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Synthesis and characterisation of 1-(diphenylphosphino)-1′-(methylsulfanyl)ferrocene and a series of metal (Cu^I, Ag^I)–ferrocenylene complexes

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A novel phosphorus/sulfur-substituted ferrocenylene ligand, 1-(diphenylphosphino)-1′-(methylsulfanyl)ferrocene has been synthesized by two routes and fully characterised. The co-ordination chemistry of this species and analogous phosphorus/phosphorus- and sulfur/sulfur-substituted ferrocenylene ligands, 1,1′-bis(diphenylphosphino)ferrocene, 1,1′-bis(methylsulfanyl)ferrocene and 1,1′-bis(isopropylthio)ferrocene has been demonstrated by reaction with copper and silver tetrakis(acetonitrile) salts to form a series of metal–ferrocenylene complexes where the metal atom acts as a bridging group of two ring systems. Crystal structure determinations have been carried out on $[Ag\{(C_5H_4P(C_6H_5)_2)_2Fe\}_2]BF_4$ and $[Cu\{(C_5H_4SCH_3)_2Fe\}_2]PF_6$ and illustrate that the former shows a distorted tetrahedral geometry around silver and a significant asymmetry in the geometries of the two pseudo six-membered chelate rings and that the latter possesses S_4 symmetry with a pronounced *exo* orientation of the four methyl groups.

Introduction

Ferrocene-containing complexes are currently undergoing something of a renaissance due to their increasing role in the rapidly growing area of materials science.[1] The substitution of ferrocenes by various donor heteroatoms has led to a series of chelating ligands that have found wide application, *e.g.* incorporation of phosphines for homogeneous catalysis in organic synthesis, chiral phosphines for enantiomeric synthesis and amino alcohols for asymmetric catalysis.[1,2] Efforts have been made to control the 1,1′-hetero- or homo-substitution of ferrocene, normally *via* lithio intermediates,[3–10] to allow the formation of a number of useful substituted-ferrocenyl synthetic precursors, *i.e.* halides,[11,12] aldehydes,[13] phosphines,[14–17] amines,[18] and stannyl species.[19] By linking the heteroatoms, or by the incorporation of a preformed linkage, metallocenophanes (or *ansa*-metallocenes) (species that feature linking of the cyclopentadienyl rings by the introduction of a heteroannular bridge or bridges) can be formed. Bridged Group 4 metallocenes have come to the fore as catalysts in stereoselective olefin polymerisation[20] and strained, ring-tilted iron group metallocenophanes have been found to undergo thermal ring-opening polymerisation (ROP), leading to rare examples of well defined, high molecular mass, soluble polymers with transition metals in the main polymer chain.[21]

Ferrocenyl dichalcogenide ligands and the Group 4 elements Si, Ge and Sn are known to form 'spiro'[22] compounds in which two [3]ferrocenophane rings share the bridge atom in position 2,[23–26] *e.g.* $[Z(E_2Fc)_2]$ (where Z = Si, Ge or Sn; E = S, Se or Te; $Fc = \{(C_5H_4)_2Fe\}$). Whilst metal complexes with two 1,1′-bis(diphenylphosphino)ferrocene ligands are well known,[1,27,28] to date the only transition metal complex with two chelating ferrocenyl dichalcogenide ligands is the anion of the diamagnetic brown rhenate(V) salt, *e.g.* $[P(C_6H_5)_4][ReO(S_2Fc)_2]$.[29]

To explore the formation of novel ferrocenophanes further, we have synthesized the first mixed phosphorus/sulfur-substituted ferrocenylene ligand, 1-(diphenylphosphino)-1′-(methylsulfanyl)ferrocene (PSF) L^1, along with the more well known phosphorus/phosphorus- and sulfur/sulfur-substituted species, 1,1′-bis(diphenylphosphino)ferrocene (BPPF) L^2, 1,1′-bis(methylsulfanyl)ferrocene (BMSF) L^3 and 1,1′-bis(isopropylsulfanyl)ferrocene (BIPSF) L^4 respectively and treated them with labile tetrakis(acetonitrile)-copper(I) or -silver(I) centres to form a series of novel metal–ferrocenylene complexes **1**–**9**.

Experimental

General

All preparations were carried out using standard Schlenk techniques.[30] All solvents were distilled over standard drying agents under nitrogen directly before use and all reactions were carried out under an atmosphere of nitrogen. Alumina gel (type UG-1) was used for chromatographic separations.

All NMR spectra were recorded on a JEOL 270 MHz instrument. Chemical shifts are reported in δ using $CDCl_3$ (^1H, δ 7.26) as the reference for ^1H spectra, whilst the ^{31}P-{^1H} spectra were referenced to 85% H_3PO_4. Mass spectra were recorded using positive FAB methods, on a Micromass Autospec Q spectrometer. Microanalyses were carried out at the Department of Chemistry, Imperial College of Science, Technology and Medicine.

Starting materials

The ligands L^2,[31] L^3[10] and L^4[10] were synthesized by following literature procedures, as were $[Cu(CH_3CN)_4]PF_6$,[32] 1,1′-dilithioferrocene[8] and 1,1′-phenylphosphinoferrocenophane[7] and were characterised by ^1H NMR and mass spectrometry; $[Ag(CH_3CN)_4]BF_4$ was purchased from Aldrich Chemical Co.

