

Metal Complexes with Mono- and Bis{[bis(2-pyridyl)amino]carbonyl}ferrocene Ligands

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The ligands {[bis(2-pyridyl)amino]carbonyl}ferrocene (**L1**) and 1,1'-bis{[bis(2-pyridyl)amino]carbonyl}ferrocene (**L2**) have been prepared by treatment of the mono- or 1,1'-bis(chlorocarbonyl)ferrocene derivatives with dipyridylamine in a 1:1 or 1:2 ratio, respectively. The ligand properties of these compounds towards group 11 and palladium complexes have been studied. Ligand **L1** coordinates to these compounds to give four-coordinate [Cu(**L1**)₂]⁺, [PdCl₂(**L1**)] and [Ag(OTf)(**L1**)(PR₃)] or three-coordinate [Ag(OTf)(**L1**)] and [Au(C₆F₅)(**L1**)] compounds. The ligand coordinates in a chelate fashion in all cases. The reactivity of **L2** is somewhat different because coordination to copper or silver atoms can

take place through several pyridine units either from different cyclopentadienyl rings, as in [Cu(**L2**)]⁺, [Ag₂(OTf)₂(**L2**)] and [Ag(OTf)(**L2**)(PPh₃)], or from the same cyclopentadienyl ring, as in [Ag₂(OTf)₂(**L2**)(PPh₃)₂]. Coordination as a bridging ligand for four gold atoms has also been achieved in [Au₄(C₆F₅)₄(**L2**)] and [Au₄(**L2**)(PPh₃)₄](OTf)₄. The ligands and some complexes have been characterized by X-ray diffraction studies and show the presence of several hydrogen bonds that lead to supramolecular structures.

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Introduction

Ferrocene is a very versatile molecule with important properties such as high electron density, aromaticity and redox reversibility. These characteristics, together with the ease of preparation of mono- and 1,1'-disubstituted ferrocene derivatives with a great variety of organic fragments that may contain O, N, S, P, etc. as donor atoms, make ferrocene an ideal building block in many fields of research.^[1–3] Current areas of interest in ferrocene chemistry include its use in catalysis, materials and bioinorganic chemistry. These functionalized ferrocene derivatives and the study of their coordination to metal centres are an important topic of research in many areas that seek special properties for such species, especially nonlinear optical properties, charge transport, liquid crystals, electrochemical recognition, catalysis, nanoparticles, immunoassay reagents or biological applications.^[1–17]

The introduction of a ferrocene group into supramolecular coordination systems not only incorporates a redox-active group but could also lead 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 and their interesting coordination properties.^[18] 1,1'-Bis(4-pyridyl)ferrocene, for example, gives supramolecular heterometallic metallamacrocycles.^[19] Supramolecular networks resulting from coordination or weak hydrogen bonding have also been achieved with other substituted ferrocenes with azolate ligands.^[20]

Continuing our studies in this field, in which we have described several ferrocene ligands that show interesting coordination properties and, in some cases, supramolecular motifs through weak hydrogen bonds,^[21–27] we report here the synthesis of two (aminocarbonyl)ferrocene derivatives that contain several pyridine groups. The coordination properties of these ligands towards group 11 metals and palladium have been studied. They can act as bidentate or tetradentate chelating or bridging ligands. The structurally characterized derivatives show supramolecular structures through weak hydrogen bonding involving the oxygen, fluorine and/or chlorine atoms.

Results and Discussion

The ligands {[bis(2-pyridyl)amino]carbonyl}ferrocene (**L1**) and 1,1'-bis{[bis(2-pyridyl)amino]carbonyl}ferrocene (**L2**) were prepared by treatment of the mono- or 1,1'-bis(chlorocarbonyl)ferrocene derivatives with dipyridylamine, in a 1:1 or 1:2 molar ratio, respectively, in dichloro-

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methane in the presence of NEt_3 [see Equations (1) and (2)]. The IR spectrum of **L1** shows a $\nu(\text{C}=\text{O})$ absorption for the amide group at 1674 cm^{-1} and $\nu(\text{C}=\text{N})$ absorptions at 1558 and 1567 cm^{-1} . The ^1H NMR spectrum shows two multiplets for the α - and β -protons of the substituted cyclopentadienido group, a singlet for the protons of the unsubstituted cyclopentadienido ring and four typical resonances

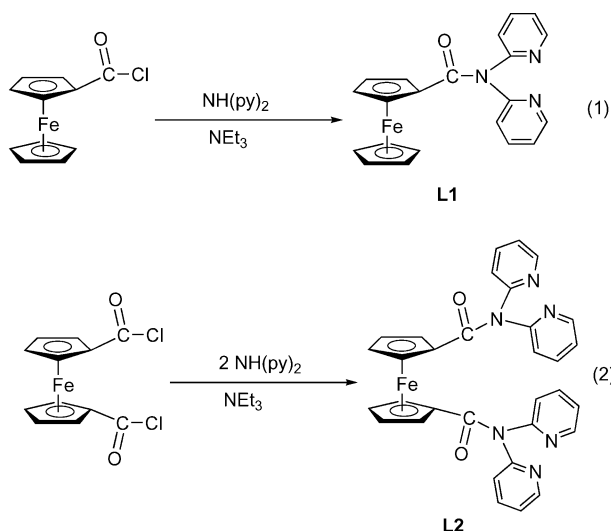


Table 1. Hydrogen bonds for **L1**, **L2**, **6** and **8** [$\text{\AA}$ and $^\circ$].

	$d(\text{H}\cdots\text{A})$	$d(\text{D}\cdots\text{A})$	$\angle(\text{DHA})$
L1			
$\text{C}(5)\text{--H}(5)\cdots\text{O}(1)\#1$	2.60	3.463(2)	150.9
$\text{C}(16)\text{--H}(16)\cdots\text{O}(1)\#2$	2.37	3.267(2)	157.3
Symmetry transformations used to generate equivalent atoms: #1: $x, y+1, z$; #2: $x, -y, z-1/2$.			
L2			
$\text{C}(16)\text{--H}(16)\cdots\text{N}(22)\#1$	2.59	3.395(2)	143.1
$\text{C}(23)\text{--H}(23)\cdots\text{O}\#2$	2.63	3.546(2)	162.8
$\text{C}(15)\text{--H}(15)\cdots\text{O}\#3$	2.67	3.609(2)	168.1
Symmetry transformations used to generate equivalent atoms: #1: $-x+1, y, -z+1/2$; #2: $x, -y+1, z-1/2$; #3: $-x+1, -y+1, -z+1$.			
Complex 6			
$\text{C}(15)\text{--H}(15)\cdots\text{O}(1)\#1$	2.48	3.259(4)	138.7
$\text{C}(22)\text{--H}(22\text{A})\cdots\text{Cl}(1)\#2$	2.85	3.669(4)	140.9
$\text{C}(18)\text{--H}(18)\cdots\text{Cl}(2)\#2$	2.87	3.524(3)	126.8
$\text{C}(20)\text{--H}(20)\cdots\text{Cl}(3)\#3$	2.84	3.645(3)	142.6
$\text{C}(21)\text{--H}(21)\cdots\text{Cl}(1)\#4$	2.87	3.510(3)	125.5
$\text{C}(16)\text{--H}(16)\cdots\text{Cl}(3)\#1$	2.87	3.595(4)	133.4
Symmetry transformations used to generate equivalent atoms: #1: $-x, -y+1, -z+1$; #2: $x+1, y, z$; #3: $x, y, z-1$; #4: $-x, -y+1, -z$.			
Complex 8			
$\text{C}(9)\text{--H}(9)\cdots\text{O}(1)\#1$	2.53	3.408(5)	154.2
$\text{C}(3)\text{--H}(3)\cdots\text{O}(2)\#2$	2.37	3.223(5)	149.0
$\text{C}(4)\text{--H}(4)\cdots\text{O}(4)\#2$	2.48	3.403(5)	164.5
$\text{C}(8)\text{--H}(8)\cdots\text{F}(1)\#2$	2.45	3.241(5)	140.7
$\text{C}(53)\text{--H}(53)\cdots\text{O}(3)$	2.35	3.096(5)	135.4
$\text{C}(33)\text{--H}(33)\cdots\text{O}(5)$	2.57	3.309(6)	134.3
Symmetry transformations used to generate equivalent atoms: #1: $-x, -y, -z+1$; #2: $-x+1, -y, -z+1$.			

