The Role of Secondary Interactions in Group 11 Metal Complexes Containing the Ferrocene Ligand $FcCH_2NHpyMe$ in Supramolecular Structures

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The ferrocene ligand 6-[(ferrocenylmethyl)amino]-2-picoline, $FcCH_2NHpyMe$ [Fc = $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$], has been prepared by treatment of $FcCH_2NMe_2$ with 6-amino-2-picoline, NH_2pyMe. The coordination chemistry with group 11 metals has been studied and several complexes with coordination of the metal atom to the pyridine nitrogen atom, such as $[M(PPh_3)(FcCH_2NHpyMe)]OTf$, $[Au(C_6F_5)(FcCH_2NHpyMe)]$ and $[AuR_3(FcCH_2NHpyMe)]$ (M = Au, Ag; R_3 = $(C_6F_5)_3$, $(C_6F_5)_2Cl$; OTf = trifluoromethanesulfonate), have been obtained. The complex $[Cu(FcCH_2NHpyMe)_2]PF_6$ has also been synthesised with a probable coordination of the copper centre to the pyridine and amine nitrogen atoms. Deprotonation of the NH group allows the synthesis of dinuclear complexes of the type $[M_2(PPh_3)_2(FcCH_2NpyMe)]X$ or $[Au_2(C_6F_5)(PPh_3)(FcCH_2NpyMe)]$ with a mixed pyridine–amide ligand. Some of the complexes have been characterised by X-ray diffraction and show the presence of intramolecular aurophilic interactions in the dinuclear complex and intermolecular interactions leading to chains in the mononuclear complex. Other types of secondary bonds are present in these structures, such as hydrogen bonding and weak η^2 interactions between the gold centre and the cyclopentadienyl ring.

Introduction

Gold complexes with nitrogen ligands, especially with amine ligands, have not been extensively studied until recently perhaps because of their limited stability.[1] This can be rationalised in terms of incompatibility between the soft metal centre and the hard nitrogen donor. Additional stabilisation of these compounds may be provided by aurophilic interactions or by formation of N−H···X hydrogen bonds. In this manner, several complexes of stoichiometry [AuClL] have been recently reported.[2] Stabilisation of these complexes with a phosphane ligand is also possible and several examples of the type $[AuL(PR_3)]^+$ are known.[3] However, complexes in which there are more than one type of nitrogen donor atoms in the same ligand are not frequent. As far as we are aware there is only one gold(I) derivative, namely $[(AuPPh_3)_4NQuin]BF_4$ (NQuin = 8-quinolinaminato),[4] with a pyridine−imido ligand as well as some gold(III) compounds with amine−amide ligands.[5] Here we report the synthesis of several gold, silver and copper complexes containing the ligand $FcCH_2NHpyMe$ which has two types of nitrogen donor atoms belonging to the amine and the pyridine groups. In our work with ferrocene derivatives[6] we have observed that the ferrocenyl group confers a great deal of stability on these types of ligands. Consequently, in this case, it is possible to coordinate the pyridine nitrogen atom to the metal fragments and also to substitute the proton in the NH group with the isolobal fragments $AgPPh_3^+$ or $AuPPh_3^+$, leading to the formation of the mixed gold or silver complexes with the pyridine−amide ligands. The crystal structure determinations provide experimental evidence for the importance of secondary bonds in the molecular architectures. Here, aurophilic interactions and hydrogen bonding are present in some of the complexes as illustrated by X-ray diffraction.

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Results and Discussion

Synthesis of the Complexes

The reaction of $FcCH_2NMe_2$ with 6-amino-2-picoline (NH_2pyMe) in acetic acid gives the ferrocene ligand $FcCH_2NHpyMe$ (**1**) [Equation (1)]. A closely related ferrocene derivative, FcCONHpyMe, has previously been reported and the effect of protonation on the spectroscopic and redox properties was studied.[7] Compound **1** has been characterised by NMR spectroscopy and its ^1H NMR spectrum shows the three resonances for the three types of pyridine protons as two doublets and a doublet of doublets

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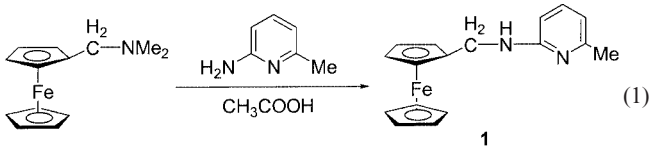
with the NH signal at $\delta = 4.73$ ppm, the signal of the methylene protons at $\delta = 4.12$ ppm and the cyclopentadienyl proton signals at $\delta = 4.10$, 4.19 and 4.22 ppm in a ratio of 2:5:2, respectively. The positive liquid secondary-ion mass spectrum (LSIMS) exhibits the molecular peak at m/z = 306 as the most intense.



(1)

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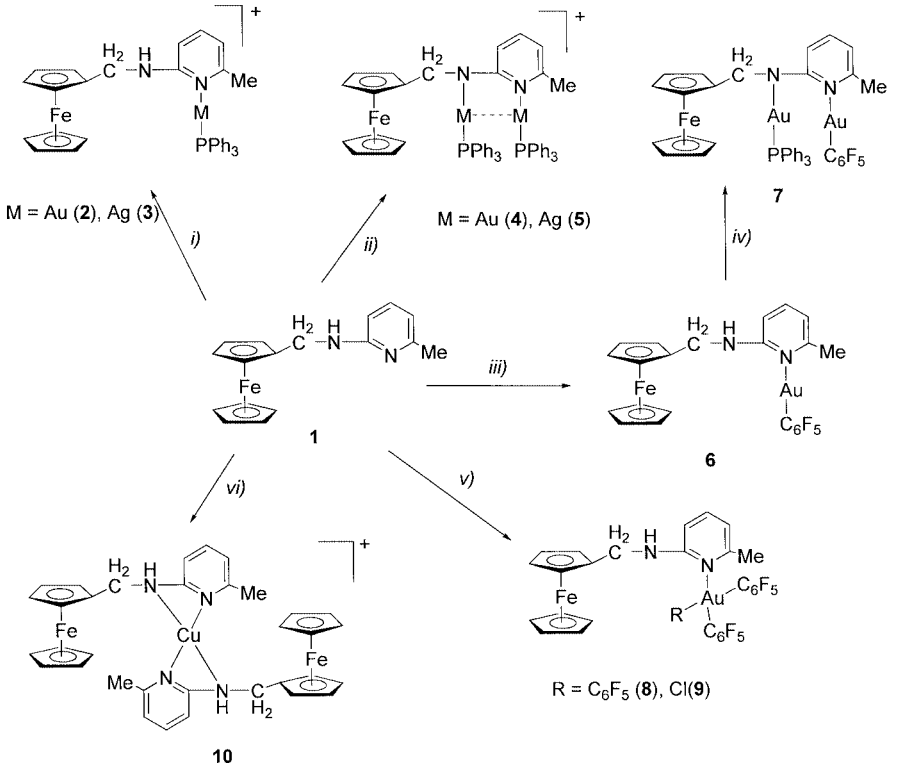
The reactivity of ligand **1** towards several gold, silver and copper compounds has been studied. Thus, treatment of **1** with $[M(OTf)PPh_3]$ in a 1:1 molar ratio affords complexes of stoichiometry $[M(PPh_3)(FcCH_2NHpyMe)]OTf$ [M = Au (**2**), Ag (**3**)] (see Scheme 1).

