [AgL]$^+$, at $m/z = 561$.

The crystal structure of complex **5** has been established by X-ray diffraction. In compound **5** the ferrocene ligand is tridentate (Fig. 3). The cyclopentadienyl rings are staggered by 4.4° around the Cp···Cp axis (Cp = centre of the cyclopentadienyl ring) as defined by the torsion angle C1–Cp–Cp–C10. The silver atom diplays a T-shaped geometry [N21–Ag–N31 179.23(7)°, N21–Ag–O2 103.79(6), N31–Ag–O2 75.56(6), see Table 2] with the silver atom 0.008 Å out of the plane formed by O2, N31 and N21. In addition, the silver atom displays a short contact with one of the oxygen atoms of another molecule [Ag–O2#1 2.7178(17) Å] leading to the formation of a chain (Fig. 4).

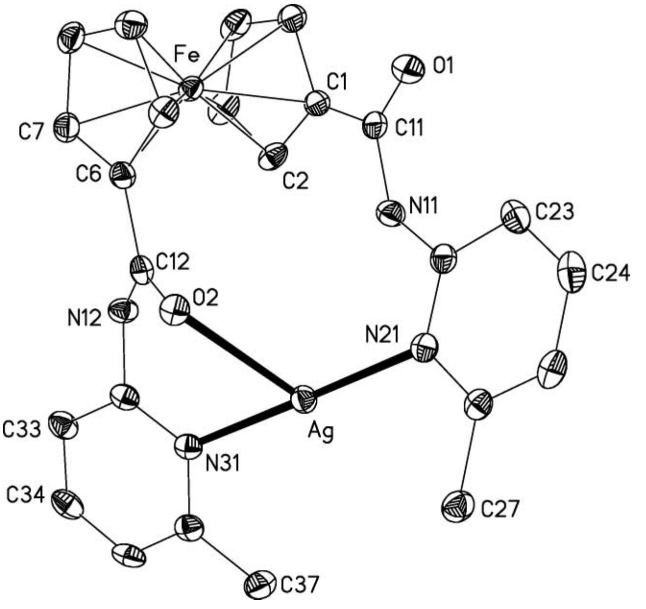


Fig. 3 Perspective view of the X-ray structure of the cation of complex **5** showing the atom labelling scheme. Hydrogen atoms have been omitted for clarity. Ellipsoids represent 50% probability levels.

An analogous arrangement, with similar Ag–N and Ag–O bond distances, is found in the compound {[Ag(bpy)][Ag(HSIP)(bpy)](H$_2$O)$_2$}$_n$ (bpy = bipyridine, H$_3$SIP = 5-sulfoisophthalic acid) for which "Ag(bpy)" units form chains, as do the "Ag(HSIP)(bpy)" units. Both types of chains are linked through Ag···O contacts (2.7598(7) Å).[14] In {[Ag(bpy)][Ag(HSIP)(bpy)](H$_2$O)$_2$}$_n$ the silver centres of the

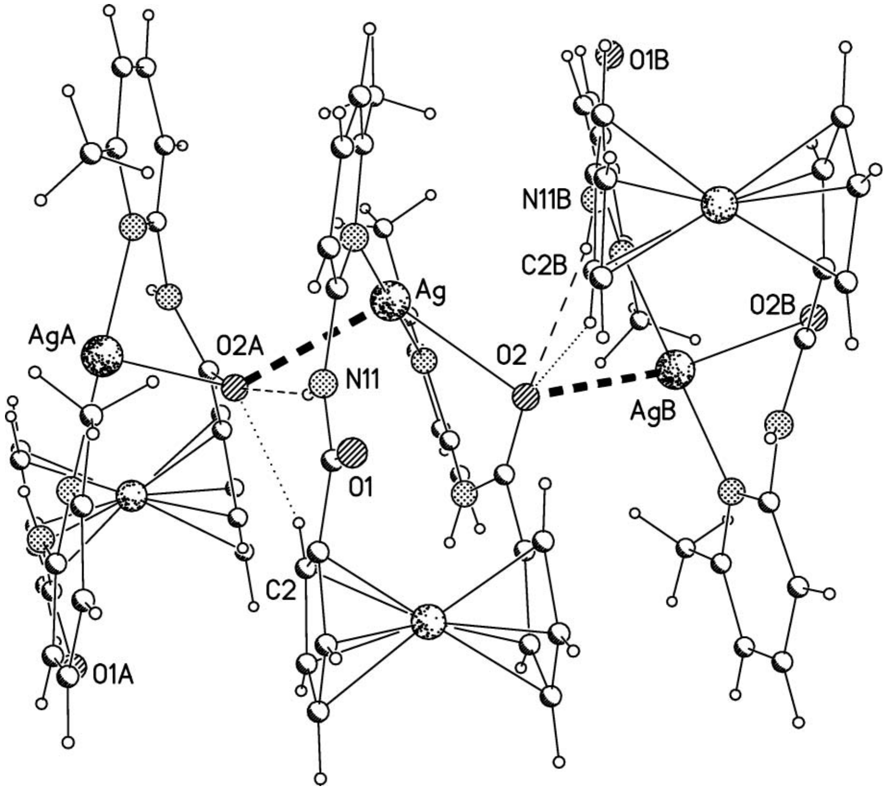


Fig. 4 Formation of chains in **5** through Ag···O contacts (width broad dashed lines) and hydrogen bonds (thin dotted lines).