Ligands

1-(Diphenylphosphino)-1′-(methylsulfanyl)ferrocene L^1. *Method 1.* 1-Diphenylphosphino-1′-lithioferrocene was prepared using the method of Seyferth and Withers[16] from 1,1′-phenylphosphinoferrocenophane (6.28 g, 21.50 mmol) and a 10–15 fold excess of C_6H_5Li (1 M solution in diethyl ether). The resultant orange-brown precipitate was treated with $(CH_3)_2S_2$

(1.93 cm^3, 21.50 mmol) in diethyl ether (20 cm^3) and the mixture stirred overnight. Water (100 cm^3) was added and stirred for 2 h, then the organic layer decanted and the aqueous layer washed with diethyl ether (2 × 20 cm^3). The extracts were combined and dried over $MgSO_4$, filtered and subjected to column chromatography using an 80% hexane–20% diethyl ether solution and isolated as an orange solid after evaporation of the solvents. Overall yield from 1,1′-phenylphosphinoferrocenophane, 1.64 g (18%).

Method 2. A suspension of 1,1′-dilithioferrocene (6.75 g, 21.50 mmol) in hexane (100 cm^3) was treated with a premixed solution of $(CH_3)_2S_2$ (1.93 cm^3, 21.50 mmol) and $P(C_6H_5)_2Cl$ (3.85 g, 21.50 mmol) in hexane (10 cm^3) and the mixture stirred overnight. Water (20 cm^3) was added and stirred for 1 h, then the organic layer decanted and the aqueous layer washed with hexane (2 × 10 cm^3). The extracts were combined and dried over $MgSO_4$, filtered, then purified by column chromatography using first hexane (to remove the starting materials), then an 80% hexane–20% diethyl ether solution, to give the product, after evaporation of the solvents, as a light orange microcrystalline powder. Further purification was achieved by recrystallisation from hexane–diethyl ether (1 : 1) as orange crystals, 3.44 g (38%) (Calc. for $C_{23}H_{21}FePS$: C, 66.35; H, 5.05. Found: C, 66.57; H, 4.87%). ^1H NMR ($CDCl_3$): δ 2.23 (s, 3 H, SCH_3), 4.06 (t, 2 H, C_5H_4), 4.11 (q, 2 H, C_5H_4), 4.20 (t, 2 H, C_5H_4), 4.38 (t, 2 H, C_5H_4) and 7.31 (m, 10 H, C_6H_5). ^{31}P-$\{^1H\}$ NMR ($CDCl_3$): δ −16.78.

Complexes

Formation of the complexes followed the same general procedure as for the formation of **5** using either $[Cu(CH_3CN)_4]PF_6$ or $[Ag(CH_3CN)_4]BF_4$ and the appropriate bidentate ligand.

$[Cu(L^1)_2]PF_6$ 1. The salt $[Cu(CH_3CN)_4]PF_6$ (0.09 g, 2.33 mmol) was added to a solution of ligand L^1 (0.19 g, 4.66 mmol) in CH_2Cl_2 (20 cm^3) and stirred for 1 h. The resulting dark brown solution was reduced under vacuum, washed with diethyl ether (10 cm^3) and dried ($MgSO_4$) to yield a brown microcrystalline solid, 0.16 g (66%) (Calc. for $C_{46}H_{42}CuF_6Fe_2P_3S_2$: C, 53.03; H, 4.04. Found: C, 53.02, H, 4.31%). ^1H NMR ($CDCl_3$): δ 2.61 (br, 3 H, SCH_3), 4.29 (br, 4 H, C_5H_4), 4.50 (br, 2 H, C_5H_4), 4.65 (br, 2 H, C_5H_4), 7.41 (br, 5 H, C_6H_5) and 7.58 (br, 5 H, C_6H_5). *m*/*z* 896 $[(L^1)_2Cu]$, 480 $[(L^1)Cu]$, 416 (L^1).

$[Ag(L^1)_2]BF_4$ 2. From the salt $[Ag(CH_3CN)_4]BF_4$ (0.14 g, 3.80 mmol) and ligand L^1 (0.32 g, 7.64 mmol). Orange microcrystalline solid, 0.30 g (77%) (Calc. for $C_{46}H_{42}AgBF_4Fe_2P_2S_2$: C, 53.75; H, 4.09. Found: C, 54.09; H, 4.07%). ^1H NMR ($CDCl_3$): δ 2.22 (s, 3 H, SCH_3), 4.14 (t, 2 H, C_5H_4), 4.19 (t, 2 H, C_5H_4), 4.29 (t, 2 H, C_5H_4), 4.61 (t, 2 H, C_5H_4) and 7.45 (m, 10 H, C_6H_5). *m*/*z* 941 $[(L^1)_2Ag]$, 523 $[(L^1)Ag]$, 416 (L^1) and 401 $[(C_5H_4PPh_2)Fe(C_5H_4S)]$.

$[Cu(L^2)_2]PF_6$ 3. From the salt $[Cu(CH_3CN)_4]PF_6$ (0.07 g, 1.81 mmol) and ligand L^2 (0.20 g, 3.61 mmol). The complex was allowed to recrystallise from the CH_2Cl_2 solution, producing light orange crystals, 0.17 g (71%) (Calc. for $C_{68}H_{56}CuF_6Fe_2P_5$: C, 61.96: H, 4.25. Found: C, 61.64; H, 4.60%). ^1H NMR ($CDCl_3$): δ 4.10 (br, 4 H, C_5H_4), 4.31 (br, 4 H, C_5H_4), 7.25 (m, 10 H, C_6H_5) and 7.40 (m, 10 H, C_6H_5). *m*/*z* 1172 $[(L^2)_2Cu]$, 617 $[(L^2)Cu]$ and 554 (L^2).