Complexes **2**–**3** are air- and moisture-stable yellow solids. Their IR spectra show bands for the trifluoromethanesulfonate group at $\tilde{\nu} \approx 1265$ [vs, br., $\nu_{as}(SO_3)$], 1223 [s, $\nu_s(CF_3)$], 1150 [s, $\nu_{as}(CF_3)$] and 1023 [s, $\nu_s(SO_3)$] cm^{-1}. The ^1H NMR spectra for both complexes show broad signals at $\delta \approx 4.3$ ppm where the resonances for the ferrocenyl, methylene and NH protons are overlapping. The signals of only two of the pyridine protons can be observed because that of the other is also overlapping with those of the phenyl protons. In the $^{31}P(^1H)$ NMR spectra one sharp (in **2**) or broad (in **3**) resonance appears. At −55 °C the broad singlet from **3** splits into two doublets because of the coupling with the $^{109,107}Ag$ nuclei. The positive liquid secondary-ion mass spectra (LSIMS+) exhibit the molecular peaks at m/z (%) = 917 (5) [**2**] or 825 (12) [**3**] or the cationic peaks [M − OTf] at m/z (%) = 765 (95) [**2**] or 676 (30) [**3**].

The reaction of ligand **1** with the oxonium compound $[O(AuPPh_3)_3]ClO_4$ proceeds with the deprotonation of the NH group and coordination of two $AuPPh_3^+$ fragments to the amine nitrogen atom and to the pyridine group, giving the complex $[Au_2(PPh_3)_2(FcCH_2NpyMe)]ClO_4$ (**4**). This derivative, with triflate as counter anion, is also accessible by treatment of complex **2** with $[Au(acac)(PPh_3)]$. The analogous silver derivative $[Ag_2(PPh_3)_2(FcCH_2NpyMe)]OTf$ (**5**) can be obtained by treatment of **3** with $[Ag(OTf)(PPh_3)]$ in the presence of triethylamine. The IR spectra show absorptions from the perchlorate anion at $\tilde{\nu} = 1096$ (vs, br.) and 623 (m) cm^{-1} for **4** and for **5** the typical absorptions for the trifluoromethanesulfonate anion can be observed. In the ^1H NMR spectra the resonances for the ferrocenyl protons appear as two singlets for the methyl and unsubstituted Cp groups, three multiplets for the α and β protons of the substituted Cp group and for the methylene protons. The resonance of the NH group disappears. For the pyridine protons, only two resonances can be observed because the third overlaps with the signals from the phenyl protons. The $^{31}P(^1H)$ NMR spectrum of complex **4** shows two resonances for the two inequivalent phosphorus atoms. For compound **5** the spectrum at room temperature consists of two



Scheme 1. i) $[M(OTf)(PPh_3)]$, ii) $[O(AuPPh_3)_3]ClO_4$ or 2 $[Ag(OTf)(PPh_3)]$ + NEt_3, iii) $[Au(C_6F_5)(tht)]$, iv) $[Au(acac)(PPh_3)]$, v) $[Au(C_6F_5)_3(OEt_2)]$ or 1/2 $[Au(C_6F_5)_2Cl]_2$, vi) 1/2 $[Cu(NCMe)_4]PF_6$

broad signals that split at −55 °C into four doublets as a consequence of the coupling of two inequivalent phosphorus atoms with the two silver nuclei. In the LSIMS+ mass spectra the cationic molecular peaks appear at *m/z* (%) = 1223 (20) [**4**] and 1044 (40) [**5**].

Treatment of **1** with an equimolar amount of $[Au(C_6F_5)(tht)]$ (tht = tetrahydrothiophene) affords the compound $[Au(C_6F_5)(FcCH_2NHpyMe)]$ (**6**). Complex **6** is an air- and moisture-stable yellow solid which is a nonconductor in acetone solution. The IR spectrum shows bands arising from the pentafluorophenyl group at $\tilde{\nu}$ = 1500 (vs), 954 (s) and 793 (m) cm^{-1}. In the ^1H NMR spectrum of **6** the typical resonances for the ferrocenyl, methyl and methylene (as a doublet) protons are apparent. The three pyridine protons appear as two doublets and a doublet of doublets and the resonance for the NH proton has shifted downfield to δ = 6.73 ppm. The ^{19}F NMR spectrum shows the three resonances for a pentafluorophenyl group as two multiplets for the *ortho*- and *meta*-fluorine atoms and a triplet for the *para*-fluorine atom. The LSIMS+ mass spectrum shows the molecular peak at *m/z* (%) = 670 (85) and a peak arising from loss of the pentafluorophenyl group at *m/z* (%) = 503 (7) can also be observed. The reaction of complex **6** with 1 equiv. of $[Au(acac)(PPh_3)]$ leads to deprotonation of the amine group and coordination of the nitrogen atom to the $AuPPh_3^+$ fragment. The compound $[Au_2(C_6F_5)(PPh_3)(FcCH_2NpyMe)]$ (**7**) is an air- and moisture-stable yellow solid which is a nonconductor in acetone solution. The ^1H NMR spectrum shows the resonances for the ferrocenyl unit, a singlet for the unsubstituted cyclopentadienyl Cp ligand and a broad multiplet for the substituted cyclopentadienyl Cp unit. The methylene and the methyl protons appear as a multiplet and a singlet, respectively, and the resonances for the phenyl and pyridine groups are overlapping. The signal for the NH proton disappears. The ^{31}P NMR spectrum shows one singlet for the phosphorus atom and the ^{19}F NMR spectrum has a typical pattern for the pentafluorophenyl group. In the LSIMS+ spectrum the molecular peak at *m/z* (%) = 1128 (5) and the $[M + AuPPh_3]^+$ fragment at *m/z* (%) = 1587 (10) may be observed.