"Ag(HSIP)(bpy)" fragment displays T-shaped geometry with Ag–N distances of 2.178(7) and 2.209(7) Å (*cf.* 2.1768(19), 2.1998(19) Å found in **5**). These distances are slightly longer than those of the two coordinated linear silver centres in the "Ag(bpy)" units (2.154(7), 2.162(7) Å). The Ag–O bonding distance in **5** (2.5605(16) Å) is longer than that in {[Ag(bpy)][Ag(HSIP)(bpy)](H$_2$O)$_2$} (2.453(7) Å). The bond lengths increase as the number of weak contacts (Ag···N, Ag···O…) increases. Thus longer distances than those in **5** are shown in [Ag$_2${1,2-bis(8-quinolyloxymethyl)benzene}$_3$][15] in which each silver centre displays two short Ag···O (2.656(2)–2.725(2) Å) and one Ag–N (2.714(2)–2.722(2) Å) contacts in addition to two Ag–N and one Ag–O bonds [Ag–N 2.213(2), 2.229(2) Å; Ag–O 2.595(2) Å].

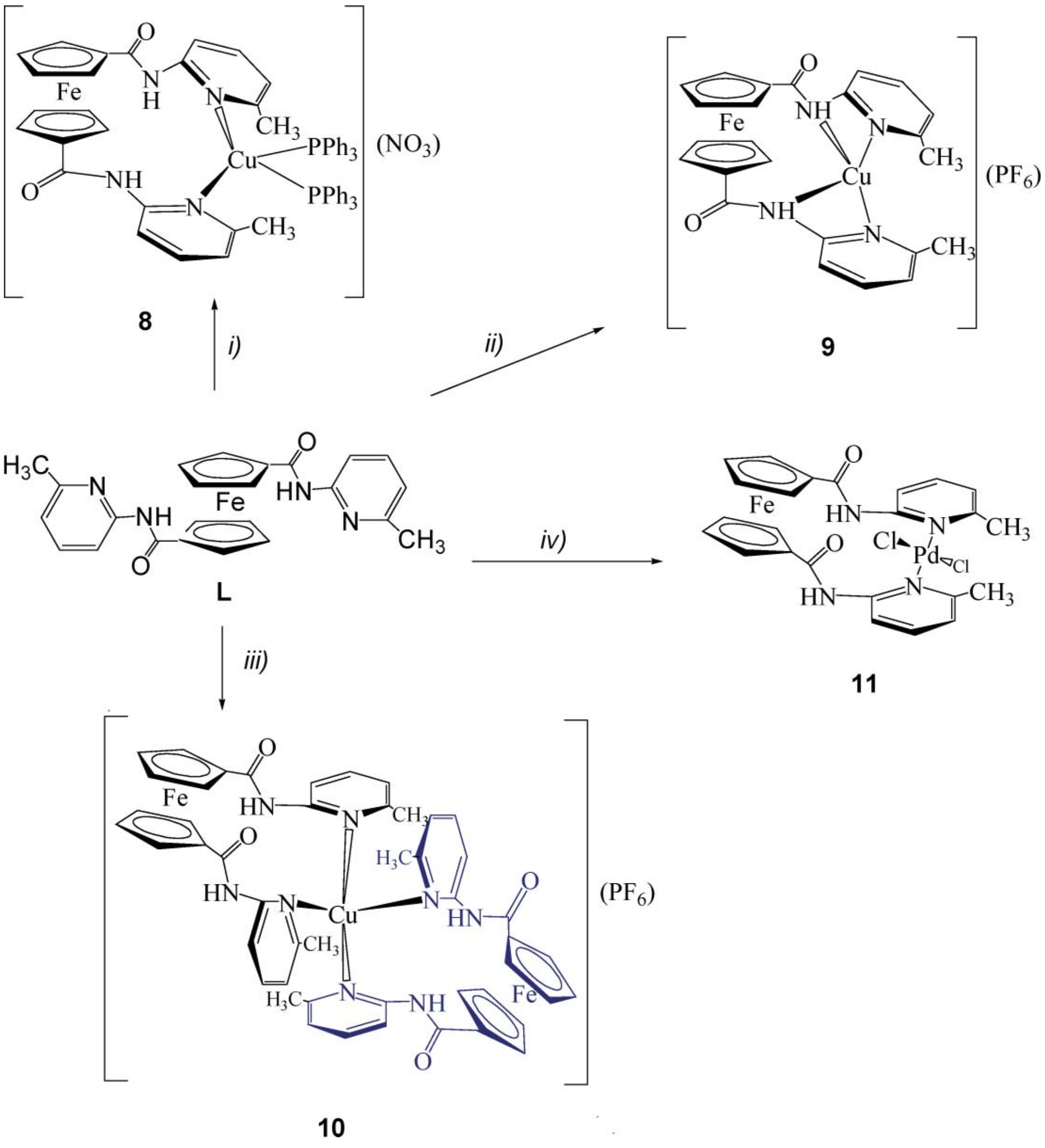
Hydrogen bonds of the type C–H···O and N–H···O are present (see ESI, Table S2†). The oxygen atoms bonded to the silver centre in the chain Ag–O···Ag–O··· are also involved in two hydrogen bonds, one with one of the hydrogen atoms of one of the cyclopentadienyl rings of the adjacent molecule [C2–H2···O2#] [*d*(C–H···O) 3.323(3) Å; *d*(H···O) 2.45 Å], the other with the hydrogen atom of the amide group [N11–H11···O2#] [*d*(N–H···O) 3.150(3) Å; *d*(H···O) 2.40(3) Å], reinforcing the chain (Fig. 4). In each chain the oxygen atoms not bonded to silver (O1) participate in hydrogen bonds with hydrogen atoms of a cyclopentadienyl ring of another molecule [C8–H8···O1#] [*d*(C–H···O 3.292(3) Å; *d*((H···O) 2.57 Å] leading to a 3D structure. The pattern is complicated further by hydrogen bonds involving the oxygen atoms of the triflate groups (*e.g.* from N12–H12 of the chain to O3 of the triflate, *d*(N–H···O) 2.956(3) Å; *d*(H···O) 2.17(3) Å).