for the equivalent pyridine moieties. The molecular peak in the mass spectrum (LSIMS+) appears at m/z (%) = 383 (100). The ligand **L2** also shows the $\nu(\text{C}=\text{O})$ absorption of the amide group at 1670 cm^{-1} in its IR spectrum. The ^1H NMR spectrum contains two multiplets for the α - and β -protons of the cyclopentadienido groups and four resonances for the pyridine units. The mass spectrum shows the molecular peak with an additional proton at m/z (%) = 581 (20).

The structures of both ligands were established by X-ray diffraction. Selected bond lengths and angles and the drawings of the molecules are available as Supporting Information. The cyclopentadienido rings in **L1** are almost eclipsed, and the pyridine units are almost perpendicular to each other (interplanar angle 98.7°). The bond lengths and angles are typical of this type of compounds. There are several contacts between the oxygen atom and the protons of the cyclopentadienido or pyridine rings in the range $2.37\text{--}2.60\text{ \AA}$ with angles close to 180° ; these can be classified as hydrogen bonds (Table 1) and lead to a supramolecular network. The shortest one [$\text{O}1\cdots\text{H}16$ $2.370(1)\text{ \AA}$] leads to the formation of chains (Figure 1). The molecule of **L2** shows crystallographic twofold symmetry with the two bis(2-pyridyl)amino units in the ferrocene moiety staggered by 72° .

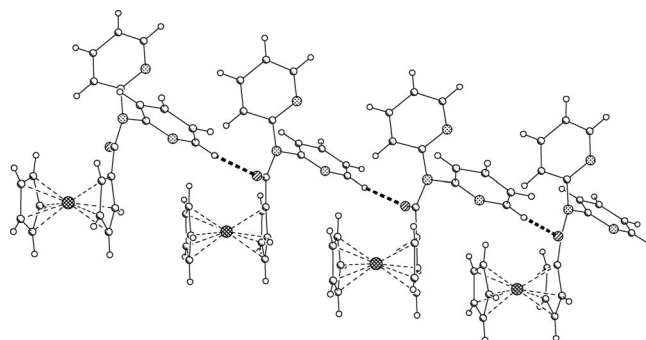


Figure 1. Formation of chains through hydrogen bonds (dotted lines) in **L1**.

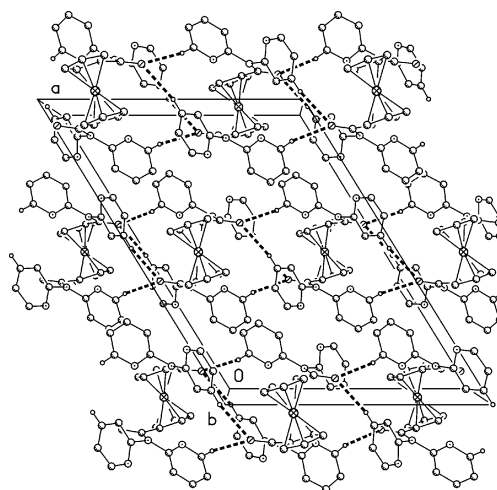


Figure 2. Chains of molecules parallel to the z axis formed by hydrogen bonds (dotted lines) in **L2**.

The two carbonyl groups point to the inside of the ferrocene moiety, with the pyridine rings perpendicular to them. The C=O and N–C distances are normal for this type of compound. This molecule also contains several hydrogen bonds with the oxygen atom as acceptor. The contacts O...H15 (2.65 Å) and O...H23 (2.63 Å) combine to form chains of molecules parallel to the *z* axis (Figure 2).

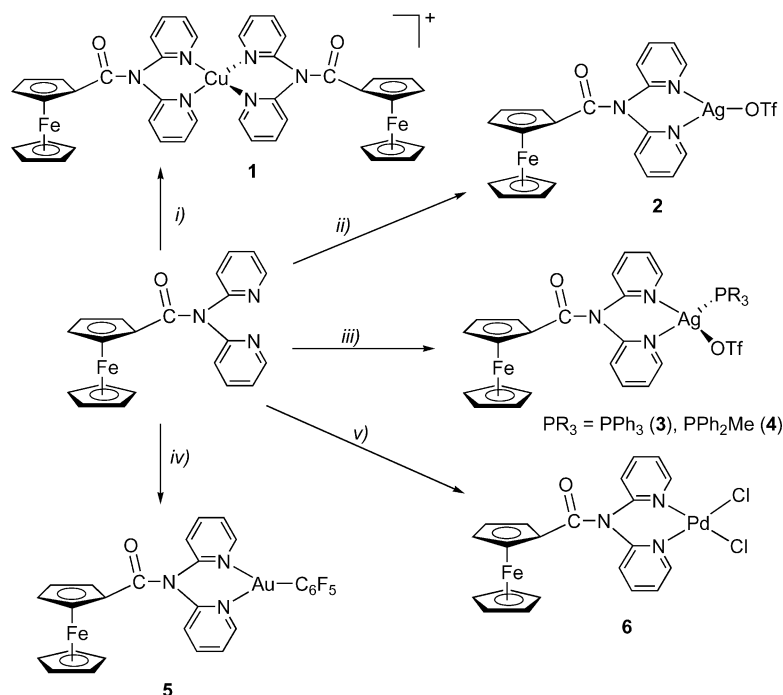
The reaction of **L1** with [Cu(NCMe)₄]PF₆ in a 2:1 molar ratio gives the complex [Cu(L1)₂]PF₆ (**1**). We assume that the structure corresponds to a four-coordinate copper atom with a tetrahedral geometry (Scheme 1). The ¹H NMR spectrum shows broad resonances with chemical shifts different from those of the uncoordinated ligand. The mass spectrum shows the cationic molecular peak [Cu(L1)₂]⁺ at *m/z* (%) = 829 (95). Treatment of **L1** with Ag(OTf) in a 1:1 molar ratio gives the mononuclear complex [Ag(OTf)(L1)] (**2**), whose spectroscopic data are consistent with the coordination of the silver centre to the ligand, presumably through the nitrogen atoms of the pyridine moieties and the oxygen atom of the triflate anion. The mass spectrum shows the cationic molecular peak [Ag(L1)]⁺ at *m/z* (%) = 490 (55). Treatment of the ligand with the silver complex [Ag(OTf)(PR₃)] gives the four-coordinate species [Ag(OTf)(L1)(PR₃)] [PR₃ = PPh₃ (**3**), PPh₂Me (**4**)] in high yields. Complexes **3** and **4** show two multiplets for the α- and β-protons of the substituted cyclopentadienido rings, a singlet for the protons of the unsubstituted cyclopentadienido units and resonances for the pyridine and phenyl protons in their ¹H NMR spectra. Compound **4** also shows a broad resonance for the methyl protons coupled to the phosphorus atom. The ³¹P{¹H} NMR spectrum contains a broad resonance at room temperature that splits into two doublets

at –55 °C due to coupling of the phosphorus atoms with the two silver nuclei ¹⁰⁷Ag and ¹⁰⁹Ag.