Ligand **1** also reacts with gold(III) complexes of the type $[Au(C_6F_5)_3(OEt_2)]$ or $[Au(C_6F_5)_2Cl]_2$ to afford the compounds $[Au(C_6F_5)_3(FcCH_2NHpyMe)]$ (**8**) or $[Au(C_6F_5)_2Cl(FcCH_2NHpyMe)]$ (**9**), respectively. Complexes **8** and **9** are air- and moisture-stable yellow solids which are nonconductors in acetone solution. Their IR spectra show typical bands for the pentafluorophenyl fragments bonded to gold(III) at $\tilde{\nu} \approx$ 1507 (s), 972 (s), 800 (s) and 795 (m) cm^{-1}. The ^{19}F NMR spectrum of **8** shows the typical pattern of an $Au(C_6F_5)_3$ group in which the *trans*-pentafluorophenyl groups are equivalent. Six resonances in a 2:1 ratio are observed corresponding to the *ortho*-, *meta*- and *para*-fluorines of the inequivalent C_6F_5 moieties. For compound **9**, two inequivalent pentafluorophenyl units may be observed corresponding to a *cis* configuration. The ^1H NMR spectrum is in agreement with the formula. In the LSIMS+ spectra the molecular peaks appear at *m/z* (%) = 1004 (5) and 872 (100), respectively.

A copper derivative $[Cu\{(FcCH_2NHpyMe)\}_2]PF_6$ (**10**) has been obtained by treatment of **1** with $[Cu(NCMe)_4]PF_6$ in a molar ratio of 2:1. Because of the tendency of Cu^I to adopt higher coordination numbers than gold, we propose a tetrahedral derivative with the copper atom bonded to both pyridine and amine nitrogen atoms. In the ^1H NMR spectrum both ferrocene units are equivalent and the protons appear as a broad resonance. A singlet for the methyl protons and a multiplet for the methylene protons also appear. The pyridine units show two multiplets for the two different types of protons.

Crystal Structure Determinations

The crystal structure of the cyclohexane solvate of $[Au_2(PPh_3)_2(FcCH_2NpyMe)]ClO_4$ (**4**) has been determined by a single-crystal X-ray diffraction study (Figure 1). A selection of bond lengths and angles are shown in Table 1. The gold atoms have a distorted linear geometry with angles N(1)−Au(1)−P(1) of 172.8(2)° and N(2)−Au(2)−P(2) of 170.26(14)°. This distortion may be a consequence of a short intramolecular gold(I)−gold(I) interaction of 2.9732(5) Å. The Au−N distances are 2.091(5) Å to the pyridine nitrogen atom and 2.052(5) Å to the amine nitrogen atom which are among the longest found in

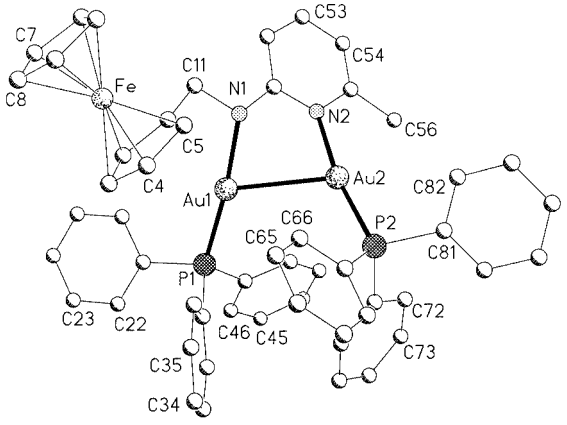


Figure 1. Structure of the cation of complex **4** showing the atom labelling scheme; radii are arbitrary, H atoms are omitted for clarity

Table 1. Selected bond lengths [Å] and angles [°] for **4**

Au(1)−N(1)	2.054(5)	Au(2)−P(2)	2.2341(18)
Au(1)−P(1)	2.2412(16)	C(11)−N(1)	1.469(8)
Au(1)−Au(2)	2.9733(5)	N(1)−C(51)	1.352(8)
Au(2)−N(2)	2.093(5)		
N(1)−Au(1)−P(1)	172.85(16)	C(61)−P(2)−Au(2)	116.3(2)
N(1)−Au(1)−Au(2)	71.67(15)	C(71)−P(2)−Au(2)	111.9(2)
P(1)−Au(1)−Au(2)	114.49(5)	C(81)−P(2)−Au(2)	110.1(2)
N(2)−Au(2)−P(2)	170.25(14)	N(1)−C(11)−C(1)	109.6(5)
N(2)−Au(2)−Au(1)	75.80(13)	C(51)−N(1)−Au(1)	119.0(4)
P(2)−Au(2)−Au(1)	113.94(5)	C(11)−N(1)−Au(1)	115.9(4)
C(31)−P(1)−Au(1)	112.6(2)	C(51)−N(2)−Au(2)	117.1(4)
C(41)−P(1)−Au(1)	112.2(2)	C(55)−N(2)−Au(2)	119.8(4)
C(21)−P(1)−Au(1)	110.9(2)		

complexes with the unit $N_{pyridinic}-Au-PPh_3$. The latter generally range from 1.986(3)[8] to 2.108[9] Å. The longer Au−P bond in **4** is opposite to the shorter Au−N bond. The values are similar to those observed in other complexes with the N−Au−P unit.[8,9] The two P−Au−N units are skewed with respect to each other as shown by the torsion angle P(1)−Au(1)−Au(2)−P(2) of −45.8(1)°. The cyclopentadienyl rings display an essentially eclipsed geometry [torsion angle C(1)−Cp−Cp−C(6) 0.3°]. The gold atom Au(1) is located close to and with short contacts to the C(1)−C(2) bond of the cyclopentadienyl group [distances to C(1) and C(2): 3.150 and 3.357 Å] indicating a weak η^2 interaction with the Cp ring in a similar manner as has already been observed in other gold and silver complexes with ferrocene derivatives.[10,11] In the lattice there are several O···H interactions involving the oxygen atoms of the perchlorate anion and the protons of the phenyl and cyclopentadienyl moieties. These contacts are around 2.6 Å and are mostly of such a linearity as to be considered hydrogen bonds.

The structure of complex **6** has been confirmed by X-ray diffraction and is shown in Figure 2. Selected bond lengths and angles are shown in Table 2. The gold centre has a linear geometry with an angle C−Au−N of 177.65(13)°. The Au−N distance is 2.073(4) Å. Few examples of compounds with the $N_{pyridinic}-Au-C_6F_5$ moiety have been characterised by X-ray analysis and this value is shorter than the Au−N bond length of 2.124(15) Å in [Au(C_6F_5)(3-Fcpy)] (3-Fcpy = 3-ferrocenylpyridine).[12] It is similar, however, to that in [Au(C_6F_5)(3-Mepy)] (2.066 Å)[2a] or the Au−N(sp^2) value of 2.069(5) Å found in [Au(C_6F_5)($N_2C_2Ph_4$)].[13] The Au−C distance is 1.988(5) Å and resembles the values found in the complexes cited above. The cyclopentadienyl ring deviates slightly from an eclipsed geometry [torsion angle C(31)−Cp−Cp−C(41) 7.7°]. The NH group does not participate in hydrogen bonding but has a short intramolecular contact of 2.55 Å to the gold atom (N−H···Au 117°). The molecules are associated through intermolecular aurophilic interactions of 3.429 Å giving a chain of gold atoms parallel to the short axis (Figure 3). The chain structure is reinforced by offset ring stacking, with a perpendicular distance of ca. 3.33 Å and a centroid−plane distance of 3.48 Å. The molecules are further linked to form a 3D structure through C−H···F hydrogen bonds.