The reaction of **L** with Ag(OTf) in a 2 : 1 molar ratio gives the species [Ag(L)$_2$]OTf **6**, in which the silver atom is probably coordinated to two bidentate chelating ligands through the pyridine nitrogen atoms. The IR and NMR data agrees with the proposed formulation.

The treatment of **L** with two equivalents of [Ag(OTf)(PPh$_3$)] leads to the dinuclear species [Ag$_2$(μ-L)(PPh$_3$)$_2$](OTf)$_2$ **7** with the ligand bridging both silver centres. The ^{1}H NMR spectrum presents the resonances for the ligand coordinated to silver and for the triphenylphosphine. The ^{31}P{^{1}H} NMR spectrum at room temperature shows a broad resonance that splits into two doublets at −55 °C because of the coupling of the phosphorus atom with the two silver nuclei, ^{109}Ag and ^{107}Ag. The mass spectrum (LSIMS+) presents the fragments at $m/z = 1343$ (2%) corresponding to the loss of a triflate anion from the molecular peak.

The reactivity of the ferrocene ligand with copper(I) complexes has also been studied and the treatment of [Cu(NO$_3$)(PPh$_3$)$_2$] with **L** gives [Cu(L)(PPh$_3$)$_2$]NO$_3$ **8**, in which presumably the copper centre has a tetrahedral geometry with a coordinated chelating ligand (see Scheme 3). The ^{1}H NMR spectrum shows the resonances for the α and β cyclopentadienyl protons as two multiplets, the protons for the pyridine moieties appear as multiplets and the methyl and amine NH protons as singlets. The ^{31}P{^{1}H} NMR spectrum shows a unique resonance for the phosphine ligands.

The reaction of **L** with [Cu(NCMe)$_4$]PF$_6$ in a 1 : 1 and a 2 : 1 molar ratio has been carried out affording the complexes [Cu(η^4-L)]PF$_6$ **9** and [Cu(L)$_2$]PF$_6$ **10**. In complex **9** we propose that the copper centre is coordinated to the four nitrogen atoms of the ligand, two from the NH groups and two from the pyridine units.



Scheme 3 i) $[Cu(NO_3)(PPh_3)_2]$, ii) $[Cu(NCMe)_4]PF_6$, iii) $\frac{1}{2}$ $[Cu(NCMe)_4]PF_6$, iv) $[PdCl_2(NCPh)_2]$

The coordination mode of the ligand thus resembles that of a macrocyclic ligand. In complex **10** the geometry around the copper atoms should be tetrahedral with two chelating ligands. The ^{1}H NMR spectrum of complex **9**, where coordination to the NH groups is proposed, shows the resonance for the NH protons shifted downfield related to the ligand. The mass spectra presents the cation molecular peak for **9** at $m/z = 517$ ($[CuL]^+$, 20%) and for **10** at $m/z = 971$ ($[CuL_2]^+$, 15%).

Finally, we have also explored the reactivity of ligand L with other transition metal as palladium. Thus the reaction of **L** with the palladium complex *trans*-$[PdCl_2(NCPh)_2]$ has been carried out and gives the complex *trans*-$[PdCl_2(L)]$ **11** (see Scheme 3). The ^{1}H NMR spectrum presents two multiplets for the α and β protons of the cyclopendienyl groups, a singlet for the methyl protons, three multiplets for the (5,5′), (4,4′) and (3,3′) pairs of the pyridine unit and a singlet for the NH protons. The mass spectrum shows the molecular peak at $m/z = 631$ (82%).

