Unusual coordination behaviour of the ferrocenyl-terpyridine ligand with group 11 complexes[1]

Javier E. Aguado, M. Concepción Gimeno, Peter G. Jones, and Antonio Laguna

Abstract: Complexes of the ligand Fcterpy (Fcterpy = 4′-ferrocenyl-2,2′:6′,2′-terpyridine) with group 11 metals display different coordination modes. The reaction with complexes $[Cu(NO_3)(PPh_3)_2]$ or $[M(OTf)(PR_3)]$ (OTf = trifluoromethylsulphonate) gives the species $[M(Fcterpy)(PR_3)]X$ (M = Cu, X = PF_6, PR_3 = PPh_3 (**1**); M = Ag, X = OTf, PR_3 = PPh_3 (**2**), PPh_2Me (**3**); M = Au, X = OTf, PR_3 = PPh_3 (**4**)) in which the ligand is coordinated as a tridentate chelate to the metal. Treatment with $[Cu(NCMe)_4]PF_6$ or Ag(OTf) in 1:1 molar ratio gives the dinuclear complexes $[M_2(Fcterpy)_2]X_2$ (M = Cu (**5**), Ag (**6**)), in which the ligand is tetradentate because the central pyridine group is bonded to two metals. The reaction with the gold(I) complex $[Au(C_6F_5)(tht)]$ (tht = tetrahydrothiophene) leads to the first example of a terpyridine ligand bonded to three metal atoms, $[Au_3(C_6F_5)_3(Fcterpy)]$ (**7**); in the product of the corresponding reaction with the gold(III) derivative $[Au(C_6F_5)_3(OEt_2)]$ to give $[Au(C_6F_5)_3(Fcterpy)]$ (**8**), the ligand is monodentate, which is also unusual for a terpyridine ligand.

Key words: copper, silver, gold, terpyridine, ferrocene derivatives

Résumé : Les complexes du ligand Fcterpy [Fcterpy = 4′-ferrocényl-2,2′:6′,2′-terpyridine] avec les métaux du groupe 11 présentent divers modes de coordination. Les réactions avec des complexes $[Cu(NO_3)(PPh_3)_2]$ ou $[M(OTf)(PR_3)]$ (Otf = trifluorométhylsulfonate) conduisent à des espèces $[M(Fcterpy)(PR_3)]X$ [M = Cu; X = PF_6; PR_3 = PPh_3 (**1**); M = Ag; X = OTf; PR_3 = PPh_3 (**2**); PPh_2R (**3**); M = Au; X = OTf; PR_3 = PPh_3 (**4**)] dans lesquels le ligand est coordiné au métal sous la forme de chélate tridentate. Le traitement avec du $[Cu(NCME)_4]PF_6$ ou du Ag(OTf), dans un rapport molaire de 1:1, conduit à la formation de complexes binucléaires $[Me_2(Fcterpy)_2]X_2$ (M = Cu (**5**); Ag (**6**)] dans lesquels le ligand est tétradentate parce que le groupe pyridine central est lié à deux métaux. La réaction avec le complexe d'or(I) $[Au(C_6F_5)(tht)]$ (tht = tétrahydrothiophène) conduit au premier exemple d'un ligand terpyridine lié à trois atomes métalliques, $[Au_3(C_6F_5)_3(Fcterpy)]$ (**7**); dans le produit de la réaction correspondante avec le dérivé d'or(III) $[Au(C_6F_5)_3(OEt_2)]$ conduisant à la formation de $[Au(C_6F_5)_3Fcterpy)]$ (**8**), le ligand est sous la forme monodentate qui est inhabituelle pour un ligand terpyridine.

Mots-clés : cuivre, argent, or, terpyridine, dérivés du ferrocène.

[Traduit par la Rédaction]

Introduction

The coordination chemistry of terpyridine ligands with various metals has been the subject of numerous studies, inspired by the exciting photophysical properties of metal–polypyridyl complexes (1). In these compounds, the terpyridine generally acts as a chelating planar tridentate ligand; only in some examples does it act as a bidentate ligand with a non-coordinating residue (2). In the last few years, interesting spiral arrays have been prepared with these ligands that, by twisting, can accommodate more than one metal center. Thus, some examples have been prepared with silver in which the terpy is bonded to two different metal centers in a supramolecular structure (3). We have previously communicated another coordination mode in which the three nitrogen atoms are bonded to three different metals in the complex $[Au_3(C_6F_5)_3(Fcterpy)]$ (4). Few terpyridine complexes of gold have been described and these are gold(III) derivatives, such as $[AuX(Rterpy)]^{2+}$ (X = Cl, OH; R = H, SMe, PhOMe) (5–8), or $[Au(CN)_2Br(\eta^2\text{-terpy})]$ (9) (terpy = terpyridine), in which the ligand acts a tridentate or bidentate chelate. For silver and copper, more examples have been described including complexes of the type $[M(PR_3)_2(terpy)]X$ (M = Cu, Ag) (10).

Here we report complexes with the group 11 metals and a substituted terpyridine ligand, 4′-ferrocenyl-2,2′:6′,2′-terpyridine (Fcterpy) (11). Several coordination modes have been achieved, including tridentate chelate in complexes of the type $[M(Fcterpy)(PR_3)]X$ (M = Cu, Ag, Au), tetradentate in the homoleptic species $[M_2(Fcterpy)_2]X_2$ (M = Cu, Ag), which represent the first examples of dinuclear rather than

Received 21 May 2008. Accepted 10 September 2008. Published on the NRC Research Press Web site at canjchem.nrc.ca on 6 January 2009.

Dedicated to Professor Richard Puddephatt.