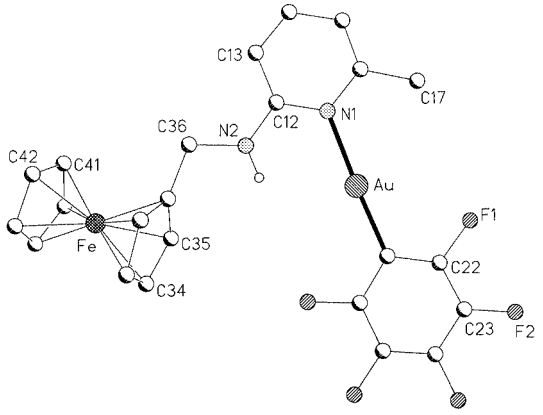


Figure 2. Molecular structure of complex **6** with the atom labelling scheme; H atoms (expect NH) are omitted for clarity

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

Au−C(21)	1.988(4)	C(21)−C(22)	1.382(6)
Au−N(1)	2.073(4)	C(21)−C(26)	1.397(6)
N(1)−C(12)	1.345(5)	C(22)−F(1)	1.362(5)
N(1)−C(16)	1.370(5)	C(22)−C(23)	1.365(6)
C(12)−N(2)	1.358(5)	C(23)−F(2)	1.343(5)
C(12)−C(13)	1.392(6)	C(23)−C(24)	1.378(7)
C(13)−C(14)	1.375(6)	C(24)−F(3)	1.338(6)
C(14)−C(15)	1.395(7)	C(24)−C(25)	1.368(7)
C(15)−C(16)	1.355(7)	C(25)−F(4)	1.345(5)
C(16)−C(17)	1.507(6)	C(25)−C(26)	1.375(7)
N(2)−C(36)	1.460(5)	C(26)−F(5)	1.352(5)
C(21)−Au−N(1)	177.65(13)	C(16)−C(15)−C(14)	119.0(4)
C(12)−N(1)−C(16)	119.1(4)	C(15)−C(16)−N(1)	121.7(4)
C(12)−N(1)−Au	120.6(3)	C(15)−C(16)−C(17)	121.7(4)
C(16)−N(1)−Au	120.3(3)	N(1)−C(16)−C(17)	116.6(4)
N(1)−C(12)−N(2)	116.5(4)	C(12)−N(2)−C(36)	124.2(4)
N(1)−C(12)−C(13)	121.9(4)	C(22)−C(21)−C(26)	113.2(4)
N(2)−C(12)−C(13)	121.6(4)	C(22)−C(21)−Au	121.3(3)
C(14)−C(13)−C(12)	118.0(4)	C(26)−C(21)−Au	125.5(3)
C(13)−C(14)−C(15)	120.4(4)		

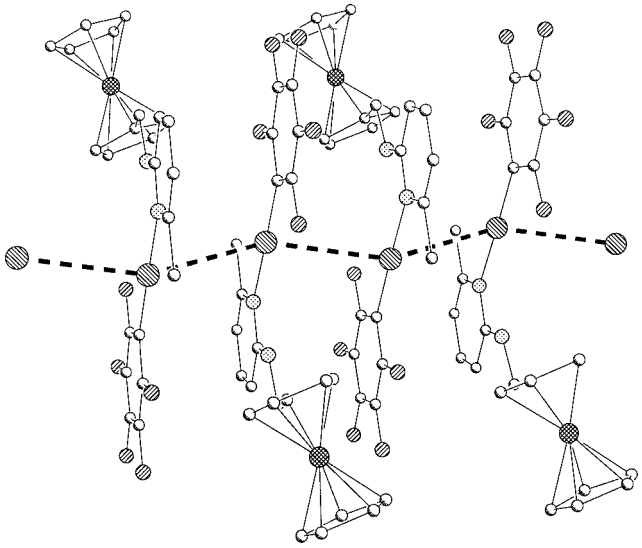


Figure 3. Association of molecules in complex **6** through aurophilic interactions; H atoms (expect NH) are omitted for clarity

The structures of complexes **8** and **9** have also been established by X-ray diffraction studies and the molecules are shown in Figures 4 and 5, respectively. Selected bond lengths and angles are collected in Tables 3 and 4. In both complexes the gold(III) centres are in a square-planar geometry with the mean deviations from the ideal angles being 3.6° (**8**) and 3.8° (**9**). In **8** the Au−C bond lengths are 2.026(6), 2.064(5) and 2.071(5) Å, the shortest is to the pentafluorophenyl group *trans* to the pyridine ligand. In **9** the distances are 2.012(2) and 2.028(3) Å which are similar to the shortest distance in compound **8**. This shows the higher *trans* influence of the pentafluorophenyl group compared with amine or chloro ligands. The Au−N distances are 2.104(4) and 2.101(2) Å and are very similar because

both have a pentafluorophenyl group *trans* to them. Few examples with the units N−Au(C_6F_5)$_3$ or N−Au−*trans*-(C_6F_5)$_2$Cl have been structurally characterised but the values are similar to those reported, as for example in [{Au(C_6F_5)$_3$}$_2${Fc(Spy)$_2$}].[6f] The cyclopentadienyl rings in these complexes are eclipsed with torsion angles C(1)−Cp−Cp−C(6) of 0.9° in **8** and 8.8° in **9**. Both complexes show intramolecular N−H···Au hydrogen contacts of 2.62(8) and 2.67(9) Å, respectively, but these are better considered as the weaker parts of three-centred interactions involving F5 or Cl, respectively, as the main hydrogen bond acceptor. Additional C−H···F (and C−H···Cl for **9**) hydrogen bonds between various molecules create a 3D extended structure in **8** or the disposition of the molecules into planes in **9** (Figure 6). Table 5 lists the hydrogen bonds found in these complexes.