The crystal structure of complex **11** has been established by X-ray diffraction studies. Complex **11** crystallizes in the monoclinic system with the palladium and the Fe atoms lying on a twofold symmetry axis; consequently its asymmetric unit contains half of the molecule (Fig. 5 shows the molecule generated by symmetry). Selected bond lengths and angles are shown in Table 3. The palladium centre is chelated by the pyridyl nitrogen atoms of the ferrocene group in a *trans* geometry with *cis* angles of 88.56(10)° and 91.60(10)°; the palladium atom displays a slightly distorted square plane coordination that tends towards tetrahedral: the dihedral angle between the planes formed by N2–Pd1–Cl1A and N2A–Pd–Cl1 is 6.7°, with the chlorine atoms oriented to the inside of the molecule. Two symmetrical intramolecular, weak but significant, hydrogen bonds between each chlorine and the nearest amido proton of the ferrocenyl ligand (H1 $\cdots$ Cl1 distance: 2.81 Å; N1–H1 $\cdots$ Cl1 angle: 134.8°) are present. They could be associated with the distortion of

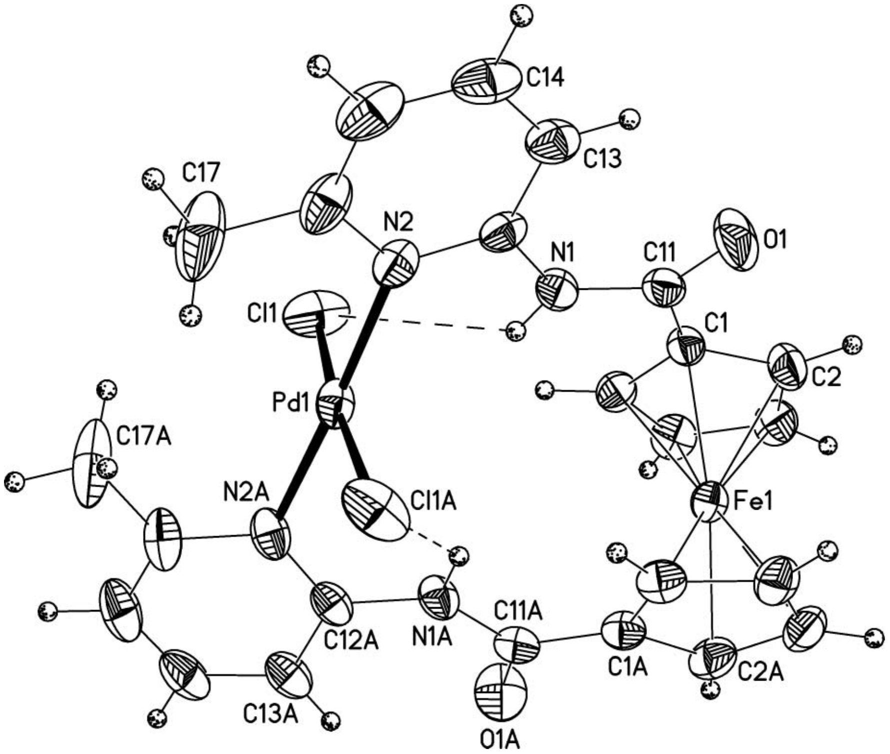


Fig. 5 Molecular structure of compound **11** showing the atom numbering scheme. Displacement parameter ellipsoids represent 50% probability surfaces.

Table 3 Selected bond lengths [Å] and angles [°] for compound **11**

Pd(1)–N(2)#1	2.046(3)	Pd(1)–Cl(1)#1	2.2825(14)
Pd(1)–N(2)	2.046(3)	Pd(1)–Cl(1)	2.2825(14)
N(2)#1–Pd(1)–N(2)	177.09(15)	N(2)#1–Pd(1)–Cl(1)	88.56(10)
N(2)#1–Pd(1)–Cl(1)#1	91.60(10)	N(2)–Pd(1)–Cl(1)	91.60(10)
N(2)–Pd(1)–Cl(1)#1	88.56(10)	Cl(1)#1–Pd(1)–Cl(1)	173.99(6)

Symmetry transformations used to generate equivalent atoms: #1 –x,y,–z+1/2.

the square planar geometry (Fig. 5). Additionally, the molecule presents two short intramolecular interactions between the oxygen of the CO and one proton of the pyridine group of each chain of the ferrocene ligand, that could be considered as hydrogen bonds (H13 · · · O1 distance: 2.29 Å; C13–H13 · · · O1 angle: 118.4°). The cyclopentadienyl rings adopt a staggered orientation with a torsion angle C1–X1–X2–C5A of 20.3°, where X1 and X2 are the centres of the cyclopentadienyl rings. The corresponding angle C1–X1–X2–C1A is 87.2°. The Pd–N (2.046(3) Å) and Pd–Cl (2.2825(14) Å) distances are of the same order than those found in related *trans* square planar palladium(II) complexes such as: $[PdCl_2(2\text{-}BPEFA)]$[16] (2-BPEFA = N,N′-bis{2-(2-pyridyl)ethyl}-1,1′-ferrocenedicarboxiamide), $[PdCl_2(2\text{-}BPMFA)]$[16] (2-BPMFA = N,N′-bis(2-pyridylmethyl)-1,1′-ferrocenedicarboxiamide), $[PdCl_2(FcNP_2)]$[17] ($FcNP_2$ = 1,1′-bis(1,8-naphthyrid-2-yl)ferrocene), $[PdCl_2\{Fc\text{-}(Ala\text{-}L\text{-}Pro\text{-}NHPy)_2\}]$[18] or $[PdCl_2\{Fc(N{=}CH\text{-}6\text{-}Me\text{-}Py)_2\}]$[19] (Pd–N bond distances range from 2.013(5) to 2.06(1) Å and Pd–Cl bond distances from 2.297(3) to 2.315(1) Å). There are no intermolecular H-bonds of note in the structure of this complex **11**.