J.E. Aguado, M.C. Gimeno,[2] and A. Laguna. Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza – C.S.I.C., E-50009 Zaragoza, Spain.
P.G. Jones. Institut für Anorganische und Analytische Chemie der Technischen Universität, Postfach 3329, D-38023 Braunschweig, Germany.

[1] This article is part of a Special Issue dedicated to Professor R. Puddephatt.

[2] Corresponding author (e-mail: gimeno@unizar.es).

doi:10.1139/V08-148

Scheme 1. Synthesis of the Fcterpy ligand.

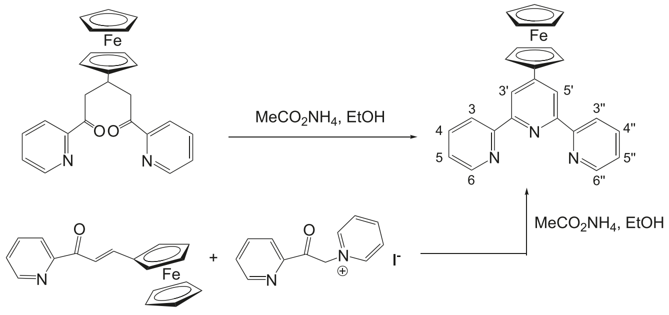
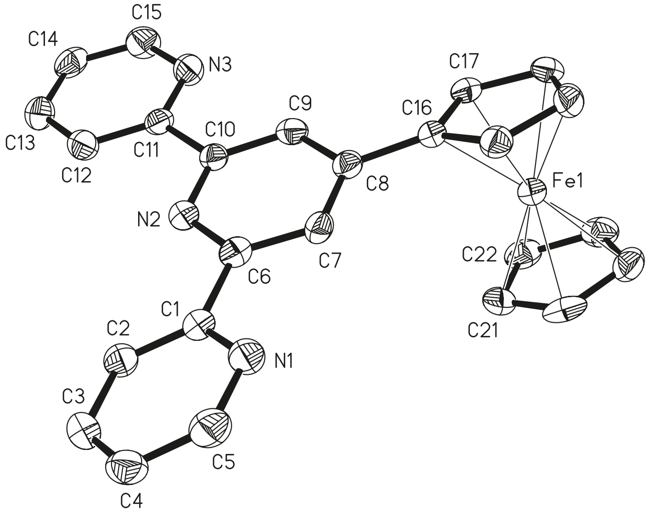


Fig. 1. Structure of compound Fcterpy showing the atom labelling scheme. Displacement parameter ellipsoids represent 50% probability surfaces. Radii are arbitrary; H atoms are omitted for clarity.



the usual polymeric derivatives, or monodentate in the gold(III) compound [Au(C$_6$F$_5$)$_3$(Fcterpy)].

Results and discussion

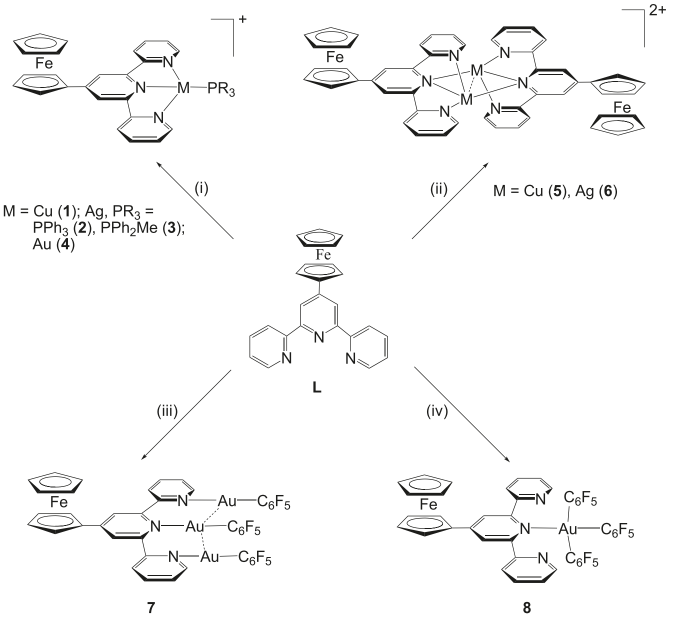
The ligand 4′-ferrocenyl-2,2′:6′,2′-terpyridine (Fcterpy) has been synthesized by aromatization of a 3-ferrocenyl-1-bis(2-pyridyl)pentane-1,5-dione, previously obtained by reaction of ferrocenaldehyde and 2-acetylpyridine, or by aromatization of the corresponding enone with a pyridonium iodide salt (see Scheme 1) as has been previously described (11). The crystal structure of this ligand has been established and the molecule is shown in Fig. 1. A selection of bond lengths and angles are collected in Table 1. The overall bond lengths and angles are within the normal values found in this type of compound (12). The cyclopentadienyl rings are almost eclipsed. In the terpyridine moiety the aromatic rings are almost coplanar themselves, but not with the cyclopentadienyl ring; the dihedral angle formed by the nitrogen atoms and the cyclopentadienyl ring is 161.6°. The nitrogen atoms of the external pyridine rings are pointed in the opposite direction to that of the central one. This configuration changes upon coordination of the ligand.

Table 1. Bond lengths and angles for the ligand Fcterpy.