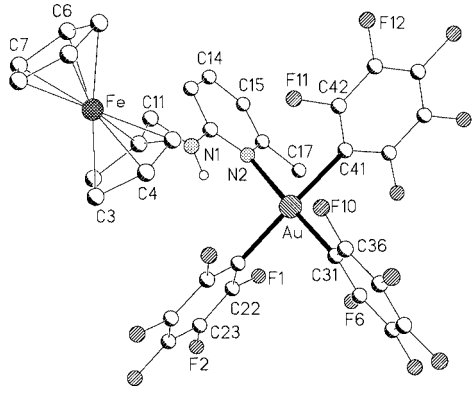


Figure 4. Perspective view of complex **8** with the atom labelling scheme; H atoms (except NH) are omitted for clarity

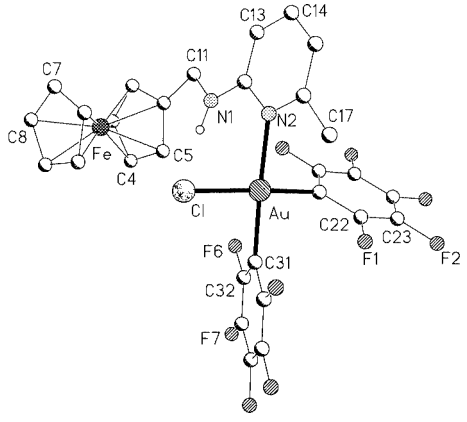


Figure 5. Molecular structure of complex **9** with the atom labelling scheme; H atoms (except NH) are omitted for clarity

Table 3. Selected bond lengths [Å] and angles [°] for **8**

Au−C(31)	2.026(6)	N(1)−C(12)	1.340(6)
Au−C(21)	2.064(5)	N(1)−C(11)	1.455(6)
Au−C(41)	2.071(5)	N(2)−C(12)	1.352(6)
Au−N(2)	2.104(4)	N(2)−C(16)	1.379(7)
C(31)−Au−C(21)	88.9(2)	C(16)−N(2)−Au	119.8(4)
C(31)−Au−C(41)	89.1(2)	C(22)−C(21)−Au	124.7(4)
C(21)−Au−C(41)	177.9(2)	C(26)−C(21)−Au	120.4(4)
C(31)−Au−N(2)	176.60(19)	C(32)−C(31)−Au	122.5(4)
C(21)−Au−N(2)	93.64(18)	C(36)−C(31)−Au	120.1(4)
C(41)−Au−N(2)	88.38(18)	C(42)−C(41)−Au	122.4(4)
C(12)−N(2)−Au	119.4(4)	C(46)−C(41)−Au	122.1(4)

Table 4. Selected bond lengths [Å] and angles [°] for **9**

Au−C(31)	2.012(2)	Au−N(2)	2.101(2)
Au−C(21)	2.028(3)	Au−Cl	2.3303(7)
C(31)−Au−C(21)	86.25(10)	N(2)−Au−Cl	91.03(6)
C(31)−Au−N(2)	177.22(9)	C(12)−N(2)−Au	120.96(17)
C(21)−Au−N(2)	91.52(9)	C(16)−N(2)−Au	118.51(17)
C(31)−Au−Cl	91.28(7)	C(22)−C(21)−Au	122.8(2)
C(21)−Au−Cl	176.22(7)	C(36)−C(31)−Au	122.39(19)

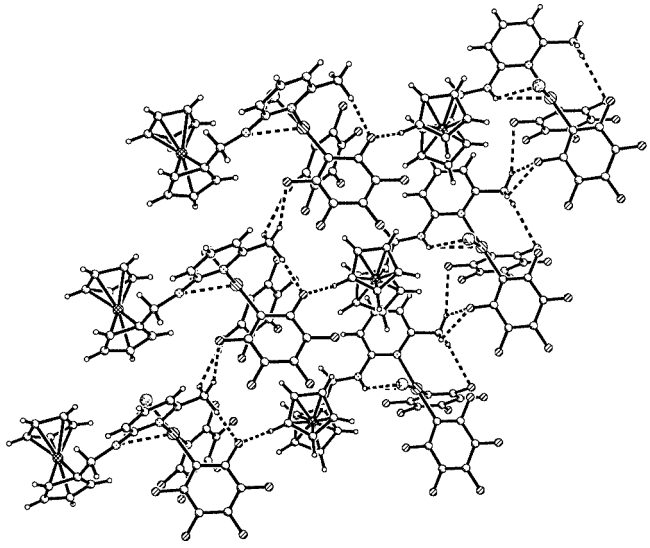


Figure 6. Supramolecular structure through hydrogen bonding in complex **9**

Conclusions

The ligand $FcCH_2NHpyMe$ can form several complexes with copper, silver or gold with different geometries and coordination modes. Coordination through the pyridine nitrogen atom is ususally preferred by the three metals but bonding to the amine nitrogen atom can be achieved using deprotonating agents causing substitution of the proton for the isolobal $AgPPh_3^+$ or $AuPPh_3^+$ fragments. In the structures of these derivatives it is worth mentioning the presence of intra- and intermolecular gold−gold interactions. In some cases the aurophilic interactions provide a supramolecular chain-like structure. The presence of other secondary interactions is also noteworthy, for example the weak η^2 interaction between the gold centre and the cyclopendienyl ring and the intra- and intermolecular hydrogen bonds.