The reaction of **L1** with 1 equiv. of [Au(C₆F₅)(tbt)] gives the complex [Au(C₆F₅)(L1)] (**5**) in which the ligand may be acting in a chelating mode to afford a three-coordinate gold(I) derivative. The ¹H NMR spectrum of **5** shows that the resonances for both pyridine groups are equivalent, which is consistent with a trigonal-planar disposition for the gold centre. The ¹⁹F NMR spectrum shows the three typical resonances for a pentafluorophenyl ring (two multiplets for the *ortho*- and *meta*-fluorine atom and a triplet for the *para*-fluorine atom). The mass spectrum contains the molecular peak at *m/z* (%) = 747 (80).

Treatment of **L1** with [PdCl₂(NCPh)₂] in a 1:1 molar ratio leads to the complex [PdCl₂(L1)] (**6**), by displacement of the benzonitrile ligands, in which the ligand coordinates as a chelate. The ¹H NMR spectrum of this complex shows the typical resonances for the coordinated ligand. The mass spectrum contains the molecular peak at *m/z* (%) = 561 (65).

The structure of complex **6** was confirmed by X-ray diffraction (Figure 3). A selection of bond lengths and angles are collected in Table 2. The coordination of the palladium centre is square-planar with very regular angles, with the largest deviation corresponding to the N–Pd–N angle [86.54(10)°]. The Pd–Cl [2.2801(8) and 2.2906(9) Å] and Pd–N distances [2.029(3) and 2.034(3) Å] are similar to those found in other palladium complexes, and the cyclopentadienido rings are almost ideally staggered. There are several secondary bonds that can be classified as hydrogen bonds, as, for example, those formed between the oxygen atom and one of the protons of a pyridine ring (H15) of



Scheme 1. (i) 1/2 [Cu(NCMe)₄]PF₆, (ii) Ag(OTf), (iii) [Ag(OTf)(PR₃)], (iv) [Au(C₆F₅)(tbt)], (v) [PdCl₂(NCPh)₂].

2.485 Å (H...O), which leads to the formation of dimers (Figure 4), or those involving the chlorine atoms bound to the palladium atom and the dichloromethane solvent, which leads to a three-dimensional network.

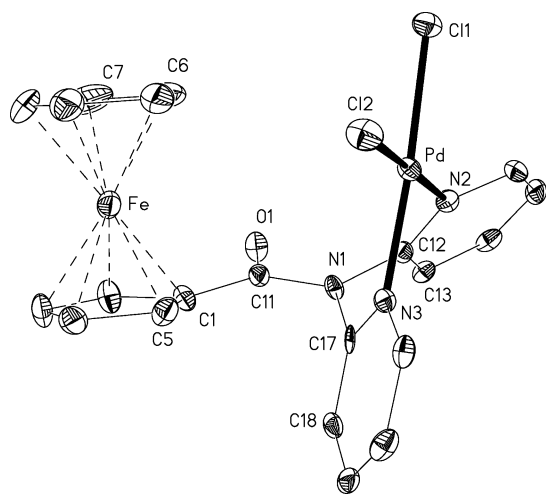


Figure 3. Molecular structure of complex **6** showing the atom-numbering scheme. Displacement parameter ellipsoids represent 50% probability surfaces. Hydrogen atoms and solvent molecules have been omitted for clarity.

Table 2. Selected bond lengths [Å] and angles [°] for complex **6**.

Pd–N(2)	2.029(3)
Pd–N(3)	2.034(3)
Pd–Cl(2)	2.2801(8)
Pd–Cl(1)	2.2906(9)
N(2)–Pd–N(3)	86.54(10)
N(2)–Pd–Cl(2)	176.60(8)
N(3)–Pd–Cl(2)	91.09(7)
N(2)–Pd–Cl(1)	90.50(8)
N(3)–Pd–Cl(1)	174.42(8)
Cl(2)–Pd–Cl(1)	92.07(3)
N(2)–C(12)–N(1)	114.9(3)
N(3)–C(17)–N(1)	116.4(3)
C(12)–N(2)–Pd	119.5(2)
C(16)–N(2)–Pd	121.8(2)

The reactivity of **L2** towards group 11 metals has also been studied (Scheme 2). Thus, the treatment of **L2** with 1 equiv. of [Cu(NCMe)₄]PF₆ gives a compound of stoichiometry [Cu(**L2**)PF₆] (**7**). The ligand possesses four pyridine groups that can coordinate to the copper centre in a tetrahedral geometry, thereby acting as a tetradentate ligand. The IR spectrum of **7** shows the absorption of the hexafluorophosphate anion at 884 cm^{−1} (vs) and the ν(C=O) absorption at 1667 cm^{−1} (s). The ¹H NMR spectrum shows two multiplets for the α- and β-protons of the cyclopentadienylidene rings and one unique broad multiplet for the pyridine protons. The mass spectrum shows the cationic molecular peak at *m/z* (%) = 644 (75).

The reaction of **L2** with 2 equiv. of Ag(OTf) gives [Ag₂(OTf)₂(μ-**L2**)] (**8**), in which each silver centre is bonded to

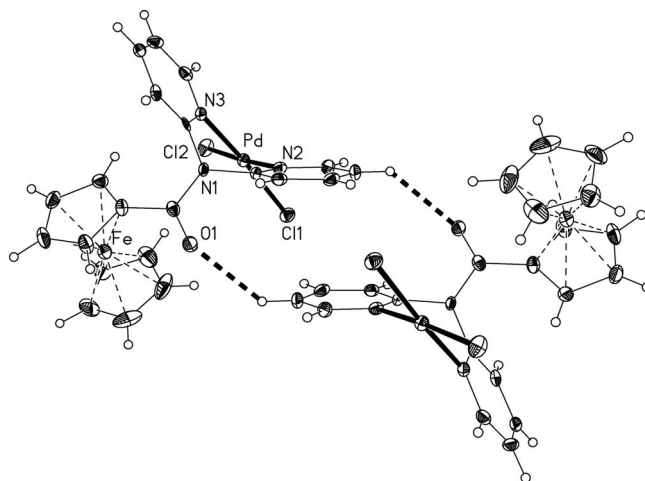


Figure 4. Some hydrogen bonds in complex **6**.

two pyridine groups of different ligands. The IR spectrum of compound **8** shows the presence of coordinated triflate ligands, with ν_s(SO₃) absorptions at 1273 and 1255 (vs), ν_s(CF₃) absorptions at 1231 (s), ν_{as}(CF₃) absorptions at 1166 (s) and ν_s(SO₃) absorptions at 1046 cm^{−1} (s). The α- and β-protons appear as two multiplets in the ¹H NMR spectrum, thereby indicating that both cyclopentadienylidene rings are equivalent. There are also three resonances for the pyridine protons, some of which are overlapped.