$[Ag(L^2)_2]BF_4$ 4. From ligand L^2 (0.10 g, 0.18 mmol) and $[Ag(CH_3CN)_4]BF_4$ (0.03 g, 0.09 mmol). Light orange solid, 0.076 g (65%) (Calc. for $C_{68}H_{56}AgBF_4Fe_2P_4$: C, 62.62; H, 4.30. Found: C, 62.66; H, 3.95%). ^1H NMR ($CDCl_3$): δ 4.10 (br, 4 H, C_5H_4), 4.40 (br, 4 H, C_5H_4), 7.10 (m, 10 H, C_6H_5) and 7.30 (m, 10 H, C_6H_5). *m*/*z* 1216 $[(L^2)_2Ag]$, 1139 $[(L^2)Ag(C_5H_4PPh_2)Fe(C_5H_4PPh)]$, 661 $[(L^2)Ag]$ and 554 (L^2).

$[Cu(L^3)_2]PF_6$ 5. From $[Cu(CH_3CN)_4]PF_6$ (0.19 g, 0.52 mmol) and ligand L^3 (0.29 g, 1.04 mmol) in CH_2Cl_2 (20 cm^3). The resulting dark brown solution was reduced under vacuum, washed with hexane (10 cm^3) and dried to yield a brown crystalline solid, 0.38 g (96%) (Calc. for $C_{24}H_{28}CuF_6Fe_2PS_4$: C, 37.65; H, 3.66. Found: C, 37.48; H, 3.14%). ^1H NMR ($CDCl_3$): δ 2.68 (br s, 3 H, SCH_3) and 4.43 (br s, 4 H, C_5H_4). *m*/*z* 620 $[(L^3)_2Cu]$, 341 $[(L^3)Cu]$, 326 $[(C_5H_4SMe)Fe(C_5H_4S)Cu]$ and 278 (L^3). Suitable crystals for X-ray analysis were grown as transparent brown pyramids by cooling a saturated CH_2Cl_2 solution.

$[Ag(L^3)_2]BF_4$ 6. From $[Ag(CH_3CN)_4]BF_4$ (0.30 g, 0.85 mmol) and ligand L^3 (0.47 g, 1.69 mmol). Dark brown solution reduced under vacuum to a brown solid, 0.42 g (67%) (Calc. for $C_{24}H_{28}AgBF_4Fe_2S_4$: C, 38.35; H, 3.73. Found: C, 38.10; H, 3.74%). ^1H NMR ($CDCl_3$): δ 2–3 (br s, 3 H, SCH_3) and 4–5 (m, 4 H, C_5H_4). *m*/*z* 664 $[(L^3)_2Ag]$, 385 $[(L^3)Ag]$ and 278 (L^3).

$[Cu(L^4)_2]PF_6$ 7. From ligand L^4 (0.52 g, 1.56 mmol) and $[Cu(CH_3CN)_4]PF_6$ (0.29 g, 0.78 mmol). Dark brown oily solid formed on evaporation of solvent, brown solid formed on cooling, 0.53 g (78%) (Calc. for $C_{32}H_{44}CuF_6Fe_2PS_4$: C, 43.79; H, 5.02. Found: C, 43.82; H, 5.06%). ^1H NMR ($CDCl_3$): δ 1.39 [d, 6 H, $SCH(CH_3)_2$], 3.30 [septet, 1 H, $SCH(CH_3)_2$], 4.40 (br, 2 H, C_5H_4) and 4.51 (br, 2 H, C_5H_4). *m*/*z* 732 $[(L^4)_2Cu]$, 471 $[(L^4)CuC_5H_4SCH(CH_3)_2Fe(C_5H_4)]$, 397 $[(L^4)Cu]$ and 334 (L^4).

$[Ag(L^4)_2]BF_4$ 8. From ligand L^4 (0.41 g, 1.2 mmol) and $[Ag(CH_3CN)_4]BF_4$ (0.22 g, 0.61 mmol). Light orange solid, 0.38 g (72%) (Calc. for $C_{32}H_{44}AgBF_4Fe_2S_4$: C, 44.50; H, 5.10. Found: C, 44.41; H, 4.84%). ^1H NMR ($CDCl_3$): δ 1.38 [d, 6 H, $SCH(CH_3)_2$], 3.22 [septet, 1 H, $SCH(CH_3)_2$], 4.34 (t, 2 H, C_5H_4) and 4.52 (t, 2 H, C_5H_4). *m*/*z* 776 $[(L^4)_2Ag]$, 472 $[(L^4)AgS]$, 442 $[(L^4)Ag]$, 398 $[AgC_5H_4SCH(CH_3)_2)Fe(C_5H_4)S]$ and 334 (L^4).

$[Cu(L^3)\{P(C_6H_5)_3\}_2]PF_6$ 9. A solution of $[Cu(L^3)_2]PF_6$ (0.35 g, 4.58 mmol) was treated with $P(C_6H_5)_3$ (0.24 g, 9.15 mmol) and stirred for 1 h. The solution was reduced under vacuum and washed with diethyl ether (2 × 10 cm^3) to leave an orange solid, 0.31 g (67%) (Calc. for $C_{48}H_{44}CuF_6FeP_3S_2$: C, 56.97; H, 4.35. Found: C, 57.71; H, 4.36%). ^1H NMR ($CDCl_3$): δ 2.29 (s, 6 H, SCH_3), 4.31 (t, 4 H, C_5H_4), 4.95 (t, 4 H, C_5H_4), 7.11 (m, 15 H, C_6H_5) and 7.41 (m, 15H, C_6H_5). *m*/*z* 603 $[(L^3)Cu(PPh_3)]$, 587 $[Cu(PPh_3)_2]$, 341 $[(L^3)Cu]$ and 278 (L^3).