Bond lengths (Å)	
N(1)–C(5)	1.337(3)
N(1)–C(1)	1.346(3)
N(2)–C(10)	1.335(3)
N(2)–C(6)	1.344(4)
N(3)–C(15)	1.336(3)
N(3)–C(11)	1.338(3)
Bond angles (°)	
C(5)-N(1)-C(1)	116.8(2)
C(15)-N(3)-C(11)	116.9(2)
N(1)-C(1)-C(2)	122.4(2)
N(1)-C(1)-C(6)	116.6(2)
N(1)-C(5)-C(4)	124.4(3)
N(2)-C(6)-C(7)	122.8(2)
N(2)-C(6)-C(1)	115.9(2)
C(10)-N(2)-C(6)	117.6(2)
N(2)-C(10)-C(9)	122.7(2)
N(3)-C(11)-C(10)	116.7(2)
N(2)-C(10)-C(11)	116.7(2)
N(3)-C(15)-C(14)	124.5(3)

The reaction of the Fcterpy ligand with [Cu(NO$_3$)(PPh$_3$)$_2$] or [Ag(OTf)(PR$_3$)] or [Au(OTf)(PPh$_3$)] affords the complexes [Cu(PPh$_3$)(Fcterpy)]NO$_3$ (**1**), [Ag(PR$_3$)(Fcterpy)]OTf (PR$_3$ = PPh$_3$ (**2**), PPh$_2$Me (**3**)), or [Au(PPh$_3$)(Fcterpy)]OTf (**4**) (see Scheme 2). The IR spectra for these compounds show the absorptions of the ferrocenyl terpyridine unit as those arising from the aromatic pyridine and cyclopentadienyl rings around 1607 (s), 1586 (s), 1104 (s), and 820 (s) cm^{-1}. In addition, complex **1** shows the absorptions of the nitrate group at 1725 (w), 1090 (m), 1026 (m), 1000 (w), and 827 (m) cm^{-1} and complexes **2**–**4** show the bands arising from the ionic trifluoromethylsulfonate anion at around 1262 (vs), 1223 (m), 1147 (vs), and 1030 (vs) cm^{-1}. Because the ^{1}H NMR spectra of all complexes show the presence of the ligand Fcterpy, it is useful to compare the resonances with those present in the free ligand. The ligand shows two multiplets for the α and β protons of the substituted cyclopentadienyl group and a singlet for the unsubstituted cyclopentadienyl unit; the proton signals for the terpyridine are a doublet of doublets for the pair 5–5″, a doublet of triplets for the pair 4–4″, a singlet for 3′–5′, and doublets for the pairs 3–3″ and 6–6″. The resonances for the coordinated ligand in complexes **1**–**4** resemble those in the free ligand but with a different chemical shift and not so well defined, and in some cases the resonances overlap with those of the phenylic protons. For complex **3**, a doublet at 1.91 ppm for the methyl protons coupled to the phosphorus atom is observed. The ^{31}P{^{1}H} NMR spectra shows a singlet for complexes **1** and **4**, whereas for compounds **2** and **3** a broad resonance appears at room temperature and splits into two doublets at –55 °C, because of the coupling of the phosphorus atom with the two silver nuclei with spin 1/2, ^{109}Ag (48.17%) and ^{107}Ag (51.83%). The mass spectra show in all the complexes the cationic molecular peak [M(PR$_3$)(Fcterpy)]$^+$ at m/z = 742 (18%, **1**), 786 (34%, **2**), 724 (36%, **3**), and 876 (45%, **4**), although for the copper and silver complexes the most abundant peaks correspond to the species [M(Fcterpy)]$^+$.

Scheme 2. (*i*) $[Cu(NO_3)(PPh_3)_2]$ or $[Ag(OTf)(PR_3)]$ or $[Au(OTf)(PPh_3)]$; (*ii*) $[Cu(NCMe)_4]PF_6$ or Ag(OTf); (*iii*) 3 $[Au(C_6F_5)(tht)]$; (*iv*) $[Au(C_6F_5)_3(OEt_2)]$.



The silver complexes have been structurally characterized, showing that the metal center is bonded to the three nitrogen atoms of the terpyridine unit, although the shortest bond is with the central nitrogen atom; we assume analogous structures for the copper and gold complexes. However in the gold complex the metal could be far more strongly bonded to the central nitrogen atom and make only very short contacts with the others, given the high tendency of gold to form two-coordinate derivatives. No crystal structure for gold(I) complexes with terpyridine ligands has been carried out, with the exception of the trinuclear complex **7**. The structures of complexes **2** and **3** have been established by X-ray diffraction and are shown in Figs. 2 and 3, respectively. A selection of bond lengths and angles are collected in Tables 2 and 3. The structure for complex **2** shows that the silver center coordinates to the three nitrogen atoms of the terpyridine moiety and to the triphenylphosphine, and although it is tetra-coordinated, the geometry is far from tetrahedral. The silver atom is located 0.11 Å out of the plane formed by the four donor atoms, P, N11, N21, and N31, and only 0.057 Å out of the trigonal plane of the P, N21, and N31 atoms. The Ag–N distances are 2.302(4), 2.435(4), and 2.492(4) Å, the shortest being to the central nitrogen atom. The angles N–Ag–P are 117.53(9) and 109.91(11)°, which corresponds to normal values found in trigonal planar complexes (13); consequently the N–Ag–N angles are very narrow, 68.98(13) and 68.35(14)°. Two of the phenyl rings are disordered in mutually perpendicular positions, although this disorder is not shown in Fig. 2. The structure of complex **3** is similar, with Ag–N distances 2.332(4), 2.421(4), and 2.488(5) Å, again with the shortest to the central pyridine ring. The geometry around the silver center is more distorted than in complex **2**; the Ag atom lies 0.27 Å out of the plane formed by the four coordinated atoms and 0.11 Å out of the plane of the N1, N3, and P atoms. The phosphorus atom is located further from the plane formed by the terpyridine and the silver atom than in complex **2**, with an N2–Ag–P angle of 152.06(11)° compared to 158.65(9)° in **2**. These structures are different from the previously reported complexes of stoichiometry $[M(terpy)(PPh_3)_2]^+$, which consist of discrete monomers of distorted trigonal-bipyramidal geometry, with the metal atoms coordinated to the distal terpyridine pyridyl rings [Cu-N 2.386(3), 2.535(4); Ag–N 2.614(2), 2.561 (2)Å] in axial sites (10). The coordination spheres are completed by the binding of the central pyridyl nitrogen atoms [Cu-N(2) 2.102(3), Ag–N(2) 2.457(2)Å] and two PPh_3 phosphorus atoms, which together define the equatorial planes.