The structure of complex **8** was confirmed by X-ray diffraction and is shown in Figure 5. No short argentophilic interaction is present [Ag(1)–Ag(2) 3.461 Å]. Each silver atom is bonded to two nitrogen atoms of the pyridine rings of different bis(2-pyridyl)amino units that are staggered by 61.5° (72° in **L2**). The geometry around the silver atoms is

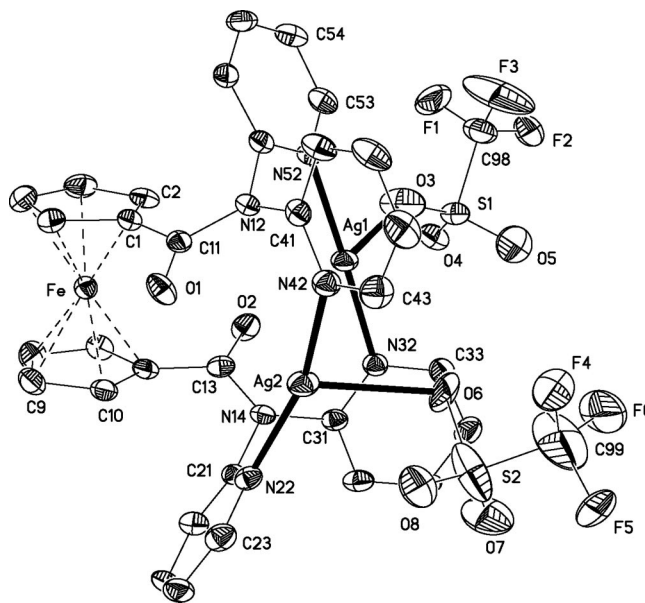
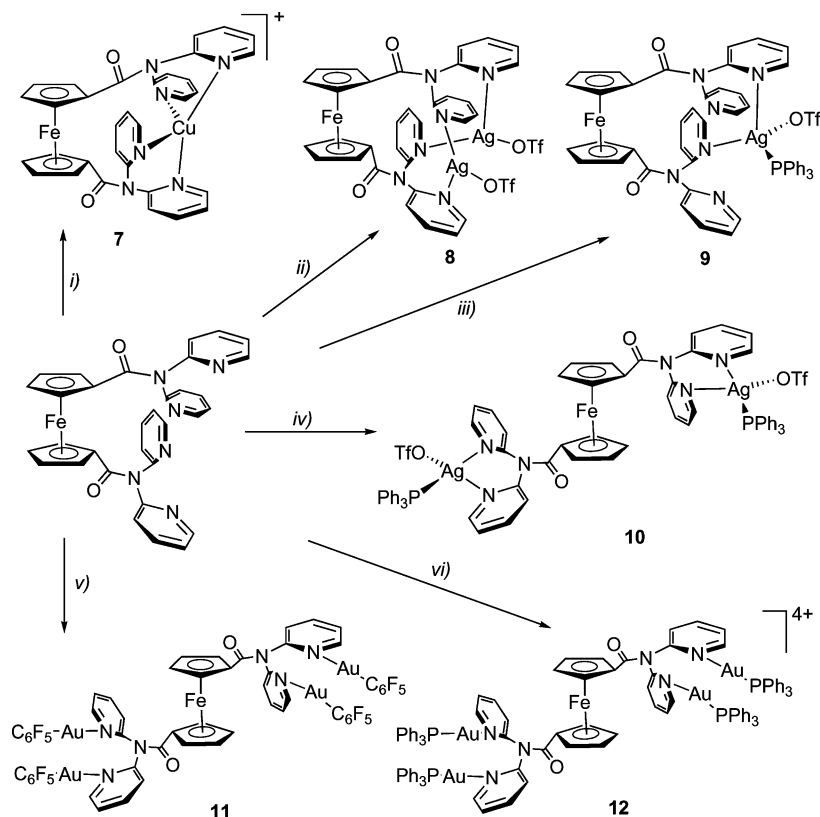


Figure 5. Molecular structure of compound **8** showing the atom-numbering scheme. Displacement parameter ellipsoids represent 30% probability surfaces. Hydrogen atoms have been omitted for clarity. Only one position of the disordered triflate group is shown.



Scheme 2. (i) $1/2$ $[\text{Cu}(\text{NCMe})_4]\text{PF}_6$, (ii) $2 \text{ Ag}(\text{OTf})$, (iii) $[\text{Ag}(\text{OTf})(\text{PPh}_3)]$, (iv) $2 [\text{Ag}(\text{OTf})(\text{PPh}_3)]$, (v) $4 [\text{Au}(\text{C}_6\text{F}_5)(\text{ttht})]$, (vi) $4 [\text{Au}(\text{OTf})(\text{PPh}_3)]$.

slightly distorted from linear $[\text{N}(32)-\text{Ag}(1)-\text{N}(52) 178.03^\circ$, $\text{N}(42)-\text{Ag}(2)-\text{N}(22) 161.37^\circ$; Table 3]. This distortion is probably due to the coordination of each silver atom to one oxygen atom belonging to one triflate group. The triflate group bonded to Ag2 is disordered, and the $\text{Ag}(2)-\text{O}(6)$ distance in Table 3 should be interpreted with caution (see refinement, special details). The $\text{Ag}(1)-\text{O}(3)$ distance $[2.641(3) \text{ \AA}]$ is shorter than those in $[\text{Ag}(\text{PPh}_2\text{Me})_2](\text{OTf})$ [$\text{Ag}-\text{O}$ $2.775(2)$, $2.854(2) \text{ \AA}$]^[28] and longer than that found in $[\text{Ag}(\text{H}_2\text{O})\text{L}]_2(\text{NO}_3)_2$ $[2.592(2) \text{ \AA}; \text{L} = 1,4\text{-bis}(2\text{-pyridoxy})\text{-benzene}]$,^[29a] in which the silver atoms are coordinated to two nitrogen atoms of pyridine rings and an oxygen atom of a water molecule. In this case, there are also weaker contacts between each atom of the pyridoxy unit with one silver atom (ca. $2.9 \text{ \AA}$). These contacts are also observed in **8** [$\text{Ag}(1)-\text{O}(2) 2.961$, $\text{Ag}(2)-\text{O}(1) 3.074 \text{ \AA}$]. The $\text{Ag}-\text{N}$ distances in $[\text{AgL}(\text{NO}_3)]_2$ [$\text{L} = 1,4\text{-bis}(2\text{-pyridylsulfanylmethyl})\text{benzene}$;^[29b] $2.166(2)$, $2.165(2) \text{ \AA}$] are longer than those in **8** $[2.159(3)-2.171(2) \text{ \AA}]$. The bond lengths in the ferrocene ligand **L2** are similar to those observed in **8**. The $\text{C}=\text{O}$ distances in **8** are very similar $[1.216(5)$ and $1.214(5) \text{ \AA}]$ and shorter than that in **L2** $[1.227(2) \text{ \AA}]$. The coordination to the silver atoms seems to have no significant effect on the $\text{N}-\text{C}$ distances or the $\text{C}-\text{N}-\text{C}$ angles.