X-Ray crystallography

Table 2 provides a summary of the crystal data, data collection and refinement parameters for complexes **4** and **5**. The structures were solved by direct methods and the heavy atom method for **5** and **4** respectively, and refined by full matrix least squares based on F^2. In **5** the complex and the PF_6 anion were found to be disordered over independent crystallographic S_4 positions. In the case of the complex two discrete half-occupancy orientations were identified, with only their copper and iron centres in common, and refined anisotropically, with the cyclopentadienyl rings treated as optimised rigid bodies. The disorder in the anion was modelled by the assignment of sufficient electron density around the central phosphorus atom to match a single quarter-occupancy (due to site symmetry) molecule, all atoms being refined anisotropically. In **4** the complex was ordered and refined anisotropically with the phenyl rings treated as optimised rigid bodies (the cyclopentadienyl rings were not optimised). The BF_4 anion was found to be distributed over three partial occupancy sites (two of which were located proximal to crystallographic special positions); only the major occupancy atoms were refined anisotropically. In both structures the hydrogen atoms were placed in calculated positions, assigned isotropic thermal parameters, $U(H) = 1.2U_{eq}(C)$, and allowed to ride on their parent atoms. The polarity of **5** was determined by *R*-factor tests [$R_1^+ = 0.031$, $R_1^- = 0.039$] and by use of the Flack parameter [$x^+ = -0.03(4)$, $x^- = +1.03(4)$]. Computations were carried out using the SHELXTL PC program system.[33]

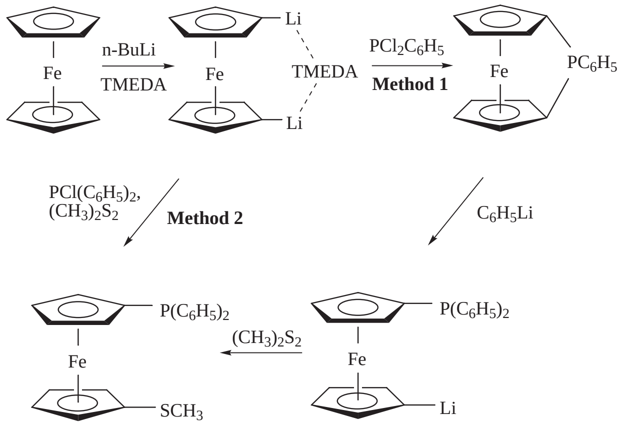
CCDC reference number 186/1452.

See http://www.rsc.org/suppdata/dt/1999/1981/ for crystallographic files in .cif format.

Results and discussion

Synthesis

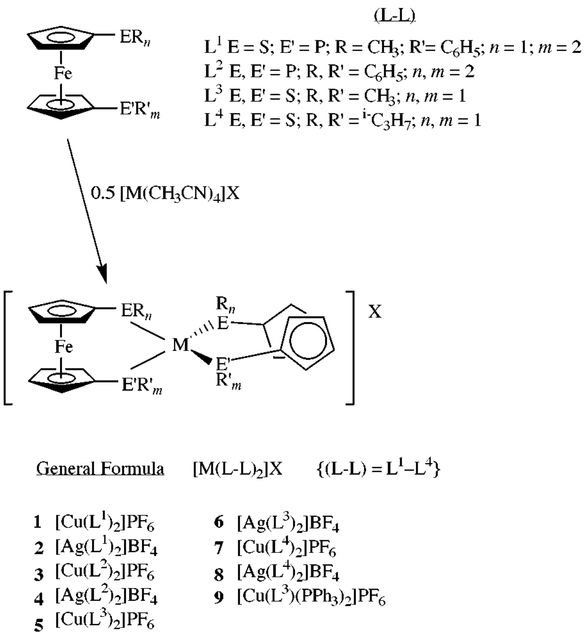
The new hetero-donor ligand, PSF (L^1), may be prepared by two methods (Scheme 1) which involve the initial formation of the well known intermediate 1,1′-dilithioferrocene. Addition of dichlorophenylphosphine produces 1,1′-phenylphosphinoferrocenophane (Method 1),[7] which was isolated and characterised spectroscopically. This [1]ferrocenophane was then treated with a 10–15 fold excess of phenyllithium (1 M solution in diethyl ether) to cleave one of the P–C bonds and yield the air- and moisture-sensitive 1-diphenylphosphino-1′-lithioferrocene.[16] The orange-brown precipitate was treated *in situ* with dimethyl disulfide to give a crude dark orange oil (L^1). Purification was effected by column chromatography on neutral grade II alumina (hexane–diethyl ether (80:20)) to give an orange solid in an overall yield from ferrocene of 11%, or 18% from 1,1′-phenylphosphinoferrocenophane.



Scheme 1 Two methods for the synthesis of ligand L^1.

Method 2 was more direct and involved treating a hexane suspension of the 1,1′-dilithioferrocene intermediate with a mixture (1:1) of dimethyl disulfide and dichlorophenylphosphine, also in hexane. Perhaps surprisingly, a reasonable yield of the desired product was obtained (along with mainly BMSF and monosubstituted ferrocenes as by-products) which was again purified by column chromatography using first hexane as eluent (to remove the starting materials) and then hexane–diethyl ether (80:20) to give the orange solid (yield 38% from ferrocene).