Conclusions

The 1,1′-bis[((6-methyl)-2-pyridyl)amido]ferrocene ligand (**L**) shows different coordination modes in its coordination to gold, silver, copper and palladium. In most of the complexes studied **L** acts as bidentate chelate or bridging ligand; it is noteworthy that in the silver and palladium species the coordination of the ligand is *trans*-chelating. Other less frequent coordination modes are as a tridentate O,N,N-, as tetradentate neutral NH,NH,N,N- or a tetradentate dianionic N,N,N,N-ligand. In the structures of some of these derivatives the presence of secondary interactions such as weak hydrogen bonds of the type C–H · · · O, C–H · · · N or C–H · · · X (X = F, Cl) or even M · · · O interactions lead to supramolecular networks.

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. 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 liquid secondary-ion mass spectra (LSIMS) technique, using nitrobenzyl alcohol as matrix. NMR spectra were recorded on a Varian Unity 300 spectrometer and a Bruker ARX 300 spectrometer in $CDCl_3$, unless otherwise stated. Chemical shifts are cited relative to $SiMe_4$ (^1H, external), $CFCl_3$ (^{19}F, external) and 85% H_3PO_4 (^{31}P, external).

Starting materials

The starting materials $Fc(COCl)_2$,[20] $[O(AuPPh_3)_3]ClO_4$,[21] $[Au(C_6F_5)(tht)]$,[22] $[Au(C_6F_5)_3(tht)]$,[23] $[Ag(OTf)(PPh_3)]$,[24] $[Cu(NO_3)(PPh_3)_2]$,[25] $[Cu(NCMe)_4]PF_6$,[25] *trans*-$[PdCl_2(NCPh)_2]$[26] were prepared according to published procedures. $[Au(OTf)(PPh_3)]$ was obtained by reaction of $[AuCl(PPh_3)]$[27] with Ag(OTf) in dichloromethane and used *in situ*. All other reagents were commercially available.

Synthesis of $[Au_2(\mu\text{-L})(PPh_3)_2](OTf)_2$ (1). To a solution of **L** (0.045 g, 0.1 mmol) in 20 mL of dichloromethane was added $[Au(OTf)(PPh_3)]$ (0.121 g, 0.2 mmol) under an argon atmosphere. The mixture was stirred for 1 h and then evaporation of the solvent to *ca.* 5 mL and addition of diethyl ether gave complex **1** as an orange solid. Yield, 0.130 g, 78%. $C_{62}H_{52}Au_2F_6FeN_4O_8P_2S_2$ (1670.94): calcd. C 44.56, H 3.13, N 3.35, S 3.83; found C 44.79, H 3.28, N 3.16, S 3.63. ^1H NMR, $\delta = 2.82$ (s, 6H, Me), 4.54 (m, 4H, α-C_5H_4), 5.08 (m, 4H, β-C_5H_4), 7.2-8.0 (m, 6H + 30H, py + Ph), 10.17 (s, 2H, NH). $^{31}P\{^1H\}$ NMR, $\delta = 29.8$ (s, PPh_3). IR: $\upsilon_s(SO_3)$ 1275, $\upsilon_s(CF_3)$ 1222 (vs), $\upsilon_{as}(CF_3)$ 1156 (s) and $\upsilon_s(SO_3)$ 1029 (vs), υ(C=O) 1672 (s) cm^{-1}.

Synthesis of $[Au_4(L\text{-}2H)(PPh_3)_4](ClO_4)_2$ (2). To a solution of **L** (0.045 g, 0.1 mmol) in 20 mL of dichloromethane was added $[O(AuPPh_3)_3]ClO_4$ (0.298 g, 0.2 mmol) under an argon atmosphere. The mixture was refluxed for 24 h and then evaporation of the solvent to *ca.* 5 mL and addition of diethyl ether gave complex **2** as an orange solid. Yield, 0.181 g, 73%. $C_{96}H_{80}Au_4Cl_2FeN_4O_{10}P_4$ (2486.22): calcd. C 46.33, H 3.24, N 2.25; found: C 46.76, H 3.28, N 2.02. ^1H NMR, $\delta = 2.02$ (s, 6H, Me), 4.33 (m, 4H, α-C_5H_4), 5.07 (m, 2H, β-C_5H_4), 5.39 (m, 2H, β-C_5H_4), 6.90 (d, 2H, $J_{HH} = 7.3$ Hz, 5,5′-py), 7.76 (t, 2H, $J_{HH} = 7.78$ Hz, 4,4′-py), 7.90 (d, 2H, $J_{HH} = 8.08$ Hz, 3,3′-py), 7.0-7.6 (m, 60H, Ph). $^{31}P\{^1H\}$ NMR, $\delta = 27.8$ (s, $NAuPPh_3$), 30.2 (s, $pyAuPPh_3$). IR: ClO_4^- 619 (m), 1103 (s).