Fig. 2. Structure of the cation of compound **2** showing the atom numbering scheme. Displacement parameter ellipsoids represent 30% probability surfaces. Radii are arbitrary; H atoms are omitted for clarity.

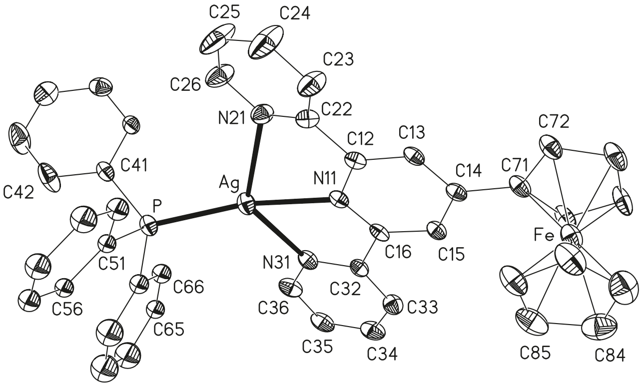
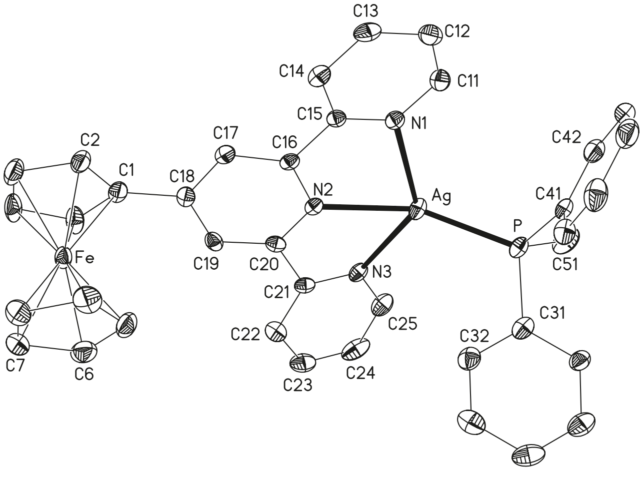


Fig. 3. Structure of the cation of compound **3** showing the atom numbering scheme. Displacement parameter ellipsoids represent 30% probability surfaces. Radii are arbitrary; H atoms are omitted for clarity.



The reaction of the ligand with an equimolar amount of $[Cu(NCMe)_4]PF_6$ or Ag(OTf) gives compounds with the stoichiometry [M(Fcterpy)]X (M = Cu, X = PF_6 (**5**); M = Ag, X = OTf (**6**)). The IR spectra show the typical absorptions of the Fcterpy ligand; the copper species show the absorption of the hexafluorophosphate at 640 (s) cm^{-1}, whereas the silver derivative presents the absorptions for the trifluoromethylsulfonate at 1259 (vs), 1223 (m), 1115 (vs),

Table 2. Selected bond lengths and angles for complex **2**.

Bond lengths (Å)	
Ag–N(11)	2.302(4)
Ag–N(31)	2.435(4)
Ag–P	2.3710(14)
Ag–N(21)	2.492(4)
Bond angles (°)	
N(11)-Ag-P	158.65(9)
N(11)-Ag-N(21)	68.35(14)
N(11)-Ag-N(31)	68.98(13)
P-Ag-N(21)	109.91(11)
P-Ag-N(31)	117.53(9)
N(31)-Ag-N(21)	132.38(13)

Table 3. Selected bond lengths and angles for complex **3**.

Bond lengths (Å)	
Ag–N(2)	2.332(4)
Ag–N(1)	2.421(4)
Ag–P	2.3783(16)
Ag–N(3)	2.488(5)
Bond angles (°)	
N(2)–Ag–P	152.06(11)
N(2)-Ag-N(3)	67.72(15)
N(2)-Ag-N(1)	69.22(15)
P-Ag-N(3)	111.19(11)
P-Ag-N(1)	113.70(11)
N(1)-Ag-N(3)	134.47(14)

and 1029 (vs) cm^{-1}. The ^{1}H NMR spectra also exhibit different ligand chemical shifts for the silver and copper derivatives; the copper species shows a broad resonance at 8.2 ppm for all the protons of the Fcterpy ligand. In the mass spectrum of complex **5** the peaks arising from $[Cu(Fcterpy)]^+$, $[Cu_2(Fcterpy)_2]^{2+}$, and $[Cu_2(Fcterpy)](PF_6)^+$ appear at *m*/*z* = 480 (100%), 960 (9%), and 1129 (15%); for complex **6** similar peaks at *m*/*z* = 524 ($[Ag(Fcterpy)]^+$, 100%), 941 ($[Ag(Fcterpy)_2]^+$, 12%), and 1119 ($[Ag_2(OTf)(Fcterpy)_2]^+$, 4%) are observed. These data could imply a dinuclear structure with two metal atoms and two ferrocenyl-terpyridine ligands. The previously reported complexes that contain a terpyridine ligand and silver atoms are usually polymeric species in which the silver center bonds asymmetrically to the terpyridine units, giving a polymeric chain structure or a helical structure for the ligand *t*-BuPh-terpy (14). In our ligand the presence of a more bulky group, the ferrocenyl unit, makes the structure different. Several crystals of complex **6** proved to be of low quality, small and poorly diffracting, but the molecule can be recognised in the structure solution and corresponds to a dinuclear derivative in which the ferrocenyl-terpyridine ligand has an unusual role; central pyridine is bonded to the two silver atoms, in a coordination mode described as “crevice” (see Scheme 1) that has only recently been reported for silver (10). We assume a similar structure for the copper species although we can not rule out other possibilities.