As mentioned in the Introduction, hetero-donor substituted ferrocenes are known but to date most have featured pnictinide substituents. The different co-ordinating abilities of the phosphorus and sulfur substituents in L^1, along with the possibility for further donor atom substitution around the same ferrocene unit,[34] opens up diverse co-ordination chemistry of these systems which is the subject of ongoing studies. As a starting point for the co-ordination chemistry and as a comparison to the more well known analogues 1,1′-bis(diphenylphosphino)ferrocene (BPPF) (L^2), 1,1′-bis(methylsulfanyl)ferrocene (BMSF) (L^3) and 1,1′-bis(isopropylsulfanyl)ferrocene (BPSF) (L^4), each ligand was treated with simple copper and silver tetrakis(acetonitrile) complexes. Using a 2:1 ratio of ligand to metal, the acetonitrile moieties could be displaced within a few minutes by stirring at room temperature, to yield a tetrasubstituted metal complex with two ferrocenylene ligands (Scheme 2). Each complex **1**–**8** appears to possess the same structure where the metal atom acts as a bridging group of two ring systems. The air- and moisture-stable orange solids were formed in excellent yields and could be recrystallised from saturated chlorocarbon solutions.



1 $[Cu(L^1)_2]PF_6$
2 $[Ag(L^1)_2]BF_4$
3 $[Cu(L^2)_2]PF_6$
4 $[Ag(L^2)_2]BF_4$
5 $[Cu(L^3)_2]PF_6$
6 $[Ag(L^3)_2]BF_4$
7 $[Cu(L^4)_2]PF_6$
8 $[Ag(L^4)_2]BF_4$
9 $[Cu(L^3)(PPh_3)_2]PF_6$

Scheme 2 The syntheses of complexes **1**–**8**.

Spectroscopy

Each complex **1**–**8** displays broadened signals in the cyclopentadienyl ring region of its room temperature ^1H NMR spectrum which was initially thought to be due to fluxional processes, such as pyramidal sulfur inversion or bridge reversal,[35] being observed in solution. However, dynamic NMR experiments and, in particular, cooling solutions to low temperatures (*ca.* −80 °C) failed to elucidate any fine structure on the cyclopentadienyl proton signals. This could be due to a lack of slowing of the fluxional processes but is thought more likely to be a dissociative process in solution (breaking of the metal–heteroatom bonds) giving rise to an averaged set of peaks. To elucidate this phenomenon, a solution of **5** was treated with two equivalents of $P(C_6H_5)_3$ and substitution of a labile ligand indeed occurred to form a [3]ferrocenophane **9** (Scheme 3). (NB **9** was also formed by the addition of $[Cu(CH_3CN)_2\{(P(C_6H_5)_3)\}_2]PF_6$ to a stirred solution of the ligand L^3). The lack of sulfur inversion is perhaps surprising but there is clearly something of a ‘potential well’ in the thermodynamics of the structure especially when considering the crystal structure determination (see later). The methyl groups are ‘locked’ into a very stable *exo* orientation and this seems to preclude any movement and therefore fluxional behaviour of these units.

Electrochemistry

A preliminary investigation on dichloromethane solutions of the reported complexes using platinum electrodes illustrated the occurrence of interfering adsorption phenomena, whereas the use of glassy-carbon electrodes overcame these problems. Figs. 1 and 2, which compare the cyclic voltammetric responses of the ligands L^1 and L^2 with those of their copper(I) and silver(I) complexes, show the subtle electronic effects that govern the redox behaviour of these species.

With respect to the ligand L^1, the bis(ferrocenediyl) copper(I) and silver(I) complexes **1** and **2** undergo anodic oxidations at potentials shifted toward more positive potential values by about 0.25 V (Fig. 1). In particular, the copper complex **1**

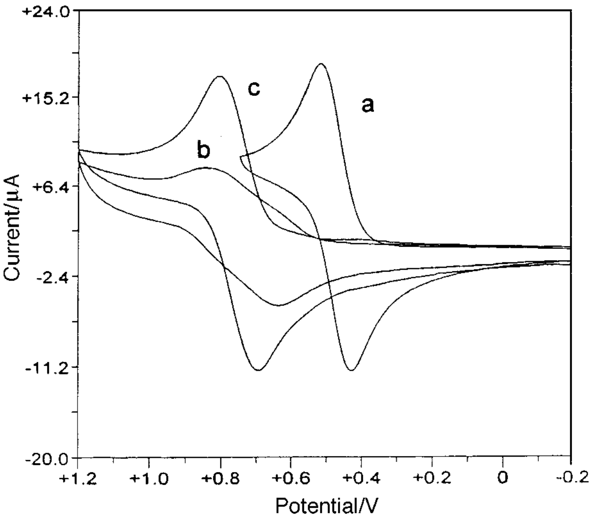


Fig. 1 Cyclic voltammetric responses recorded at a glassy-carbon electrode on CH_2Cl_2 solutions containing $[NBu_4][PF_6]$ (0.2 mol dm^{-3}) and (a) L^1 (1.0 × 10^{-3} mol dm^{-3}), (b) complex **1** (0.4 × 10^{-3} mol dm^{-3}), (c) complex **2** (0.8 × 10^{-3} mol dm^{-3}). Scan rate 0.05 V s^{-1}.