Some hydrogen bonds (Table 1) of the type $\text{C}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{F}$ ($\text{H}\cdots\text{O}$ distances between 2.35 and $2.57 \text{ \AA}$; $\text{H}\cdots\text{F}$ distance $2.45 \text{ \AA}$) have been found (those involving the oxygen atoms of the disordered triflate are not considered).

Table 3. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$] for compound **8**; see Table 1 for definition of symmetry operations used to generate equivalent atoms.

$\text{Ag}(1)-\text{N}(32)$	2.159(3)
$\text{Ag}(1)-\text{O}(3)$	2.641(13)
$\text{Ag}(2)-\text{N}(22)$	2.165(3)
$\text{Ag}(2)-\text{N}(42)$	2.164(3)
$\text{Ag}(2)-\text{O}(6)$	2.572(9)
$\text{Ag}(1)-\text{N}(52)$	2.171(3)
$\text{N}(32)-\text{Ag}(1)-\text{N}(52)$	178.03(12)
$\text{N}(32)-\text{Ag}(1)-\text{O}(3)$	94.63(11)
$\text{N}(52)-\text{Ag}(1)-\text{O}(3)\#1$	86.91(11)
$\text{N}(22)-\text{Ag}(2)-\text{N}(42)$	161.41(12)
$\text{N}(22)-\text{Ag}(2)-\text{O}(6)$	110.9(2)
$\text{N}(42)-\text{Ag}(2)-\text{O}(6)$	86.4(2)

Among them, those formed by the amide oxygen atoms join the molecules in an almost head (the part of the molecule with the ferrocene unit)-to-tail fashion. The result is the formation of chains in which the angle between the plane formed by the two silver atoms and the two hydrogen atoms ($\text{O1}, \text{H9}, \text{O1A}, \text{H9A}$) with the plane formed by atoms $\text{O2}, \text{H3}, \text{O2B}$ and H3B is 78.4° (Figure 6). Two different triflate ligands complete the pattern. One of these belongs to the same asymmetric unit and uses O5 , as well as O3 (also bonded to Ag1), to form hydrogen bonds with the hydrogen atoms of one pyridine ring. The other triflate group belongs to the same asymmetric unit as that involved in $\text{O2}\cdots\text{H3}$ hydrogen bonds and uses O4 and F1 to form hydrogen

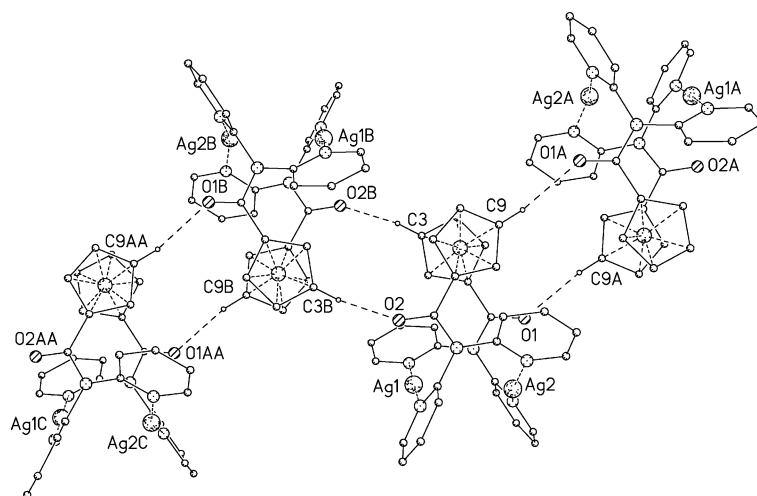


Figure 6. Formation of chains through hydrogen bonding (dotted lines) in complex **8**.

bonds with the hydrogen atoms of the ferrocene rings. C–H...X interactions, although weaker than strong hydrogen bonds with oxygen or nitrogen atoms, have been classified as real hydrogen bonds.^[30]

The reaction of **L2** with [Ag(OTf)(PPh₃)] was carried out in a 1:1 and 1:2 molar ratio to give the compounds [Ag(OTf)(**L2**)(PPh₃)] (**9**) and [Ag₂(OTf)₂(**L2**)(PPh₃)₂] (**10**), respectively. There are two possibilities for the structure of complex **9**: the silver centre coordinates to two pyridine rings of one of the substituted cyclopentadienido ligands, or the silver atom coordinates to two pyridine units from different cyclopentadienido groups. The first case would give nonequivalent cyclopentadienido units and pyridine groups. This situation is not observed in the ¹H NMR spectrum; therefore, we propose a structure in which the silver centre is coordinated to two pyridine units from different cyclopentadienido substituents for complex **9**. A coordination similar to that in complex **8** is possible for compound **10**, in other words coordination to pyridine units from different substituents, but the presence of a bulky ligand such as PPh₃ could promote coordination to pyridine moieties from the same cyclopentadienido units in an antiperiplanar fashion. The bands due to the trifluoromethanesulfonate anion in the IR spectra suggest that it is covalent. In both cases the ¹H NMR spectra show two multiplets for the α- and β-protons of the cyclopentadienido groups, thereby indicating that they are equivalent, along with several multiplets, some of which are overlapped, for the pyridine protons. The ³¹P{¹H} NMR spectra show one broad resonance at room temperature that splits into two doublets at –90 °C in dichloromethane as a consequence of the coupling of the phosphorus atoms with the silver nuclei.

Finally, the reactions of **L2** with the gold derivatives [Au(C₆F₅)(tht)] (tht = tetrahydrothiophene) and [Au(OTf)(PPh₃)] in a 1:4 molar ratio were carried out to afford the tetranuclear gold species [Au₄(C₆F₅)₄(μ-**L2**)] (**11**) and [Au₄(μ-**L2**)(PPh₃)₄](OTf)₄ (**12**). The IR spectrum of **11** shows absorptions due to the pentafluorophenyl groups at 1505 (vs), 954 (vs) and 799 cm^{–1} (s) together a ν(C=O) ab-

sorption at 1652 cm^{–1}; the most significant absorptions for compound **10** are those due to the triflate anion and ν(C=O). The ¹H NMR spectra contain one (**11**) or two multiplets (**12**) for the α- and β-protons of the cyclopentadienido units and four multiplets for the equivalent pyridine protons in each case. Compound **11** shows three resonances in its ¹⁹F NMR spectrum, thereby indicating the equivalence of the pentafluorophenyl groups. The ³¹P{¹H} NMR spectrum of complex **12** contains a singlet at δ = 29.8 ppm due to the equivalent phosphorus atoms whose chemical shift is typical of N–Au–P units.

Conclusions

The ligands {[bis(2-pyridyl)amino]carbonyl}ferrocene (**L1**) and 1,1'-bis{[bis(2-pyridyl)amino]carbonyl}ferrocene (**L2**) show different coordination modes in their coordination to copper, silver, gold and palladium. In the complexes studied **L1** always acts as a bidentate chelating ligand, whereas the coordination of **L2** is governed by the metal and the stoichiometric ratio. Thus, with copper it acts as a tetradentate chelate, with silver as a bidentate chelate and with gold as a tetradentate bridging ligand. 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), which lead to supramolecular networks in the structures of some of these derivatives, is noteworthy.