The reaction of the ferrocenyl-terpyridine ligand with three equivalents of $[Au(C_6F_5)(tht)]$ in dichloromethane leads to the synthesis of the compound $[Au_3(C_6F_5)_3(\eta^3\text{-}Fcterpy)]$ (**7**), which has been previously communicated and represents the first example of a terpyridine ligand bonded to three metal atoms (4) The treatment of the ligand with the gold(III) derivative, $[Au(C_6F_5)_3(OEt_2)]$, gives an orange solid $[Au(C_6F_5)_3(Fcterpy)]$ (**8**). The IR spectrum shows the typical absorptions arising from the pentafluorophenyl groups bonded to gold(III) at 1509 (vs), 965 (vs), 821 (m), and 794 (vs) cm^{-1}. The ^{19}F NMR spectrum also confirms the presence of an $Au(C_6F_5)_3$ moiety because six resonances appear, three for the pentafluorophenyl rings in a mutually *trans* position and the other three for the other pentafluorophenyl ring (ratio 2:1). The ^{1}H NMR spectrum presents the resonances for the ferrocenyl-terpyridine, shifted compared to the free ligand. The protons of the ferrocenyl and terpyridine unit have the same pattern as in the free ligand and, consequently, we assume a symmetrical coordination. Furthermore, since gold(III) is mainly square planar and pentacoordination is not easily achieved, we propose a coordination of the gold(III) center to the central pyridine group.

Electrochemistry

The electrochemical behaviour of the ligand Fcterpy and some of these complexes has been studied by cyclic voltammetry at a platinum electrode in CH_2Cl_2. The ligand Fcterpy undergoes a reversible one-electron oxidation process at 0.64 eV; this is based on the ferrocene unit although at higher potential than the ferrocene itself. The cyclic voltammogram of the gold derivative **8**, at a scan rate of 100 mV s^{-1}, shows an essentially reversible wave arising from the oxidation-reduction of the ferrocene moiety at slightly lower potential than the free ligand, 0.61 eV. The copper(I) and silver(I) compounds $[M(PPh_3)(Fcterpy)]^+$ show, in addition to the wave from the ferrocene oxidation at 0.54 and 0.59 eV, respectively, a more anodic irreversible wave that can be assigned to the one electron oxidation of Cu^+ to Cu^{2+} and Ag^+ to Ag^{2+} at 0.70 and 1.12 eV. The dinuclear silver derivative $[Ag_2(Fcterpy)_2](OTf)_2$ also shows a quasi reversible wave for the oxidation-reduction of the ferrocene moieties at 0.60 eV and it is possible to distinguish two oxidation waves at 1.08 and 1.17 eV for the two Ag^+ atoms.

Experimental section[3]

Reagents and general procedures

Infrared spectra were recorded in the range 4000–200 cm^{-1} on a PerkinElmer 883 spectrophotometer using Nujol mulls

---

[3] Supplementary data for this article are available on the journal Web site (canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 3856. For more information on obtaining material refer to cisti-icist.nrc-cnrc.gc.ca/cms/unpub_e.shtml. CCDC 688756–688758 contain the crystallographic data for this manuscript. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

between polyethylene sheets. C, H, N, and S analyses were carried out with a PerkinElmer 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 $SiMe_4$ (^{1}H, external), $CFCl_3$ (^{19}F, external), and 85% H_3PO_4 (^{31}P, external). Cyclic voltammetric experiments were performed by employing an EG&G PARC Model 273 potentiostat. A three-electrode system was used, consisting of a platinum disk working electrode, a platinum wire auxiliary electrode, and a saturated calomel reference electrode. The measurements were carried out in CH_2Cl_2 solutions with 0.1 mol/L Bu_4NPF_6 as a supporting electrolyte. Under the present experimental conditions, the ferrocenium–ferrocene couple was located at 0.47 V vs. SCE. The starting materials Fcterpy (11), $[Au(C_6F_5)(tht)]$ (15), $[Ag(OTf)(PR_3)]$ (16), $[Cu(NO_3)(PPh_3)_2]$ (17), $[Cu(NCMe)_4]PF_6$ (17), and $[Au(C_6F_5)_3(OEt_2)]$ (18) were prepared according to published procedures. $[Au(OTf)(PPh_3)]$ was obtained by reaction of $[AuCl(PPh_3)]$ (19) with Ag(OTf) in dichloromethane and used in situ. All other reagents were commercially available.

Preparation of $[Cu(PPh_3)(Fcterpy)]NO_3$ (1)

To a solution of Fcterpy (0.041 g, 0.1 mmol) in 20 mL of dichloromethane was added $[Cu(NO_3)(PPh_3)_2]$ (0.063 g, 0.1 mmol) under an argon atmosphere, and the mixture was left to react for 40 min. Evaporation of the solvent to ca. 2 mL and addition of hexane gave a deep red solid of complex **1**; yield 53%. ^{1}H NMR δ: 4.09 (s, 5H, C_5H_5), 4.63 (m, 2H, C_5H_4), 5.0 (m, 2H, C_5H_4), 6.9–7.5 (m, 15H + 4H, Ph + H5,H5″ + H6,H6″), 7.66 (t, 2H, *J*(HH) = 7.45 Hz, H4,H4′), 7.97 (d, 2H, *J*(HH) = 8.06 Hz, H3,H3″), 8.01 (s, 2H, H3′,H5′). ^{31}P NMR {^{1}H} δ: 1.2 (s, 1 P, PPh_3). MS *m/z*: 742 (18%, $[Cu(PR_3)(Fcterpy)]^+$), 480 (100%, $[Cu(Fcterpy)]^+$). Anal.calcd.. for $C_{43}H_{34}CuFeN_4O_3P$: C 64.14, H 4.25, N 6.95; found: C 64.53, H 4.62, N 6.74.