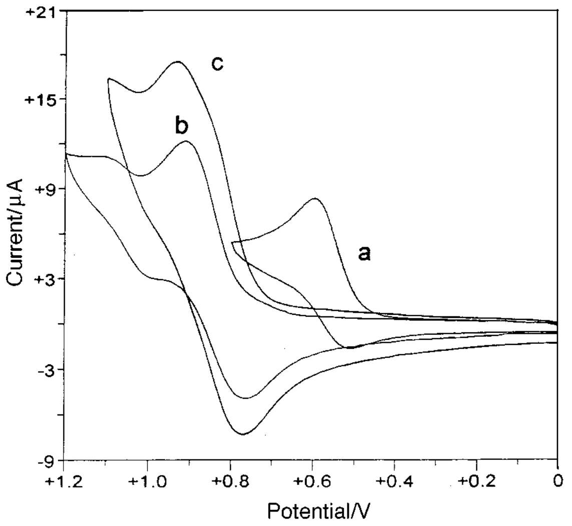


Fig. 2 Cyclic voltammetric responses recorded at a glassy-carbon electrode on CH_2Cl_2 solutions containing $[NBu_4][PF_6]$ (0.2 mol dm^{-3}) and (a) L^2 (0.8 × 10^{-3} mol dm^{-3}), (b) complex **3** (1.0 × 10^{-3} mol dm^{-3}), (c) complex **4** (0.9 × 10^{-3} mol dm^{-3}). Scan rates: (a, c) 0.05; (b) 0.1 V s^{-1}.

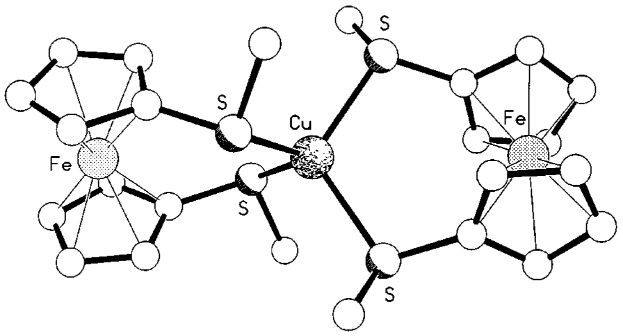
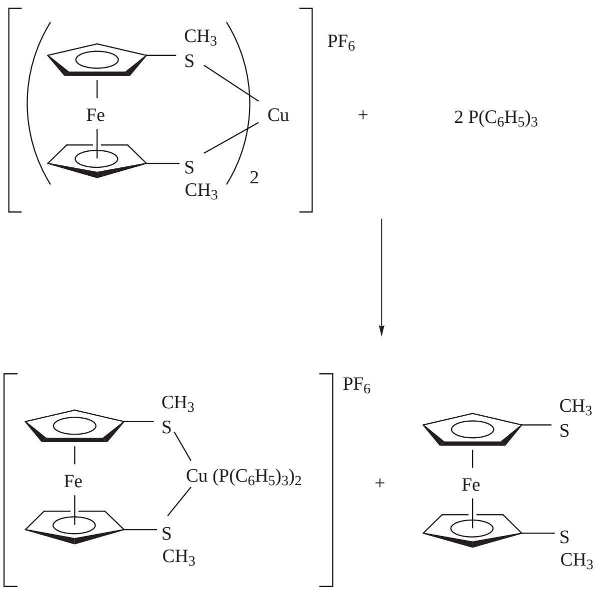


Fig. 3 The molecular structure of one of the two 50% orientations of the S_4-symmetric cation present in the structure of complex **5**. The Cu–S and S–C_5 bond lengths are 2.331(2) [2.327(2)] and 1.746(5) [1.755(6) Å] respectively. The associated bite and interligand S–Cu–S angles are 112.28(10) [112.33(10)] and 108.08(5) [108.06(5)°] respectively; the Cu–S–C_5 angles are 109.2(3) [109.6(3)°], the number in [ ] referring to the alternative orientation present in the crystal.



Scheme 3 The synthesis of complex **9**.

exhibits two substantially overlapping one-electron oxidations, which could not be resolved with additional use of differential pulse voltammetry, and simply afforded a rounded peak. On the other hand, the silver complex **2** displays a single two-electron oxidation. In spite of the apparent chemical reversibility of these anodic processes on the cyclic voltammetric timescale, cyclic voltammetric tests on solutions from exhaustive two-electron oxidation of both complexes showed partial decomposition of the corresponding trications.

Interestingly, L^2, which is known to undergo a one-electron oxidation coupled to chemical complications,[36] when part of the metal complexes **3** and **4** gives rise to oxidation processes with features of chemical reversibility (also in these cases it is limited to the cyclic voltammetric timescale), Fig. 2. In addition, a slight wave splitting occurs for the silver complex **4**.

As Table 1 summarises, analogous behaviour is seen for the remaining complexes. The oxidations of the metal complexes occur at potentials which range from 0.25 to 0.42 V higher than those of the corresponding ligands. It has to be taken into account that these shifts must be attributed either to the electrostatic effect of removing electrons from monocations, or to the metals themselves. The minor wave splittings observed for some complexes suggest slight communication between the two ferrocene units, but it can be deduced that the communication is probably attributable to the nature of the ferrocene ligands rather than to that of the metals.