Table 5. Hydrogen bonds for compounds **4**, **6**, **8** and **9**

Compound **4** D−H···A	*d*(D−H)	*d*(H···A)	*d*(D···A)	∠(DHA)
C(32)−H(32)···O(1)	0.95	2.53	3.256(8)	133.5
C(83)−H(83)···O(2)#1	0.95	2.57	3.500(9)	165.1
C(53)−H(53)···O(3)#2	0.95	2.57	3.465(11)	158.2
C(73)−H(73)···O(3)#3	0.95	2.58	3.258(9)	128.6
C(23)−H(23)···O(4)	0.95	2.55	3.232(10)	128.6
C(64)−H(64)···O(4)#4	0.95	2.47	3.376(9)	160.4
C(10)−H(10)···N(1)#5	0.95	2.64	3.492(8)	149.6
Symmetry transformations used to generate equivalent atoms: #1: $x + 1, -y + 3/2, z - 1/2$; #2: $-x + 1, y - 1/2, -z + 1/2$; #3: $x + 1, y, z$; #4: $x, -y + 3/2, z - 1/2$; #5: $-x + 1, -y + 1, -z$.				
Compound **6** D−H···A	*d*(D−H)	*d*(H···A)	*d*(D···A)	∠(DHA)
C(32)−H(32)···F(1)#1	0.95	2.49	3.130(6)	125.0
C(35)−H(35)···F(1)#2	0.95	2.55	3.316(6)	137.7
C(42)−H(42)···F(2)#3	0.95	2.43	3.335(7)	159.9
C(34)−H(34)···F(3)#4	0.95	2.60	3.520(6)	164.3
C(17)−H(17C)···F(4)#5	0.98	2.52	3.299(6)	136.2
Symmetry transformations used to generate equivalent atoms: #1: $-x + 1, -y + 1, -z + 1$; #2: $-x, -y + 1, -z + 1$; #3: $x + 1, y, z - 1$; #4: $-x, -y + 2, -z + 1$; #5: $x, y - 1, z$.				
Compound **8** D−H···A	*d*(D−H)	*d*(H···A)	*d*(D···A)	∠(DHA)
C(11)−H(11B)···F(3)#1	0.99	2.35	3.328(7)	169.4
C(10)−H(10)···F(4)#1	0.95	2.57	3.459(8)	155.6
N(1)−H(1)···F(5)	0.88	2.26	3.105(6)	161.8
C(13)−H(13)···F(9)#2	0.95	2.47	3.404(7)	169.5
C(14)−H(14)···F(5)#2	0.95	2.38	3.112(7)	134.0
C(9)−H(9)···F(15)#3	0.95	2.59	3.435(8)	147.7
N(1)−H(1)···Au	0.88	2.62	3.128(5)	117.6
C(4)−H(4)···F(14)#3	0.95	2.59	3.435(8)	147.7
Symmetry transformations used to generate equivalent atoms: #1: $x - 1, y, z$; #2: $x - 1/2, -y + 1/2, z - 1/2$; #3: $-x + 3/2, y - 1/2, -z + 1/2$.				
Compound **9** D−H···A	*d*(D−H)	*d*(H···A)	*d*(D···A)	∠(DHA)
N(1)−H(01)···Au	0.88	2.67	3.143(2)	115.2
N(1)−H(01)···Cl	0.88	2.93	3.580(2)	132.1
C(8)−H(8)···F(1)#1[a]	0.95	2.60	3.298(4)	130.8
C(17)−H(17A)···F(6)#2	0.98	2.51	2.967(3)	108.3
C(17)−H(17B)···F(6)#2	0.98	2.56	2.967(3)	108.3
C(4)−H(4)···Cl#3	0.95	2.86	3.759(3)	157.4
C(11)−H(11A)···Cl#4	0.99	2.91	3.882(3)	167.9
Symmetry transformations used to generate equivalent atoms: #1: $x + 1/2, -y + 1/2, z - 1/2$, #2: $x - 1, y, z$; #3: $x + 1, y, z$; #4: $0.5 + x, 0.5 + y, 0.5 - z$.				

Experimental Section

Instrumentation: Infrared spectra were recorded in the range 4000−200 cm^{-1} with a Perkin−Elmer 883 spectrometer 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 microanalyser. Mass spectra were recorded with a VG Autospec instrument with the liquid secondary-ion mass spectroscopy (LSIMS) technique using nitrobenzyl alcohol as a matrix. NMR spectra were recorded with a Varian Unity 300 spectrometer or a Bruker ARX 300 spectrometer in $CDCl_3$. Chemical shifts are given relative to $SiMe_4$ (^1H, external), $CFCl_3$ (^{19}F, external) or 85% H_3PO_4 (^{31}P, external).

Starting Materials: The starting materials [Au(acac)(PPh_3)],[14] [$O(AuPPh_3)_3$]ClO_4,[15] [Au(C_6F_5)(tht)],[16] [Au(C_6F_5)$_3$(OEt_2)],[17] [Au(C_6F_5)$_2$Cl]$_2$ [18] and [Ag(OTf)(PPh_3)][19] were prepared according to published procedures. All other reagents were commercially available.

Synthesis of $FcCH_2NHpyMe$ (1): To a solution of 6-amino-2-picoline (0.756 g, 7 mmol) in acetic acid (30 mL) was added $FcCH_2NMe_2$ (1.7 g, 14 mmol) and the mixture was heated at 80 °C for 3 h. The solution was then cooled and an aqueous solution of $NaHCO_3$ was added in order to raise the pH to 7. The organic phase was extracted with CH_2Cl_2 (3 × 1 mL) and dried with $MgSO_4$. The solution was then concentrated to ca. 2 mL and chromatographed on alumina with diethyl ether/hexane (4:1) as eluent. Evaporation of the solvent to ca. 5 mL and addition of hexane gave the ligand **1** as an orange solid. Yield 40%, 856.9 mg. Λ_M = 0.4 Ω^{-1}·cm^2·mol^{-1}. $C_{17}H_{18}FeN_2$ (306.2): calcd. C 66.69, H 5.92, N 9.15; found C 66.57, H 5.90, N 9.10. ^1H NMR: δ = 2.39 (s, 3 H, Me), 4.10 (m, 2 H, C_5H_4), 4.12 (m, 2 H, CH_2), 4.19 (s, 5 H, C_5H_5), 4.22 (m, 2 H, C_5H_4), 4.73 (br. m, 1 H, NH), 6.23 [d, *J*(H,H) = 8.3 Hz, 1 H, py], 6.46 [d, *J*(H,H) = 7.7 Hz, 1 H, py], 7.35 [dd, *J*(H,H) = 8.3, 7.7 Hz, 1 H, py] ppm.

Synthesis of [M(PPh_3)($FcCH_2NHpyMe$)]OTf, M = Au (2), Ag (3): To a solution of **1** (0.031 g, 0.1 mmol) in dichloromethane (20 mL) 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 30 min. Evaporation of the solvent to ca. 5 mL and addition of hexane (10 mL) gave complexes **2** or **3** as orange solids.

Complex 2: Yield 72%, 65.8 mg. Λ_M = 120 Ω^{-1}·cm^2·mol^{-1}. $C_{36}H_{33}AuF_3FeN_2O_3PS$ (914.27): calcd. C 47.30, H 3.63, N 3.06, S 3.50; found C 46.86, H 3.29, N 2.90, S 3.64. ^1H NMR: δ = 2.58 (s, 3 H, Me), 4.3 (br. m, 10 H, C_5H_4, C_5H_5, NH, CH_2), 6.46 [d, *J*(H,H) = 6.6 Hz, 1 H, py], 6.63 [d, py, *J*(H,H) = 7.4, 1 H], 7.2−7.8 (m, 16 H, Ph, py) ppm. $^{31}P(^1H)$ NMR: δ = 30.6 (s, 1 P, PPh_3) ppm.

Complex 3: Yield 85%, 70.31 mg. Λ_M = 110 Ω^{-1}·cm^2·mol^{-1}. $C_{36}H_{33}AgF_3FeN_2O_3PS$ (827.171): calcd. C 52.38, H 4.03, N 3.41, S 3.88; found C 52.24, H 4.22, N 3.33, S 3.87. ^1H NMR: δ = 2.44 (s, 3 H, Me), 4−5 (br. m, 10 H, C_5H_4, C_5H_5, CH_2), 6.47 (m, 1 H, py), 6.52 (m, 1 H, py), 6.76 (s, 1 H, NH), 7.2−7.8 (m, 16 H, py, Ph) ppm. $^{31}P(^1H)$ NMR (−55 °C): δ = 11.3 [2 d, *J*(^{107}AgP) = 475.1, *J*(^{109}AgP) = 547.4 Hz, 1 P, PPh_3] ppm.