Experimental Section

Instrumentation: Infrared spectra were recorded in the range 4000–200 cm^{–1} with a Perkin–Elmer 883 spectrophotometer as Nujol mulls between polyethylene sheets. Conductivities were measured in ca. 5 × 10^{–4} M acetone solutions with a Philips 9509 conductimeter. C, H, N and S analyses were performed with a Perkin–Elmer 2400 microanalyzer. Mass spectra were recorded with a VG Autospec, with the liquid secondary-ion mass spectra (LSIMS) technique, using nitrobenzyl alcohol as matrix. NMR spectra were recorded with 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 $\text{Fc}(\text{COCl})_2$,^[32] $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$,^[33] $[\text{Ag}(\text{OTf})(\text{PR}_3)]$,^[28] $[\text{Cu}(\text{NCMe})_4]\text{PF}_6$,^[34] and $[\text{PdCl}_2(\text{NCPh})_2]$ ^[35] were prepared according to published procedures. $[\text{Au}(\text{OTf})(\text{PPh}_3)]$ was obtained by treatment of $[\text{AuCl}(\text{PPh}_3)]$ ^[36] with $\text{Ag}(\text{OTf})$ in dichloromethane and used in situ. All other reagents were commercially available.

Synthesis of L1: NEt_3 (0.61 mL, 1 mmol) was added to a solution of $\text{HN}(\text{py})_2$ (0.712 g, 1 mmol) in dichloromethane (20 mL) under argon, and a solution of FcCOCl (0.248 g, 1 mmol) in dichloromethane (20 mL) was added dropwise at 0°C . When the addition was complete, the solution was stirred at 0°C for 1 h, and the mixture was left to react for 24 h. After chromatography on alumina, with a dichloromethane/ethanol (99:1) mixture as eluent, **L1** was obtained as a red solid. Yield: 0.182 g (49%). $M_{\text{M}} = 0.1 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. $\text{C}_{21}\text{H}_{17}\text{FeN}_3\text{O}$ (383.22): calcd. C 65.81, H 4.47, N 10.96; found C 65.51, H 4.27, N 10.93. ^1H NMR: $\delta = 4.21$ (m, 4 H, C_5H_4), 4.27 (m, 9 H, $\text{C}_5\text{H}_4 + \text{C}_5\text{H}_5$), 7.16 (m, 2 H, py), 7.36 (m, 2 H, py), 7.70 (m, 2 H, py), 8.42 (m, 2 H, py) ppm.

Synthesis of L2: NEt_3 (0.42 mL, 4.2 mmol) was added to a solution of $\text{HN}(\text{py})_2$ (0.684 g, 4 mmol) in dichloromethane (20 mL) under argon, and a solution of 1,1'-bis(chlorocarbonyl)ferrocene (0.510 g, 2 mmol) in dichloromethane (20 mL) was added dropwise at 0°C . When the addition was complete, the solution was stirred at 0°C for 1 h, and the mixture was left to react for 24 h. After chromatography on alumina, using a dichloromethane/ethanol (95:5) mixture as eluent, **L2** was obtained as a red solid. Yield: 0.371 g (32%). $M_{\text{M}} = 1.1 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. $\text{C}_{32}\text{H}_{24}\text{FeN}_6\text{O}_2$ (580.41): calcd. C 66.21, H 4.16, N 14.48; found C 66.34, H 4.19, N 14.22. ^1H NMR: $\delta = 4.31$ (m, 4 H, $\alpha\text{-C}_5\text{H}_4$), 4.40 (m, 4 H, $\beta\text{-C}_5\text{H}_4$), 7.16 (t, $J_{\text{H,H}} = 5.84 \text{ Hz}$, 4 H, py), 7.70 (t, $J_{\text{H,H}} = 7.21 \text{ Hz}$, 4 H, py), 7.30 (d, $J_{\text{H,H}} = 8.24 \text{ Hz}$, 4 H, py), 8.43 (m, 4 H, py) ppm.

Synthesis of $[\text{Cu}(\text{L1})_2]\text{PF}_6$ (1): $[\text{Cu}(\text{NCMe})_4]\text{PF}_6$ (0.038 g, 0.1 mmol) was added to a solution of **L1** (0.073 g, 0.2 mmol) in dichloromethane (20 mL) under argon. 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 a yellow solid. Yield: 0.073 g (75%). $M_{\text{M}} = 98 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. $\text{C}_{42}\text{H}_{34}\text{CuF}_6\text{Fe}_2\text{N}_6\text{O}_2\text{P}$ (974.75): calcd. C 51.74, H 3.51, N 8.62; found C 51.35, H 3.28, N 8.35. ^1H NMR: $\delta = 4.24$ (m, 18 H, $\text{C}_5\text{H}_4 + \text{C}_5\text{H}_5$), 7.52 (m, 4 H, py), 7.65 (m, 4 H, py), 7.94 (m, 4 H, py), 8.41 (m, 4 H, py) ppm.

Synthesis of $[\text{Ag}(\text{OTf})(\text{L1})]$ (2): $\text{Ag}(\text{OTf})$ (0.026 g, 0.1 mmol) was added to a solution of **L1** (0.038 g, 0.1 mmol) in dichloromethane (20 mL), and the mixture was stirred for 1 h. Evaporation of the solvent to ca. 5 mL and addition of diethyl ether gave complex **2** as an orange solid. Yield: 0.039 g (61%). $M_{\text{M}} = 62 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. $\text{C}_{22}\text{H}_{17}\text{AgF}_3\text{FeN}_3\text{O}_4\text{S}$ (640.16): calcd. C 41.27, H 2.67, N 6.56, S 5.01; found C 41.53, H 2.87, N 6.78, S 4.79. ^1H NMR: $\delta = 4.40$ (m, 9 H, $\text{C}_5\text{H}_4 + \text{C}_5\text{H}_5$), 7.38 (m, 2 H, py), 7.49 (m, 2 H, py), 7.89 (m, 2 H, py), 8.54 (m, 2 H, py) ppm.

Synthesis of $[\text{Ag}(\text{OTf})(\text{L1})(\text{PR}_3)]$ [$\text{PR}_3 = \text{PPh}_3$ (3), PPh_2Me (4)]: $[\text{Ag}(\text{OTf})(\text{PPh}_3)]$ (0.052 g, 0.1 mmol) or $[\text{Ag}(\text{OTf})(\text{PPh}_2\text{Me})]$ (0.045 g, 0.1 mmol) was added to a solution of **L1** (0.038 g, 0.1 mmol) in dichloromethane (20 mL), and the mixture was stirred for 1 h. Evaporation of the solvent to ca. 5 mL and addition of diethyl ether gave complexes **3** or **4** as yellow-orange solids. **Complex 3:** Yield: 0.060 g (67%). $M_{\text{M}} = 93 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. $\text{C}_{40}\text{H}_{32}\text{AgF}_3\text{FeN}_3\text{O}_4\text{PS}$ (902.44): calcd. C 53.23, H 3.57, N 4.65, S 3.55; found C 53.46, H 3.82, N 4.41, S 3.20. ^1H NMR: $\delta = 3.93$