Preparation of $[Ag(PR_3)(Fcterpy)]OTf$ (PR_3 = PPh_3 (2) and PPh_2Me (3))

To a solution of Fcterpy (0.041 g, 0.1 mmol) in 20 mL of dichloromethane was added $[Ag(OTf)(PPh_3)]$ (0.051 g, 0.1 mmol) or $[Ag(OTf)(PPh_2Me)]$ (0.045 g, 0.1 mmol) and the mixture was left to react for 40 min. Evaporation of the solvent to ca. 2 mL and addition of hexane gave deep red solids of complex **2** or **3**. Complex **2**: yield, 92%. ^{1}H NMR δ: 4.10 (s, 5H, C_5H_5), 4.54 (m, 2H, C_5H_4), 5.08 (m, 2H, C_5H_4), 7.2–7.4 (m, 15H, Ph), 7.45 (d, 2H, *J*(HH) = 7.33 Hz, H5,H5″), 7.97 (t, 2H, *J*(HH) = 7.69 Hz, H4,H4′), 8.17 (d, 2H, *J*(HH) = 4.17 H6,H6″), 8.21 (s, 2H, H3′,H5′), 8.45 (d, 2 H, *J*(HH) = 7.92 Hz, H3,H3″). ^{31}P NMR {^{1}H, –55 °C} δ: 12.3 (2d, 1 P, *J*(^{109}AgP) = 707, *J*(^{107}AgP) = 615 Hz, PPh_3). MS *m/z*: 786 (34%, $[Ag(PPh_3)(Fcterpy)]^+$), 524 (100%, $[Ag(Fcterpy)]^+$). Anal. calcd. for $C_{44}H_{34}AgF_3FeN_3O_3PS$: C 56.43, H 3.65, N 4.48, S 3.42; found: C 56.57, H 3.70, N 4.72,S 3.20. Complex **3**; yield 80%. ^{1}H NMR δ: 1.91 (d, 3H, *J*(HP) = 6 Hz, Me), 4.45 (s, 5H, C_5H_5), 4.84 (m, 2H, C_5H_4), 5.35 (m, 2H, C_5H_4), 7.2–7.4 (m, 10H, Ph), 7.41 (2H, H5,H5″), 7.89 (t, 2H, *J*(HH) = 7.57 Hz, H4,H4′), 7.98 (s, 2H, H3′,H5′), 7.98 (s, 2H, H3′,H5′), 8.37 (d, 2H, *J*(HH) = 3.91 Hz, H6,H6″). ^{31}P NMR{^{1}H, –55 °C) δ: –6.7 (2d, 1 P, *J*(^{109}AgP) = 733 Hz, *J*(^{107}AgP) = 631 Hz, PPh_2Me). MS *m/z*: 724 (36%, $[Ag(PPh_2Me)(Fcterpy)]^+$), 524 (100%, $[Ag(Fcterpy)]^+$). Anal.calcd. for $C_{39}H_{32}AgF_3FeN_3O_3PS$: C 53.56, H 3.68, N 4.80, S 3.66; found: C 53.69, H 3.71, N 5.12, S 3.83.

Preparation of $[Au(PPh_3)(Fcterpy)]OTf$ (4)

To a solution of Fcterpy (0.041 g, 0.1 mmol) in 20 mL of dichloromethane was added $[Au(OTf)(PPh_3)]$ (0.060 g, 0.1 mmol) and the mixture was left to react for 40 min. Evaporation of the solvent to ca. 2 mL and addition of hexane gave a deep red solid of complex **4**; yield 65%. ^{1}H NMR δ: 4.31 (s, 5H, C_5H_5), 4.67 (m, 2H, C_5H_4), 5.30 (m, 2H, C_5H_4), 7.2–7.5 (m, 15H + 2H, Ph + H5,H5″), 7.89 (m, 2H, H4,H4′), 8.59 (m, 2H, H6,H6″), 8.32 (m, 2 H, H3,H3″), 8.71 (s, 2H, H3′,H5′). ^{31}P NMR{^{1}H} δ: 33.6 (s, 1P, PPh_3). MS *m/z*: 876 (45%, $[Au(PPh_3)(Fcterpy)]^+$). Anal. calcd. for $C_{44}H_{34}AuF_3FeN_3O_3PS$: C 51.52, H 3.34, N 4.09, S 3.12; found: C 51.74, H 3.44, N 4.10, S 3.31.