X-Ray crystallography

The X-ray analysis of complex **5** reveals a structure that has 50/50 reflection disorder about a non-crystallographic mirror plane perpendicular to the *a* direction, the two orientations having essentially identical geometries. The complex has crystallographic S_4 symmetry, the copper lying at the S_4 position and the two iron atoms on the C_2 axis (Fig. 3). The geometry at copper is slightly distorted tetrahedral, the bite angles of the two chelating ligands being 112.3(1)°. The Cu–S distance of 2.33(1) Å is unexceptional. There is a marked departure from tetrahedral geometry at sulfur with the C_5–S–Me angles contracted to 101(1)°, the other two angles being 109(1) [Cu–S–C_5] and 110(1)° [Cu–S–Me]. The ferrocenyl C_5H_4 rings are staggered (48°), the two S–C_5 vectors being skewed by *ca.* 24°, with an essentially parallel orientation of the two rings. The Cu···Fe distance of 4.02 Å is too long for any significant metal–metal interaction.

When viewed down the metal–metal–metal axis the *exo* orientation of the four methyl groups is particularly pronounced (Fig. 4), a geometry that is dominant in solution as

Table 1 Formal electrode potentials (in V, *vs.* SCE) and peak-to-peak separations (in mV) for the anodic oxidation of the ferrocenediyl ligands L^1–L^4 and their metal derivatives **1**–**8** in CH_2Cl_2 solutions

Compound	$E°$ (0/+)	ΔE_p[a]	$E°$ (+/2+)	$E°$ (2+/3+)	$E°$ (+/3+)	ΔE_p[a]
L^1	+0.48	85				
L^2	+0.56[b]	69				
L^3	+0.37[c]	94				
L^4	+0.43	180				
1			+0.68[d]	+0.78[d]		
2					+0.75	115
3					+0.84	140
4			+0.89[d]	+0.84[d]		
5			+0.74[d]	+0.64[d]		
7					+0.85[e]	
8					+0.85[f]	90

[a] Measured at 0.1 V s^{-1}. [b] Coupled to chemical complications. [c] See ref. 37. [d] Measured according to ref. 38. [e] Irreversible two electron step. [f] Coupled to slight adsorption of the reagent.

Table 2 Selected bond lengths (Å) and angles (°) for complex **4**

Ag–P(1)	2.662(3)	Ag–P(2)	2.558(3)
Ag–P(3)	2.622(3)	Ag–P(4)	2.553(3)
P(1)–C(17)	1.790(12)	P(2)–C(22)	1.775(12)
P(3)–C(51)	1.811(14)	P(4)–C(56)	1.832(13)
P(1)–Ag–P(2)	105.51(10)	P(1)–Ag–P(3)	114.65(11)
P(1)–Ag–P(4)	109.34(11)	P(3)–Ag–P(3)	110.98(11)
P(2)–Ag–P(4)	118.92(11)	P(3)–Ag–P(4)	97.76(10)
Ag–P(1)–C(17)	106.4(4)	Ag–P(2)–C(22)	113.5(4)
Ag–P(3)–C(51)	106.4(4)	Ag–P(4)–C(56)	110.0(4)

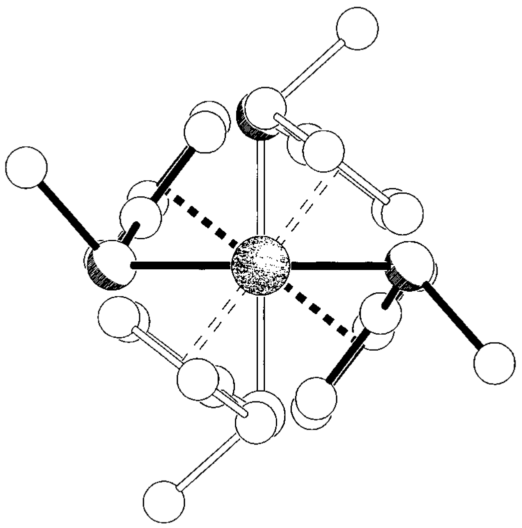


Fig. 4 The view down the Fe$\cdots$Cu$\cdots$Fe direction in the structure of complex **5** showing the radial orientation of the SMe groups.

shown by the NMR experiments. There are no intermolecular interactions of note, the packing being normal van der Waals.

In the solid state structure of complex **4** (Fig. 5) the geometry at silver is distorted tetrahedral with angles ranging between 97.8(1) and 118.9(1)°. There is a pronounced asymmetry in the geometries of the two pseudo six-membered chelate rings (Fig. 6), an asymmetry that includes both the bond lengths and angles (Table 2) and their conformations. The Ag/Fe(1) ring has a skewed "l" conformation, the C_2Fe plane being "rotated" by 23° out of the P_2Ag plane about the Fe$\cdots$Ag axis. In contrast the Ag/Fe(2) ring has a slightly twisted envelope conformation, the Ag atom being 1.38 Å out of the plane of the other five atoms which are coplanar to within 0.09 Å, corresponding to a fold about the P(3)$\cdots$P(4) vector of *ca.* 54°. The angle at silver within the skewed ring is 105.5(1)° whereas that in the ring with the envelope conformation is 97.8(1)°. Possibly most surprising is the disparity in the Ag–P distances within each pseudo chelate ring, though the asymmetry is remarkably consistent there being one "short" and one "long" bond in each ring, 2.662(3) [P(1)] and 2.558(3) Å [P(2)] in the skewed ring and 2.622(3) [P(3)] and 2.553(3) Å [P(4)] in the envelope ring. The transannular Ag$\cdots$Fe(1) and Ag$\cdots$Fe(2) distances are 4.25 and 4.15 Å respectively. The analogous complex $[Ag(L^2)_2]ClO_4\cdot 2CHCl_3$[27] has also been studied and shows a more regular tetrahedral geometry around Ag with the bite angles of the diphosphine P(1)–Ag–P(2) and P(3)–Ag–P(4) being 105.71(4) and 98.39(4)° respectively. However, no mention is made of any asymmetry in the pseudo six-membered chelate rings.