(m, 4 H, $\alpha\text{-C}_5\text{H}_4$), 4.03 (s, 4 H, C_5H_5), 3.93 (m, 4 H, $\beta\text{-C}_5\text{H}_4$), 7.38 (m, 2 H, py), 7.41 (m, 17 H, py + Ph), 7.88 (m, 2 H, py), 8.69 (m, 2 H, py) ppm. $^{31}\text{P}(\text{H})$ NMR: $\delta = 14.5$ (2 d, $J_{\text{Ag,P}} = 738.1$ and 651.8 Hz , PPh_3) ppm. **Complex 4:** Yield: 0.058 g (69%). $M_{\text{M}} = 85 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. $\text{C}_{35}\text{H}_{30}\text{AgF}_3\text{FeN}_3\text{O}_4\text{PS}$ (840.37): calcd. C 50.02, H 3.60, N 5.0, S 3.81; found C 50.17, H 3.69, N 4.85, S 3.58. ^1H NMR: $\delta = 2.15$ (m, 3 H, Me), 4.26 (m, 4 H, $\alpha\text{-C}_5\text{H}_4$), 4.33 (s, 4 H, C_5H_5), 4.38 (m, 4 H, $\beta\text{-C}_5\text{H}_4$), 7.50 (m, 17 H, py + Ph), 7.72 (m, 2 H, py), 8.09 (m, 2 H, py), 8.65 (m, 2 H, py). $^{31}\text{P}(\text{H})$ NMR: $\delta = -4.1$ (2 d, $J_{\text{Ag,P}} = 759.1$ and 658 Hz , PPh_3) ppm.

Synthesis of $[\text{Au}(\text{C}_6\text{F}_5)(\text{L1})]$ (5): $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$ (0.045 g, 0.1 mmol) was added to a solution of **L1** (0.038 g, 0.1 mmol) in dichloromethane (20 mL), and the mixture was stirred for 1 h. Evaporation of the solvent to ca. 5 mL and addition of *n*-hexane gave complex **5** as a yellow solid. Yield: 0.066 g (80%). $M_{\text{M}} = 4.5 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. $\text{C}_{33}\text{H}_{17}\text{AuF}_5\text{FeN}_3\text{O}$ (819.31): calcd. C 43.39, H 2.29, N 5.62; found C 43.68, H 2.37, N 5.86. ^1H NMR: $\delta = 4.34$ (m, 9 H, $\text{C}_5\text{H}_4 + \text{C}_5\text{H}_5$), 7.34 (m, 2 H, py), 7.69 (m, 2 H, py), 7.88 (m, 2 H, py), 8.51 (m, 2 H, py) ppm. ^{19}F NMR: $\delta = -116.0$ (m, 2 F, *o*-F), -159.9 (t, $^3J_{\text{F,F}} = 20.9 \text{ Hz}$, 1 F, *p*-F), -163.4 (m, 2 F, *m*-F) ppm.

Synthesis of $[\text{PdCl}_2(\text{L1})]$ (6): $[\text{PdCl}_2(\text{NCPh})_2]$ (0.038 g, 0.1 mmol) was added to a solution of **L1** (0.038 g, 0.1 mmol) in dichloromethane (20 mL), and the mixture was stirred for 1 h. Evaporation of the solvent to ca. 5 mL and addition of *n*-hexane gave complex **6** as a yellow-orange solid. Yield: 0.070 g (92%). $M_{\text{M}} = 11 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. $\text{C}_{21}\text{H}_{17}\text{AuCl}_2\text{FeN}_3\text{OPd}$ (757.51): calcd. C 44.99, H 3.05, N 7.49; found C 44.78, H 2.97, N 7.16. ^1H NMR: $\delta = 4.35$ (m, 2 H, $\alpha\text{-C}_5\text{H}_4$), 4.40 (m, 2 H, $\beta\text{-C}_5\text{H}_4$), 4.50 (s, 5 H, C_5H_5), 7.46 (m, 2 H, py), 7.63 (m, 2 H, py), 7.93 (m, 2 H, py), 9.10 (m, 2 H, py) ppm.

Synthesis of $[\text{Cu}(\text{L2})]\text{PF}_6$ (7): $[\text{Cu}(\text{NCMe})_4]\text{PF}_6$ (0.038 g, 0.1 mmol) was added to a solution of **L2** (0.058 g, 0.1 mmol) in dichloromethane (20 mL) under argon. The mixture was stirred for 1 h, and then evaporation of the solvent to ca. 5 mL and addition of diethyl ether gave complex **7** as an orange solid. Yield: 0.047 g (60%). $M_{\text{M}} = 99 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. $\text{C}_{32}\text{H}_{24}\text{CuF}_6\text{FeN}_6\text{O}_2\text{P}$ (788.92): calcd. C 48.71, H 3.06, N 10.65; found C 48.68, H 2.77, N 11.04. ^1H NMR: $\delta = 4.01$ (m, 4 H, $\alpha\text{-C}_5\text{H}_4$), 4.39 (m, 4 H, $\beta\text{-C}_5\text{H}_4$), 8.42 (br. m, 8 H, py) ppm.

Synthesis of $[\text{Ag}_2(\text{OTf})_2(\text{L2})]$ (8): $\text{Ag}(\text{OTf})$ (0.051 g, 0.2 mmol) was added to a solution of **L2** (0.058 g, 0.1 mmol) in dichloromethane (20 mL), and the mixture was stirred for 1 h. Evaporation of the solvent to ca. 5 mL and addition of diethyl ether gave complex **8** as a yellow solid. Yield: 0.061 g (56%). $\text{C}_{34}\text{H}_{24}\text{Ag}_2\text{F}_6\text{FeN}_6\text{O}_8\text{S}_2$ (1094.3): calcd. C 37.31, H 2.21, N 7.68, S 5.86; found C 37.45, H 2.46, N 8.04, S 6.07. ^1H NMR: $\delta = 4.12$ (m, 4 H, $\alpha\text{-C}_5\text{H}_4$), 4.31 (m, 4 H, $\beta\text{-C}_5\text{H}_4$), 7.45 (m, 4 H, py), 7.85 (m, 8 H, py), 8.79 (m, 4 H, py) ppm.

Synthesis of $[\text{Ag}(\text{OTf})(\text{L2})(\text{PPh}_3)]$ (9): $[\text{Ag}(\text{OTf})(\text{PPh}_3)]$ (0.051 g, 0.1 mmol) was added to a solution of **L2** (0.058 g, 0.1 mmol) in dichloromethane (20 mL), and the mixture was stirred for 1 h. Evaporation of the solvent to ca. 5 mL and addition of diethyl ether gave complex **9** as a yellow solid. Yield: 0.062 g (56%). $\text{C}_{51}\text{H}_{39}\text{AgF}_3\text{FeN}_6\text{O}_5\text{PS}$ (1099.6): calcd. C 55.70, H 3.57, N 7.64, S 2.98; found C 55.51, H 3.48, N 7.49, S 2.98. ^1H NMR: $\delta = 4.18$ (m, 4 H, $\alpha\text{-C}_5\text{H}_4$), 4.32 (m, 4 H, $\beta\text{-C}_5\text{H}_4$), 7.37 (m, 15 H, py), 7.73 (m, 8 H, py), 8.48 (m, 8 H, py). $^{31}\text{P}(\text{H})$ NMR: $\delta = 14.4$ (2d, $J_{\text{Ag,P}} = 745$ and 645 Hz , PPh_3) ppm.