Preparation of $[M_2(Fcterpy)_2]X_2$ (M = Cu, X =PF_6 (5) and M = Ag, X = OTf = (6))

To a solution of Fcterpy (0.041 g, 0.1 mmol) in 20 mL of dichloromethane was added $[Cu(NCMe)_4]PF_6$ (0.038 g, 0.1 mmol), at 0 °C and under an argon atmosphere, or Ag(OTf) (0.025 g, 0.1 mmol), and the mixture was left to react for 30 min. Evaporation of the solvent to ca. 2 mL and addition of hexane gave deep red solids of complexes **5** or **6**. Complex **5**: yield 53%. ^{1}H NMR δ: 4.10 (s, 5H, C_5H_5), 5.06 (m, 2H, C_5H_4), 4.52 (m, 2H, C_5H_4), 8.2 (m, 10H, terpy). MS *m/z*: 1129 (15%, $[Cu_2(Fcterpy)_2](PF_6)^+$), 960 (9%, $[Cu_2(Fcterpy)_2]^+$), 480 (100%, $[Cu(Fcterpy)]^+$). Anal. calcd. for $C_{50}H_{38}Cu_2F_{12}Fe_2N_6P_2$: C 47.98, H 3.06, N 6.71; found: C 47.97, H 3.27, N 7.03. Complex **6**: yield 61%. ^{1}H NMR δ: 4.19 (s, 5H, C_5H_5), 4.65 (m, 2H, C_5H_4), 5.32 (m, 2H, C_5H_4), 7.43 (dq, 2H, *J*(HH) = 5.0, 1.1 Hz, H5,H5″), 8.06 (dt, 2H, *J*(HH) = 7.69, 1.71 Hz, H4,H4′), 8.31 (d, 2H, *J*(HH) = 5.0 Hz, H6,H6″), 8.48 (d, 2 H, *J*(HH) = 8.05 Hz, H3,H3″), 8.51 (s, 2H, H3′,H5′). MS *m/z*: 1119 (4%, $[Ag_2(OTf)(Fcterpy)_2]^+$), 941 (12%, $[Ag_2(Fcterpy)_2]^+$), 524 (100%, $[Ag(Fcterpy)]^+$). Anal. calcd. for $C_{52}H_{38}Ag_2F_6Fe_2N_6O_6S_2$: C 46.31, H 2.84, N 6.23, S 4.75; found: C 46.55, H 3.02, N 6.37, S 4.66.

Preparation of $[Au(C_6F_5)_3(Fcterpy)]$ (8)

To a solution of Fcterpy (0.041 g, 0.1 mmol) in 20 mL of dichloromethane was added $[Au(C_6F_5)_3(OEt_2)]$ (0.077 g, 0.1 mmol) at 0 °C and under an argon atmosphere, and the mixture was left to react for 40 min. Evaporation of the solvent to ca. 2 mL and addition of hexane gave a deep red solid of complex **8**; yield 63%. ^{1}H NMR δ: 4.15 (s, 5H, C_5H_5), 4.57 (m, 4H, C_5H_4), 5.04 (m, 4H, C_5H_4), 7.51 (m, 2H, H5,H5″), 8.01 (s, 2H, H3′,H5′), 8.03 (m, 2H, H3,H3″), 8.40 (m, 2H, H4, H4′), 8.69 (d, 2H, *J*(HH) = 5.13, H6,H6″). ^{19}F NMR δ: –121.6 (m, 6F, *m*-F), –156.4 (t, 2F, *p*-F, *J*(FF) = 21.12 Hz), –156.7 (t, 1F, *p*-F, *J*(FF) = 21.33 Hz), –160.8 (m, 4F, *o*-F), –161.9 (m, 2F, *o*-F). Anal. calcd. for $C_{43}H_{19}AuF_{15}FeN_3$: C 46.30, H 1.71, N 3.76; found: C 46.25, H 1.54, N 3.49.

Table 4. X-ray data for the compound Fcterpy and complexes **2** and **3**.

Compound	Fcterpy	**2**·0.59 H_2O	**3**·1/2 CH_2Cl_2
Formula	$C_{50}H_{38}Fe_2N_6$	$C_{44}H_{35.19}AgF_3FeN_3O_{3.6}PS$	$C_{39.5}H_{33}AgClF_3N_3O_3PS$
M_r	834.56	947.25	916.89
Habit	Red prism	Red tablet	Red prism
Crystal size (mm)	0.20 × 0.20 × 0.12	0.40 × 0.20 × 0.20	0.40 × 0.30 × 0.25
Crystal system	Monoclinic	Tetragonal	Triclinic
Space group	$P2_1/c$	$I4_1/a$	$P\bar{1}$
a (Å)	7.7987(8)	29.326(3)	11.397(2)
b (Å)	22.030(2)	29.326(3)	12.093(2)
c (Å)	11.3629(11)	18.561(2)	15.574(3)
α (°)	90	90	108.38(3)
β (°)	107.306(2)	90	105.79(3)
γ (°)	90	90	98.61(3)
V (Å^3)	1863.8(3)	15964(3)	1893.8(6)
Z	2	16	2
D (Mg m^{-3})	1.487	1.577	1.608
μ (mm^{-1})	0.826	1.007	1.125
F(000)	864	7680	926
T (°C)	–173	–100	–100
$2\theta_{max}$	51	50	50
Reflections collected	10 474	8828	7569
Independent reflections	3462	7006	6469
Transmissions	0.8522–0.9074	0.704–0.816	0.885–0.968
R_{int}	0.052	0.035	0.032
Parameters	302	466	482
Restraints	0	393	2
$wR(F^2$, all refl.)	0.09	0.088	0.131
$R(I, > 2\sigma(I))$	0.039	0.043	0.05
S	0.936	0.822	0.917
Max. $\Delta\rho$ (e Å^{-3})	0.499	0.599	1.36

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 (Fcterpy) or Siemens P4 (**2**, **3**) diffractometer equipped with a low-temperature attachment. Data were collected using monochromated Mo Kα radiation (λ = 0.710 73 Å) and scan type ω, or ω and ϕ. Absorption corrections based on psi-scans (**2**, **3**) or multiple scans with the program SADABS (20) (Fcterpy), were applied. The structures were refined on F^2 using the program SHELXL-97 (21). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included using a riding model. A special refinement was required for **2**: Two rings of the PPh_3 ligand are disordered over two positions and were refined isotropically. A peak of ca. 3 e/Å^3 was interpreted as a partially occupied water site. It is also involved in a contact of ca. 2.9 Å to itself, which could represent an H bond. Further details of the data collection and refinement are given in Table 4.