Synthesis of $[Au_2(C_6F_5)_2(\mu\text{-L})]$ (3). A solution of **L** (0.045 g, 0.1 mmol) in 20 mL of dichloromethane and $[Au(C_6F_5)(tht)]$ (0.090 g, 0.2 mmol) under an argon atmosphere was stirred for 30 min. The solvent was evaporated to *ca.* 5 mL and addition of n-hexane gave complex **3** as a yellow solid. Yield, 0.096 g, 82%. $C_{36}H_{22}Au_2F_{10}FeN_4O_2$ (1182.02): calcd. C 36.54, H 1.87, N 4.73; found: C 36.61, H 1.77, N 4.51. ^1H NMR, $\delta = 2.82$ (s, 6H, Me), 4.46 (m, 4H, α-C_5H_4), 4.81 (m, 4H, β-C_5H_4), 6.82 (d, 2H, $J_{HH} = 7.58$ Hz, 5,5′-py), 7.50 (t, 2H, $J_{HH} = 7.84$ Hz, 4,4′-py), 7.90 (d, 2H, $J_{HH} = 8.34$ Hz, 3,3′-py), 8.52 (s, 2H, NH). ^{19}F NMR, $\delta = -114.9$ (m, 2F, *m*-F), −116.3 (m, 1F, *m*-F), −116.6 (m, 1F, *m*-F), −158.5 (t, 1F, $J_{FF} = 20.2$ Hz, *p*-F), −159.3 (t, 1F, $J_{FF} = 20.2$ Hz, *p*-F), −162.1 (m, 1F, *o*-F), −162.4 (m, 1F, *o*-F), −162.9 (m, 1F, *o*-F), −163.6 (m, 1F, *o*-F). IR: C_6F_5 1505 (vs), 961 (s), 791 (s), ν(C=O) 1664 (s), υ(NH) at 3294 cm^{-1}.

Synthesis of $[Au_2(C_6F_5)_6(\mu\text{-L})]$ (4). To a solution of **L** (0.045 g, 0.1 mmol) in 20 mL of dichloromethane was added $[Au(C_6F_5)(tht)]$ (0.154 g, 0.2 mmol) under an argon atmosphere. The mixture was stirred for 30 min and then evaporation of the solvent to *ca.* 2 mL and addition of n-hexane gave complex **4** as a yellow solid. Yield, 0.124 g, 67%. $C_{60}H_{22}Au_2F_{30}FeN_4O_2$ (1849.99): calcd. C 38.92, H 1.19, N 3.02; found: C 39.12, H 1.17, N 3.0. ^1H NMR, $\delta = 2.95$ (s, 6H, Me), 4.78 (m, 4H, α-C_5H_4), 5.08 (m, 4H, β-C_5H_4), 7.3 (m, 2H, 5,5′-py), 7.92 (t, 2H, $J_{HH} = 8.1$ Hz, 4,4′-py), 8.30 (d, 2H, $J_{HH} = 9.0$ Hz, 3,3′-py), 8.52 (s, 2H, NH). ^{19}F NMR, $\delta = -121.9$ (m, 4F, *m*-F), −122.7 (m, 1F, *m*-F), −122.8 (m, 1F, *m*-F), −155.1 (t, 2F, $J_{FF} = 20.6$ Hz, *p*-F), −155.8 (t, 1F, $J_{FF} = 20.6$ Hz, *p*-F), −160.1 (m, 4F, *o*-F), −160.7 (m, 1F, *o*-F), −161.0 (m, 1F, *o*-F). IR: C_6F_5, 1510 (vs), 967 (vs), 817 (m) and 795 (m) cm^{-1}.

Synthesis of $[Ag(\eta^3\text{-L})]OTf$ (5). To a solution of **L** (0.045 g, 0.1 mmol) in 20 mL of dichloromethane was added Ag(OTf) (0.025 g, 0.1 mmol) under an argon atmosphere. The mixture was stirred for 30 min and then evaporation of the solvent to *ca.* 5 mL and addition of diethyl ether gave complex **5** as an orange solid. Yield, 0.042 g, 60%. $C_{25}H_{22}AgF_3FeN_4O_5S$ (709.96): calcd. C 42.25, H 3.12, N 7.89, S 4.50; found C 42.21, H 3.19, N 7.70, S 4.41. ^1H NMR, $\delta = 2.69$ (s, 6H, Me), 4.47 (m, 4H, α-C_5H_4), 5.08 (m, 4H, β-C_5H_4), 7.0.2 (m, 2H, 5,5′-py), 7.66 (m, 4H, 4,4′-py + 3,3′-py), 9.41 (s, 2H, NH). IR: υ(C=O) 1610 (m) and 1659 (m) cm^{-1}, $\upsilon_s(SO_3)$ 1281 (vs), $\upsilon_s(CF_3)$ 1224 (vs), $\upsilon_{as}(CF_3)$ 1165 (s) and $\upsilon_s(SO_3)$ 1028 (vs) cm^{-1}.