Synthesis of [M_2(PPh_3)$_2$($FcCH_2NpyMe$)]X, M = Au, X = ClO_4 (4), M = Ag, X = OTf (5)

Complex 4: To a solution of **1** (0.031 g, 0.1 mmol) in dichloromethane (20 mL) was added [$O(AuPPh_3)_3$]ClO_4 (0.149 g, 0.1 mmol) and the mixture was stirred for 2 h. Evaporation of the solvent to ca. 5 mL and addition of diethyl ether (10 mL) gave complex **4** as a yellow solid. Yield 95%, 124.33 mg. Λ_M = 110 Ω^{-1}·cm^2·mol^{-1}. $C_{52}H_{45}Au_2ClFeN_2O_4P_2$ (1308.806): calcd. C 48.11, H 3.58, N 2.12; found C 47.98, H 3.39, N 1.99. ^1H NMR: δ = 2.56 (s, 3 H, Me), 4.04 (m, 2 H, C_5H_4), 4.16 (s, 5 H, C_5H_5), 4.18 (m, 2 H, CH_2), 4.23 (m, 2 H, C_5H_4), 6.44 [d, *J*(H,H) = 7.0 Hz, 2 H, py], 6.68 [d, *J*(H,H) = 8.4 Hz, 2 H, py], 7.1−7.8 (m, 31 H, py, Ph) ppm. $^{31}P(^1H)$ NMR: δ = 30.5 (s, 1 P, PPh_3), 24.3 (s, 1 P, PPh_3) ppm.

The triflate salt $[Au_2(PPh_3)_2(FcCH_2NpyMe)]OTf$ is also accessible by treatment of complex **2**, $[Au(PPh_3)(FcCH_2NHpyMe)]OTf$, with $[Au(acac)(PPh_3)]$ in dichloromethane. Yield, 89%.

Complex 5: To a solution of **1** (0.031 g, 0.1 mmol) in dichloromethane (20 mL) was added $[Ag(OTf)(PPh_3)]$ (0.104 g, 0.2 mmol) and NEt_3 (0.021 mL, 0.15 mmol) and the mixture was stirred for 1 h. Evaporation of the solvent to ca. 5 mL and addition of hexane (10 mL) gave complex **5** as a red solid. Yield 70%, 82.61 mg. Λ_M = 100 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$. $C_{53}H_{45}Ag_2F_3FeN_2O_3P_2S$ (1180.226): calcd. C 54.30, H 3.96, N 1.17, S 2.68; found C 54.13, H 4.05, N 1.31, S 2.34. ^1H NMR: δ = 2.50 (s, 3 H, Me), 4.04 (m, 2 H, C_5H_4), 4.10 (m, 2 H, CH_2), 4.14 (s, 5 H, C_5H_5), 4.23 (m, 2 H, C_5H_4), 6.49 (m, 1 H, py), 6.56 (m, 1 H, py), 7.1−7.8 (m, 31 H, py, Ph) ppm. $^{31}P(^1H)$ NMR (−55 °C): δ = 10.4 [2 d, $J(^{107}AgP)$ = 402.9, $J(^{109}AgP)$ = 465.9 Hz, 1 P, PPh_3], 11.2 [2 d, $J(^{107}AgP)$ = 430.1, $J(^{109}AgP)$ = 492.5 Hz, 1 P, PPh_3] ppm.

Synthesis of $[Au(C_6F_5)(FcCH_2NHpyMe)]$ (6): To a solution of **1** (0.031 g, 0.1 mmol) in dichloromethane (20 mL) was added $[Au(C_6F_5)(tht)]$ (0.045 g, 0.1 mmol) and the mixture was stirred for 30 min. Evaporation of the solvent to ca. 5 mL and addition of hexane (10 mL) gave complex **6** as a yellow solid. Yield 76%, 49.86 mg. Λ_M = 4 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$. $C_{22}H_{16}AuF_5FeN_2$ (656.056): calcd. C 41.22, H 2.71, N 4.18; found C 41.09, H 2.50, N 3.99. ^1H NMR: δ = 2.80 (s, 3 H, Me), 4.07 [d, J(H,H) = 5.1 Hz, 2 H, CH_2], 4.20 (s, 5 H, C_5H_5), 4.20 (m, 2 H, C_5H_4), 4.27 (m, 2 H, C_5H_4), 6.55 [d, J(H,H) = 7.2 Hz, 1 H, py], 6.64 [d, J(H,H) = 8.7 Hz, 1 H, py], 6.73 (m, 1 H, NH), 7.58 [dd, J(H,H) = 8.7, 7.2 Hz, 1 H, py] ppm. ^{19}F NMR: δ = −117.3 (m, 2 F, *m*-F), 160.5 [t, J(F,F) = 20.6 Hz, 1 F, *p*-F], −164.1 (m, 2 F, *o*-F) ppm.

Synthesis of $[Au_2(C_6F_5)(PPh_3)(FcCH_2NpyMe)]$ (7): To a solution of complex **6** (0.067 g, 0.1 mmol) in dichloromethane (20 mL) was added $[Au(acac)(PPh_3)]$ (0.056 g, 0.1 mmol) and the mixture was stirred for 2 h. Evaporation of the solvent to ca. 5 mL and addition of diethyl ether (10 mL) gave complex **7** as a yellow solid. Yield 66%, 72.74 mg. Λ_M = 8 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$. $C_{39}H_{30}Au_2F_5FeN_2P$ (1102.21): calcd. C 43.64, H 2.86, N 2.48; found C 43.42, H 2.80, N 2.33. ^1H NMR: δ = 2.67 (s, 3 H, Me), 3.80 (m, 2 H, CH_2), 4.12 (s, 5 H, C_5H_5), 4.31 (m, 4 H, C_5H_4), 6.26 [d, J(H,H) = 6.0 Hz, 1 H, py], 6.53 [d, J(H,H) = 8.7 Hz, 1 H, py], 7.1−7.8 (m, py, Ph) ppm. ^{19}F NMR: δ = −116.0 (m, 2 F, *m*-F), 163.3 [t, 1 F, *p*-F, J(F,F) = 20.6 Hz], −164.5 (m, 2 F, *o*-F) ppm. $^{31}P(^1H)$ NMR: δ = 30.7 (s, 1 P, PPh_3) ppm.