Acknowledgments

We thank the Dirección General de Investigación Científica y Técnica (CTQ2007–67273-C02–01) for financial support.

References

1. E. C. Constable. Adv. Inorg. Chem. Radiochem. **30**, 69 (1986).
2. See for example: (*a*) G. B. Deacon, J. M. Patrick, B. W. Skelton, N. C. Thomas, and A. H. White. Aust. J. Chem. **37**, 929 (1984); (*b*) N. C. Thomas and J. Fischer. J. Coord. Chem. **21**, 119 (1990); (*c*) E. C. Constable, M. J. Hannon, A. M. W. Cargill Thompson, D. A. Tocher, and J. V. Walker. Supramol. Chem. **3**, 243 (1993); (*d*) R. C. Chotalia, E. C. Constable, M. J. Hannon, and D. A. Tocher. J. Chem. Soc. Dalton Trans. 3571 (1995).
3. See for example: (*a*) K. T. Potts, M. Keshavarz, K. F. S. Tham, H. D. Abruña, and C. R. Arana. Inorg. Chem. **32**, 4422 (1993); (*b*) E. C. Constable, A. J. Edwards, M. J. Hannon, and P. R. Raithby. J. Chem. Soc. Chem. Commun. 1991 (1994); (*c*) G. Baum, E. C. Constable, D. Fenske, C. E. Housecroft, and T. Kulke. Chem. Commun. (Cambridge), 2659 (1998); (*d*) G. Baum, E. C. Constable, D. Fenske, C. E. Housecroft, T. Kulke, M. Neuburger, and M. Zehnder. J. Chem. Soc. Dalton Trans. 945 (2000); (*e*) M. H. Hannon, C. L. Painting, E. A. Plummer, L. J. Childs, and N. W. Alcock. Chem. Eur. J. **8**, 2225 (2002); (*f*) Y. Cui and C. He. J. Am. Chem. Soc. **125**, 16202 (2003).
4. J. E. Aguado, M. J. Calhorda, M. C. Gimeno, and A. Laguna. Chem. Commun. 3355 (2005).

5. L. S. Hollis and S. J. Lippard. J. Am. Chem. Soc. **105**, 4293 (1983).
6. H.-Q. Liu, T. C. Cheung, S. M. Peng, and C.-M. Che. J. Chem. Soc. Chem. Commun. 1787 (1995).
7. B. Pitteri, G. Marangoni, F. Visentin, T. Bobbo, V. Bertolasi, and P. Gilli. J. Chem. Soc. Dalton Trans. 677 (1999).
8. U. Sampath, W. C. Putnam, T. A. Osiek, S. Touami, J. Xie, D. Cohen, A. Cagnolini, P. Droege, D. Klug, C. L. Bernes, A. Modak, J. K. Bashkin, and S. S. Jurisson. J. Chem. Soc. Dalton Trans. 677 (1999).
9. V. Ferreti, P. Gilli, V. Bertolasi, G. Marangoni, P. Pitteri, and G. Ghessa. Acta Crystallogr. Sect. C, **48**, 814 (1992).
10. (*a*) Effendy, F. Marchetti, C. Pettinari, R. Pettinari, B. W. Skelton, and A. H. White. Inorg. Chim. Acta, **360**, 1414 (2007); (*b*) C. Di Nicola, Effendy, F. Marchetti, C. Pettinari, B. W. Skelton, and A. H. White. Inorg. Chim. Acta, **360**, 1433 (2007); (*c*) E. W. Ainscough, A. M. Brodie, S. L. Ingham, and J. M. Waters. J. Chem. Soc. Dalton Trans. 215 (1994).
11. E. C. Constable, A. J. Edwards, R. Martínez-Mánez, P. R. Raithby, and A. M. W. Cargill Thompson. J. Chem. Soc. Dalton Trans. 645 (1994).
12. U. Siemeling, U. Vorfeld, B. Neumann, H.-G. Stammler, M. Fontani, and P. Zanello. J. Organomet. Chem. **637**, 733 (2001).
13. (*a*) E. M. Barranco, O. Crespo, M. C. Gimeno, P. G. Jones, A. Laguna, and C. Sarroca. J. Chem. Soc. Dalton Trans. 2523 (2001); (*b*) O. Crespo, M. C. Gimeno, P. G. Jones, and A. Laguna. J. Chem. Soc. Dalton Trans. 4583 (1996).
14. P. K.-K. Ho, S.-M. Peng, K.-Y. Wong, and C.-M. Che. J. Chem. Soc. Dalton Trans. 1829 (1996).
15. R. Usón, A. Laguna, and M. Laguna. Inorg. Synth. **26**, 85 (1989).
16. M. Bardají, O. Crespo, A. Laguna, and A. K. Fischer. Inorg. Chim. Acta, **304**, 7 (2000).
17. G. J. Kubas. Inorg. Synth. **19**, 90 (1979).
18. R. Usón, A. Laguna, M. Laguna, J. Jiménez, and E. Durana. Inorg. Chim. Acta, **168**, 89 (1990).
19. R. Usón and A. Laguna. Inorg. Synth. **21**, 71 (1982).
20. G. M. Sheldrick. SADABS [computer program]. University of Göttingen, Göttingen, Germany. 1996.
21. G. M. Sheldrick. SHELXL-97 [computer program]. University of Göttingen, Göttingen, Germany. 1997.