Synthesis of $[Ag(L)_2]OTf$ (6). To a solution of **L** (0.090 g, 0.2 mmol) in 20 mL of dichloromethane was added Ag(OTf) (0.025 g, 0.1 mmol) under an argon atmosphere. The mixture was stirred for 30 min and then evaporation of the solvent to *ca.* 5 mL and addition of diethyl ether gave complex **5** as a yellow solid. Yield, 0.093 g, 80%. $C_{49}H_{44}AgF_3Fe_2N_8O_7S$ (1164.07): calcd. C 50.51, H 3.81, N 9.62, S 2.74; found C 50.57, H 3.94, N 9.77, S 2.64. ^1H NMR, $\delta = 2.69$ (s, 6H, Me), 4.50 (m, 4H, α-C_5H_4), 5.01 (m, 4H, β-C_5H_4), 7.02 (d, 2H, $J_{HH} = 7.32$ Hz, 5,5′-py), 7.69 (t, 2H, $J_{HH} = 7.58$ Hz, 4,4′-py), 7.76 (d, 2H, $J_{HH} = 7.58$ Hz, 3,3′-py), 9.08 (s, 2H, NH). IR υ(C=O) at 1611 (s) and 1687 (s), $\upsilon_s(SO_3)$ 1279 (vs), $\upsilon_s(CF_3)$ 1225 (vs), $\upsilon_{as}(CF_3)$ 1160 (s) and $\upsilon_s(SO_3)$ 1024 (vs) cm^{-1}.

Synthesis of $[Ag_2(\mu\text{-L})(PPh_3)_2](OTf)_2$ (7). To a solution of **L** (0.045 g, 0.1 mmol) in 20 mL of dichloromethane was added $[Ag(OTf)(PPh_3)]$ (0.103 g, 0.2 mmol) under an argon atmosphere. The mixture was stirred for 30 min and then evaporation of the solvent to *ca.* 5 mL and addition of diethyl ether gave complex **6** as an orange solid. Yield, 0.108 g, 73%. $C_{62}H_{52}Ag_2F_6FeN_4O_8P_2S_2$ (1490.0): calcd. C 49.93, H 3.51, N 3.76, S 4.29; found C 49.70, H 3.62, N 3.56, S 4.33. ^1H NMR, $\delta = 2.63$ (s, 6H, Me), 4.55 (m, 4H, α-C_5H_4), 5.12 (m, 4H, β-C_5H_4), 6.81 (m, 2H, 5,5′-py), 7.3-7.8 (m, 30H + 4H, Ph + 4,4′-py + 3,3′-py), 9.56 (s, 2H, NH). $^{31}P\{^1H\}$ NMR, r.t. $\delta = 13.5$ (s, br); -55 °C $\delta = 13.1$ (2d, $J_{109AgP} = 756$ Hz, $J_{107AgP} = 656$ Hz). IR: υ(C=O) 1652 (s), $\upsilon_s(SO_3)$ 1289 (vs), $\upsilon_s(CF_3)$ 1233 (vs), $\upsilon_{as}(CF_3)$ 1169 (s) and $\upsilon_s(SO_3)$ 1024 (vs) cm^{-1}.

Synthesis of $[Cu(\mu\text{-L})(PPh_3)_2]NO_3$ (8). To a solution of **L** (0.045 g, 0.1 mmol) in 20 mL of dichloromethane was added $[Cu(NO_3)(PPh_3)_2]$ (0.065 g, 0.1 mmol) under an argon atmosphere. The mixture was stirred for 30 min and then evaporation of the solvent to *ca.* 5 mL and addition of diethyl ether gave complex **6** as an orange solid. Yield, 0.088 g, 80%. $C_{60}H_{52}CuFeN_5O_5P_2$ (1103.20): calcd. C 65.26, H 4.75, N 6.34; found C 65.30, H 4.90, N 6.19. ^1H NMR, $\delta = 2.63$ (s, 6H, Me), 4.64 (m, 4H, α-C_5H_4), 5.12 (m, 4H, β-C_5H_4), 7.11 (m, 2H, 5,5′-py), 7.3–7.4 (m, 30H + 2H, Ph + 4,4′-py), 7.96 (m., 2H, 3,3′-py), 8.43 (s, 2H, NH). $^{31}P\{^1H\}$ NMR, $\delta = -1.7$ (s). IR: υ(C=O) 1693 (s), NO_3^- 1770 (w), 1067 (w), 1041 (m), 996 (w), 838 (m) and 693 (s) cm^{-1}.