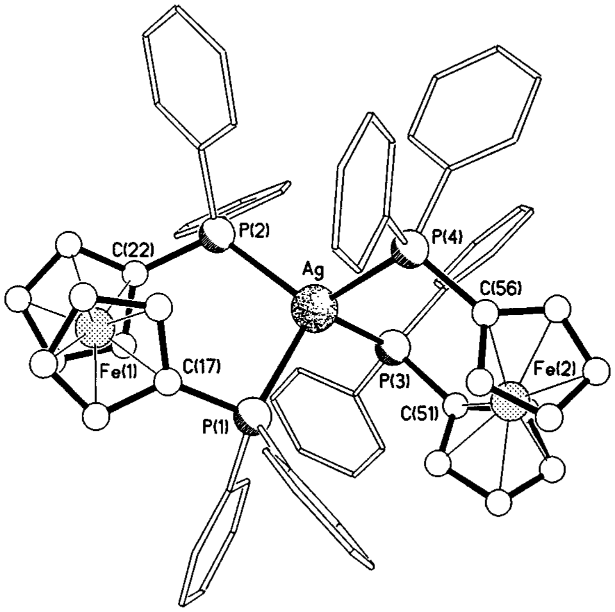


Fig. 5 The molecular structure of the cation in complex **4**.

Both ferrocenyl ring systems have slightly staggered geometries [*ca.* 15° for Fe(1) and *ca.* 11° for Fe(2)], though whereas the C_5 rings are essentially parallel in the Fe(1) ferrocenyl unit [2°] they are significantly inclined in the Fe(2) unit [8°]. Accompanying the aforementioned staggering of the rings are very different relative orientations of the P–C_5 bonds which are skewed by 53° for the Fe(1) chelate but by only 10° in the Fe(2) chelate which has the "envelope" conformation. There are no noteworthy intermolecular interactions.

Conclusion

A new 1,1′-heterodisubstituted ferrocenediyl ligand featuring P and S substituents has been synthesized by two routes. Its coordination chemistry with labile copper(I) and silver(I) centres gives metal-bridged bis(ferrocenylene) species in analogy to other more well known P/P- and S/S-substituted ligands,

Table 3 Crystal data, data collection and refinement parameters for complexes **4** and **5**[a]

	5	**4**
Formula	$C_{24}H_{28}CuF_6Fe_2PS_4$	$C_{68}H_{56}AgBF_4Fe_2P_4$
M	764.9	1303.4
Colour, habit	Orange tetrahedra	Orange-yellow prisms
Crystal size/mm	0.33 × 0.33 × 0.27	0.18 × 0.16 × 0.09
Lattice type	Tetragonal	Monoclinic
Space group symbol, number	$I\bar{4}$, 82	$I2/a$, 15
a/Å	10.493(1)	22.627(5)
b/Å	—	23.575(6)
c/Å	13.340(1)	22.970(6)
β/°	—	100.92(1)
V/Å^3	1468.8(2)	12031(5)
Z	2[b]	8
D_c/g cm^{-3}	1.730	1.439
$F(000)$	772	5312
Radiation used	Mo-Kα	Cu-Kα
μ/mm^{-1}	2.08	7.84
θ Range/°	2.5–30.0	2.7–60.0
No. unique reflections measured	1209	7891
No. observed reflections, $\lvert F_o\rvert > 4\sigma(\lvert F_o\rvert)$	1060	4658
Absorption correction	Semi-empirical	Semi-empirical
Maximum, minimum transmission	0.50, 0.38	0.99, 0.45
No. variables	164	651
$R1$	0.031	0.085
$wR2$	0.078	0.197
Largest difference peak, hole/e Å^{-3}	0.21, −0.41	1.08, −1.81

[a] Details in common: graphite monochromated radiation, ω scans, Siemens P4 diffractometer, 293 K. [b] The molecule has crystallographic S_4 symmetry.

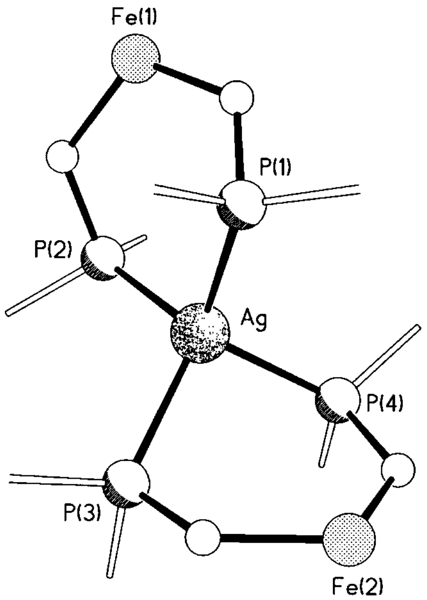


Fig. 6 The two "pseudo six-membered chelate" rings in complex **4**, showing their skewed [Fe(1)] and envelope [Fe(2)] conformations respectively.

though structural determinations illustrate some significant distortion and asymmetry within the structures. Electrochemical investigations show some subtle electronic effects and there are significant shifts to more positive potentials of the cyclic voltammetric responses of the complexes with respect to those of the ligands.

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