Synthesis of $[\text{Ag}_2(\text{OTf})_2(\mu\text{-L2})(\text{PPh}_3)_2]$ (10): $[\text{Ag}(\text{OTf})(\text{PPh}_3)]$ (0.103 g, 0.2 mmol) was added to a solution of **L2** (0.058 g, 0.1 mmol) in dichloromethane (20 mL), and the mixture was stirred

Table 4. X-ray data for complexes **L1**, **L2**, **6** and **8**.

Compound	L1	L2	6 ·CH ₂ Cl ₂	8
Empirical formula	C ₂₁ H ₁₇ FeN ₃ O	C ₃₂ H ₂₄ FeN ₆ O ₂	C ₂₂ H ₁₉ Cl ₄ FeN ₃ OPd	C ₃₅ H ₂₆ Ag ₂ Cl ₂ F ₆ FeN ₆ O ₈ S ₂
<i>M_r</i>	383.23	580.42	645.45	1179.23
Habit	yellow prism	orange prism	orange prism	orange plate
Crystal size [mm]	0.22 × 0.17 × 0.15	0.22 × 0.07 × 0.04	0.24 × 0.20 × 0.12	0.25 × 0.06 × 0.06
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	<i>C2/c</i>	<i>C2/c</i>	<i>P</i> $\bar{1}$	<i>P2₁/n</i>
<i>a</i> [Å]	41.434(2)	20.886(2)	8.7095(6)	12.6165(12)
<i>b</i> [Å]	6.4855(3)	9.2643(10)	11.8124(8)	18.723(2)
<i>c</i> [Å]	12.8719(6)	15.5288(18)	11.9898(8)	17.1694(18)
<i>a</i> [°]	90	90	86.322(1)	90
<i>β</i> [°]	104.7110(10)	121.626(3)	69.849(1)	97.933(3)
<i>γ</i> [°]	90	90	84.157(1)	90
<i>V</i> [Å ³]	3345.6	2558.5(5)	1151.43(14)	4016.9(7)
<i>Z</i>	8	4	2	4
<i>D_x</i> [Mg m ^{−3}]	1.522	1.507	1.862	1.950
<i>μ</i> [mm ^{−1}]	0.917	0.634	1.896	1.6
<i>F</i> (000)	1584	1200	640	2328
<i>T</i> [°C]	−173	−130	−173	−130
<i>2θ</i> _{max} [°]	56.78	56.56	57.14	52
No. measured reflections	10404	14779	7661	57967
No. independent reflections	3873	3179	5119	8219
Transmissions	0.82–0.87	—	0.65–0.80	0.82–0.96
<i>R</i> _{int}	0.023	0.061	0.022	0.066
Parameters	235	186	289	632
Restraints	0	0	0	375
<i>wR</i> (<i>F</i> ² , all reflections)	0.095	0.083	0.069	0.080
<i>R</i> [<i>F</i> , >4σ(<i>F</i>)]	0.038	0.036	0.037	0.033
<i>S</i>	1.062	0.965	0.923	0.964
Max. Δρ [e Å ^{−3}]	0.63	0.357	0.862	1.038

for 1 h. Evaporation of the solvent to ca. 5 mL and addition of diethyl ether gave complex **10** as a yellow solid. Yield: 0.105 g (65%). C₇₀H₅₄Ag₂F₆FeN₆O₈P₂S₂ (1618.9): calcd. C 51.93, H 3.36, N 5.19, S 3.96; found C 52.21, H 3.56, N 5.21, S 4.11. ¹H NMR: δ = 4.06 (m, 4 H, α-C₅H₄), 4.27 (m, 4 H, β-C₅H₄), 7.43 (m, 38 H, py + Ph), 7.74 (m, 4 H, py), 8.50 (m, 4 H, py). ³¹P(¹H) NMR: δ = 14.6 (2d, *J*_{Ag,P} = 744 and 644 Hz, PPh₃) ppm.

Synthesis of [Au₄(C₆F₅)₄(μ-L2)] (11**):** [Au(C₆F₅)(tht)] (0.180 g, 0.4 mmol) was added to a solution of **L2** (0.058 g, 0.1 mmol) in dichloromethane (20 mL), and the mixture was stirred for 1 h. Evaporation of the solvent to ca. 5 mL and addition of *n*-hexane gave complex **11** as a yellow solid. Yield: 0.130 g (64%). C₅₆H₂₄Au₄F₂₀FeN₆O₂ (2036.5): calcd. C 33.02, H 1.18, N 4.12; found C 33.30, H 1.12, N 4.41. ¹H NMR: δ = 4.51 (m, 8 H, C₅H₄), 7.25 (m, 2 H, py), 7.68 (m, 2 H, py), 7.85 (m, 2 H, py), 8.38 (m, 2 H, py) ppm. ¹⁹F NMR: δ = −115.4 (m, 2 F, *o*-F), −159.8 (t, ³*J*_{F,F} = 19.9 Hz, 1 F, *p*-F), −163.1 (m, 2 F, *p*-F) ppm.

Synthesis of [Au₄(μ-L2)(PPh₃)₄](OTf)₄ (12**):** [Au(OTf)(PPh₃)] (0.243 g, 0.4 mmol) was added to a solution of **L2** (0.058 g, 0.1 mmol) in dichloromethane (20 mL), and the mixture was stirred for 1 h. Evaporation of the solvent to ca. 5 mL and addition of *n*-hexane gave complex **12** as a yellow solid. Yield: 0.238 g (79%). C₁₀₈H₈₄Au₄F₁₂FeN₆O₁₄P₄S₄ (3013.7): calcd. C 43.04, H 2.80, N 2.78, S 4.62; found C 43.41, H 3.07, N 2.55, S 4.49. ¹H NMR: δ = 4.09 (m, 4 H, C₅H₄), 4.37 (m, 4 H, C₅H₄), 7.20 (m, 2 H, py), 7.37 (m, 60 H, Ph), 7.75 (m, 2 H, py), 7.88 (m, 2 H, py), 8.39 (m, 2 H, py). ³¹P(¹H) NMR: δ = 29.8 (s, PPh₃) ppm.

Crystal Structure Determinations: Crystals were mounted in inert oil on glass fibers and transferred to the cold gas stream of a Bruker Smart 1000 CCD (**L2**, **8**) or Smart Apex CCD (**L1**, **6**) diffractometer equipped with a low-temperature attachment. Data

were collected using monochromated Mo-*K*_α radiation (λ = 0.71073 Å). Scan type ω and φ. Absorption correction based on multiple scans were applied with the program SADABS^[37] for **L1**, **6** and **8**. The structures were refined on *F*² using the program SHELXL-97.^[38] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included using a riding model. Special refinement details for **8**: One of the triflate anions was severely disordered. The model used in the refinement was based on two positions, but this could be too simple, and it is not possible to compare its coordination to silver with that of AgI and O3. Further details of the data collection and refinement are given in Table 4. CCDC-661893 (for **L1**), -661894 (for **L2**), -661895 (for **6**), and -661896 (for **8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Selected bond lengths and angles and molecular structures of **L1** and **L2**.

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