Table 4 X Ray data for complexes **1**, **5** and **11**

Compound	**1**	**5**	**11**
Formula	$C_{62}H_{52}Au_2F_6FeN_4O_8P_2S_2$	$C_{25}H_{22}AgF_3FeN_4O_5S$	$C_{24}H_{22}Cl_2FeN_4O_2Pd$
M_r	1670.92	711.25	631.63
Habit/Colour	Needle/Yellow	Needle/Orange	Prism/Orange
Crystal size/mm	0.23 × 0.06 × 0.06	0.46 × 0.07 × 0.05	0.24 × 0.18 × 0.08
Crystal system	Triclinic	Tetragonal	Monoclinic
Space group	$P\bar{1}$	$P4_3$	$C2/c$
Cell constants:			
a/Å	9.494(3)	12.0259(6)	18.883(13)
b/Å	11.430(4)	12.0259(6)	12.044(7)
c/Å	16.213(6)	17.3790(14)	12.081(8)
α (°)	100.608(12)	90	90
β (°)	102.036(12)	90	121.67(2)
γ (°)	110.857(12)	90	90
Z	1	4	4
D_x (Mg m^{-3})	1.799	1.880	1.794
μ/mm^{-1}	5.172	1.509	1.649
F(000)	816	1424	1264
T/°C	–100	–100	–173
$2\theta_{max}$	56	56	54
No. of refl.:			
measured	28783	4889	7208
independent	7642	6237	2541
Transmissions	0.928, 0.477	0.962, 0.776	0.8794, 0.6930
R_{int}	0.0743	0.0432	0.0382
Parameters	472	371	156
Restraints	579	1	0
$wR(F^2$, all Refl.)	0.1267	0.0491	0.0728
$R(I, >2\sigma(I))$	0.0507	0.0230	0.0348
S	1.023	1.030	0.947
max. $\Delta\rho$/e Å^{-3}	4.071	0.456	0.522

Synthesis of [Cu(η^4-L)]PF$_6$ (9). To a solution of **L** (0.045 g, 0.1 mmol) in 20 mL of dichloromethane was added [Cu(NCMe)$_4$]PF$_6$ (0.038 g, 0.1 mmol) under an argon atmosphere. The mixture was stirred for 30 min and then evaporation of the solvent to *ca.* 5 mL and addition of diethyl ether gave complex **9** as an orange solid. Yield, 0.047 g, 71%. $C_{24}H_{22}CuF_6FeN_4O_2P$ (662.0): calcd. C 43.50, H 3.34, N 8.46; found C 43.54, H 3.42, N 8.58. ^{1}H NMR, $\delta = 2.81$ (s, 6H, Me), 4.71 (m, 4H, α-C_5H_4), 5.0 (m, 4H, β-C_5H_4), 7.20 (m, 2H, 5,5′-py), 7.88 (m, 2H, 4,4′-py), 7.82 (m., 2H, 3,3′-py), 8.90 (s, 2H, NH). IR: υ(C=O) 1682 (s), PF_6^- 844 (s) cm^{-1}.

Synthesis of [Cu(L)$_2$]PF$_6$ (10). To a solution of **L** (0.090 g, 0.2 mmol) in 20 mL of dichloromethane was added [Cu(NCMe)$_4$]PF$_6$ (0.038 g, 0.1 mmol) under an argon atmosphere. The mixture was stirred for 30 min and then evaporation of the solvent to *ca.* 5 mL and addition of diethyl ether gave complex **10** as an orange solid. Yield, 0.083 g, 75%. $C_{48}H_{44}CuF_6Fe_2N_8O_4P$ (1116.11): calcd. C 51.60, H 3.97, N 10.03; found C 51.83, H 4.18, N 9.90. ^{1}H NMR, $\delta = 2.57$ (s, 6H, Me), 4.59 (m, 4H, α-C_5H_4), 4.92 (m, 4H, β-C_5H_4), 6.99 (m, 2H, 5,5′-py), 7.65 (m, 2H, 4,4′-py), 7.84 (m, 2H, 3,3′-py), 8.70 (s, 2H, NH). IR: υ(C=O) 1163 (s), PF_6^- 844 (s) cm^{-1}.

Synthesis of [PdCl$_2$L] (11). To a solution of **L** (0.045 g, 0.1 mmol) in 20 mL of dichloromethane was added *trans*-[PdCl$_2$(NCPh)$_2$] (0.038 g, 0.1 mmol) under an argon atmosphere. The mixture was stirred for 30 min and then evaporation of the solvent to *ca.* 5 mL and addition of n-hexane gave complex **11** as an orange solid. Yield, 0.083 g, 71%. $C_{24}H_{22}Cl_2FeN_4O_2Pd$ (629.95): calcd. C 45.71, H 3.52, N 8.89; found C 46.03, H 3.88, N 9.13. ^{1}H NMR, $\delta = 3.48$ (s, 6H, Me), 3.62 (m, 4H, α-C_5H_4), 4.72 (m, 4H, β-C_5H_4), 7.06 (m, 2H, 5,5′-py), 7.73 (m, 2H, 4,4′-py), 8.20 (m., 2H, 3,3′-py), 10.47 (s, 2H, NH).

X-ray crystallography

Data were recorded with a Bruker SMART 1000 CCD diffractometer. Data collection type: ω-scans and ϕ-scans. Absorption corrections were based on multiple scans with the program SADABS.[28] The structures were refined on F^2 using the program SHELXL-97.[29] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were including using a rigid (methyl groups) or riding model. Refinement special details: The triflate anion in **1** is disordered over two positions with occupation factors 0.54, 0.46. The residual electronic density can be attributed to the irregular broad reflections associated with the needle shape of the crystal. Compound **5** crystallizes by chance in a chiral space group. The absolute structure and thus the space group $P4_3$ (rather than $P4_1$) were determined by the Flack parameter –0.014(11). Further crystallographic details are given in Table 4.

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