Synthesis of $[Au(C_6F_5)_2X(FcCH_2NHpyMe)]$, X = C_6F_5 (8), Cl (9): To a solution of **1** (0.031 g, 0.1 mmol) in dichloromethane (20 mL) was added $[Au(C_6F_5)_3(OEt_2)]$ (0.077 g, 0.1 mmol) or $[Au(C_6F_5)_2Cl]_2$ (0.056 g, 0.05 mmol) and the mixture was stirred for 1 h. Evaporation of the solvent to ca. 5 mL and addition of hexane (10 mL) gave complexes **8** or **9** as yellow solids.

Complex 8: Yield 75%, 75.25 mg, Λ_M = 4 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$. $C_{35}H_{18}AuF_{15}FeN_2$ (1004.35): calcd. C 41.86, H 1.81, N 2.79; found C 41.79, H 1.56, N 2.34. ^1H NMR: δ = 2.71 (s, 3 H, Me), 4.11 (m, 2 H, CH_2), 4.20 (m, 9 H, C_5H_5, C_5H_4, NH), 5.89 (m, 1 H, py), 6.57 (m, 2 H, py), 7.53 (m, 1 H, py) ppm. ^{19}F NMR: δ = −121.6

Table 6. X-ray data for complexes **4**, **6**, **8** and **9**

Compound	**4**·C_6H_{12}	**6**	**8**·C_5H_{12}	**9**
Formula	$C_{59}H_{59}Au_2ClFeN_2O_4P_2$	$C_{23}H_{18}AuF_5FeN_2$	$C_{40}H_{30}AuF_{15}FeN_2$	$C_{29}H_{18}AuClF_{10}FeN_2$
M_r	1407.26	670.21	1076.48	872.72
Habit	orange tablet	orange prism	orange pyramid	orange tablet
Crystal size [mm]	0.45 × 0.25 × 0.15	0.55 × 0.45 × 0.3	0.50 × 0.45 × 0.25	0.18 × 0.15 × 0.09
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P(-1)$	$P2_1/n$	$P2_1/n$
Cell constants:				
a [Å]	10.879(2)	6.641(3)	10.3534(16)	8.1587(8)
b [Å]	21.245(3)	11.151(4)	22.911(3)	14.5039(14)
c [Å]	23.773(3)	14.737(5)	16.993(2)	23.688(2)
α [°]	90	84.66(2)	90	90
β [°]	97.687(10)	77.56(2)	100.170(12)	94.312(3)
γ [°]	90	85.54(2)	90	90
V [Å^3]	5445.3	1059.2	3967.6	2795.1
Z	4	2	4	4
D_x [Mg·m^{-3}]	1.717	2.101	1.802	2.074
μ [mm^{-1}]	5.8	7.7	4.2	5.9
F(000)	2760	640	2096	1672
T [°C]	−100	−130	−100	−130
$2\theta_{max.}$ [°]	50	50	50	60
No. of reflections				
Measured	10394	4425	7479	59912
Independent	9552	3723	6936	8194
Transmissions	0.45−0.96	0.46−0.81	0.50−0.99	0.69−0.86
R_{int}	0.036	0.024	0.025	0.059
Parameters	641	295	498	398
Restraints	632	274	149	138
$wR(F^2$, all refl.)	0.073	0.062	0.069	0.052
R [F, > 4σ(F)]	0.034	0.024	0.033	0.023
S	0.88	1.07	0.89	0.99
max. $\Delta\rho$ [e·Å^{-3}]	1.9	1.7	0.8	1.8

(m, 4 F, *m*-F), −123.0 (m, 2 F, *m*-F), −156.2 [t, *J*(F F) = 19.5 Hz, 2 F, *p*-F], −156.7 (t, *J*(F,F) = 19.6 Hz, 1 F, *p*-F], −160.8 (m, 4 F, *o*-F), −161.4 (m, 2 F, *o*-F) ppm.

Complex 9: Yield 74%, 64.39 mg, Λ_M = 18 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$. $C_{29}H_{18}AuClF_{10}FeN_2$ (872.61): calcd. C 39.91, H 2.08, N 3.22; found C 39.89, H 1.65, N 2.93. ^{1}H NMR: δ = 2.85 (s, 3 H, Me), 4.12 (m, 2 H, CH_2), 4.20 (m, 9 H, C_5H_5, C_5H_4), 4.41 (m, 1 H, NH), 6.04 (m, 1 H, py), 6.60 [2 d, *J*(H,H) = 7.3, 8.5 Hz, 2 H, py], 7.58 [dd, *J*(H,H) = 7.3, 8.5 Hz, 1 H, py] ppm. ^{19}F NMR: δ = −122.0 (m, 2 F, *m*-F), −123.0 (m, 2 F, *m*-F), −154.7 [t, *J*(F,F) = 19.6 Hz, 1 F, *p*-F], −156.0 [t, *J*(F,F) = 19.6 Hz, 1 F, *p*-F], −160.0 (m, 2 F, *o*-F), −161.2 (m, 2 F, *o*-F) ppm.

Synthesis of $[Cu(FcCH_2NHpyMe)_2]PF_6$ (10): To a solution of **1** (0.031 g, 0.1 mmol) in dichloromethane (20 mL) was added $[Cu(NCMe)_4]PF_6$ (0.037 g, 0.1 mmol) and the mixture was stirred for 2 h. Evaporation of the solvent to ca. 5 mL and addition of hexane (10 mL) gave complex **10** as a yellow solid. Yield 72%, 54.83 mg. Λ_M = 134 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$. $C_{32}H_{32}CuF_6Fe_2N_4$ (761.592): calcd. C 49.75, H 4.42, N 6.82; found C 49.55, H 4.40, N 6.83. ^{1}H NMR: δ = 2.53 (s, 6 H, Me), 4.0 (m, 4 H, CH_2), 4.35 (m, 18 H, C_5H_5, C_5H_4), 5.60 (m, 2 H, NH), 6.58 (m, 3 H, py), 7.57 (m, 1 H) ppm.

X-ray Crystallography: Data were recorded with a Stoe-STADI-4 (**6**), Siemens P4 (**4**, **8**) or Bruker SMART 1000 CCD (**9**) diffractometer. Data collection type: ω/θ-scans (**6**), ω-scans (**4**, **8**) or ω- and φ-scans (**9**). The structures were refined on F^2 using the program SHELXL-97.[20] All non-hydrogen atoms were refined anisotropically. Aminic hydrogen atoms were identified from difference syntheses but were refined freely only for **6**. Other hydrogen atoms were included either as rigid methyl groups (not well resolved for **4** and **8**) or using a riding model. Refinement special details: The structure of **4** contains one well-resolved cyclohexane solvate molecule. Additionally, two peaks of ca. 2 e/Å^3 near the cyclohexane may represent an alternative disordered solvent site. The structure of **8** contains one poorly resolved pentane solvate molecule which was refined isotropically. The molecular weights and related parameters correspond to the idealised compositions including solvent. Further crystallographic data are collected in Table 6. CCDC-229959 to -229962 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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