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Synthesis, electrochemistry and complexation studies of new redox active bisferrocene acyclic and macrocyclic thioethers

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Abstract

The syntheses and electrochemical studies of new bisferrocene acyclic and macrocyclic ligands are described. Preliminary coordination investigations with palladium(II) and rhodium(I) transition metals produced, in most cases, polymeric complex species. Mono- and bi-metallic copper(II) complexes of two macrocyclic ligands and a nickel(II) complex of an acyclic analogue have been isolated and characterized.

Introduction

The incorporation of metallocene redox-active centres into various macrocyclic host structural frameworks is of considerable interest for the future design of novel sensory devices and/or homogeneous catalytic systems [1–4]. With reference to the latter, the activation of small molecules such as carbon monoxide, olefins *etc.*, bound to a co-ordinated transition metal centre of such a redox ligand system may produce new synthetic pathways to coupled redox reaction products in a stoichiometric or catalytic fashion [4,5]. We report here syntheses, co-ordination and electrochemical studies of new bisferrocene acyclic and macrocyclic thioethers including the X-ray structure of one macrocyclic ligand.

Experimental

Solvent pre-treatment

Where necessary, solvents were purified by distillation prior to use. Acetonitrile and dichloromethane were distilled from CaH_2, hexane from sodium, toluene and

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tetrahydrofuran (THF) from sodium with benzophenone as indicator. Methanol was distilled from $MgSO_4$ and stored under 4A molecular sieves with exclusion of moisture.

Unless otherwise stated, commercial grade chemicals were used without further purification. Hydroxymethylferrocene (**1**) [6], 2,6-bis(mercaptomethyl)pyridine [7] and 1,1'-bis(hydroxymethyl)ferrocene (**7**) [8] were prepared by published procedures.

Instrumental methods

Melting points were recorded with a Gallenkamp melting point apparatus in open capillaries and are uncorrected. Infrared spectra were obtained on a Perkin–Elmer 297 instrument (4000–600 cm^{-1}) as KBr discs and NaCl plates, and solution infrared spectra were obtained on a Nicolet 601A variable temperature and pressure instrument. Nuclear magnetic resonance (NMR) spectra were recorded on Jeol FX 90 and GX 270 machines, using tetramethylsilane (TMS) as internal standard (TMS = 0ppm). Mass spectra and fast atom bombardment spectra were recorded on a Kratos MS80 RF mass spectrometer, the latter with argon primary beam and with 3-nitrobenzyl-alcohol as the matrix. The UV-visible spectra were recorded on a Perkin–Elmer 330 spectrophotometer. Electron paramagnetic resonances were recorded on a Jeol spectrometer. All elemental analyses were performed at the University of Birmingham.

Electrochemical measurements

Cyclic voltammetry and differential pulse polarography were carried out with a PAR 174A potentiostat. All the electrochemical measurements were performed under nitrogen with $[N^nBu_4][PF_6]$ as the supporting electrolyte.

The cyclic voltammetry and differential pulse polarography measurements were carried out by use of a three electrode cell, which incorporated a saturated calomel reference electrode, a platinum wire auxiliary electrode, and a platinum bead working electrode. The current-voltage curves were recorded with a Phillips X–Y recorder.

2,6-Bis((methylferrocene)methylthio)pyridine (**2**)

To a solution of hydroxymethylferrocene (**1**) (0.25 g, 1 mmol) in dichloromethane (70 ml) was added 2,6-bis(mercaptomethyl)pyridine (0.10 g, 0.6 mmol) in dichloromethane (30 ml) followed by three drops of trifluoroacetic acid. The solution was refluxed for 12 h, after which thin layer chromatography showed that reaction had occurred. The solution was washed with 1.0 *M* sodium hydroxide (3 × 50 ml), the organic layer was separated and dried over $MgSO_4$ and the solvent removed to leave an oily yellow solid (0.10 g, 40%). This was purified by column chromatography on alumina (100% dichloromethane). M.p. = 78–79°C. IR (KBr) = 3100, 2900 cm^{-1} (Fc-H and alkyl CH) 1580, 1560 cm^{-1} (pyridine C=N str.). ^1H NMR ($CDCl_3$) = 7.40 (3H, m, py-H), 4.22 (4H, t, H_2, H_5), 4.11 (16H, s, $H_{3,4}$ unsubst. Fe-H), 3.79 (4H, S, SCH_2Py), 3.53 (4H, s, $FcCH_2S$). EIMS = *m/e* 567 (M^+). Analysis. Found: C, 61.80; H, 5.30; N, 2.70. $C_{29}H_{29}FeNS_2$ calc.: C, 61.38; H, 5.11; N, 2.47%.

1,3-Bis(methylferrocene)propyl disulphide (3)

This was made by the procedure used for **2** but from 1,3-propanethiol. The product was isolated as a yellow solid after column chromatography (alumina, dichloromethane), yield 0.40 g (44%). M.p. = 62–63°C. IR (KBr) = 3100 cm^{-1} (Fc-H str.), 1100 and 1000 cm^{-1} (monosubst. Fc). ^{1}H NMR ($CDCl_3$) = 4.11 (22H, s, Fc-H and $FcCH_2S$), 3.5 (6H, s, $SCH_2CH_2CH_2S$). EIMS = *m/e* 504 (M^+). Analysis. Found: C, 59.60; H, 6.0. $C_{25}H_{28}FeS_2$ calc.: C, 59.52; H, 5.6%.

1,3-Bis(methylferrocene)phenyl disulphide (4)

The same procedure was used but starting from 2,6-(methylthio)benzene. The product was purified by column chromatography on alumina (dichloromethane) and isolated as an orange powder, yield 0.17 g (32%). M.p. = 112–113°C. IR (KBr) = 3100 cm^{-1} (arom. H. str.), 2900 cm^{-1} (alkyl C-H str.), 1600, 1580, 1500 cm^{-1} (arom. C=C), 1100, 1000 cm^{-1} (monosubst. Fc). ^{1}H NMR ($CDCl_3$) = 7.2 (4H, m, arom. H), 3.4 (8H, s, alkyl CH_2). EIMS = *m/e* 566 (M^+). Analysis. Found: C, 62.80; H, 5.80. $C_{30}H_{30}FeS_2$ calc.: C, 63.60; H, 5.30%.

2-Ethyl(1,3-bis(methylferrocene) disulphide (5)

The usual procedure was used starting from 2-mercaptoethyl sulphide. The product was a yellow oil, purified by column chromatography on alumina (100% dichloromethane), yield 0.35 g (35%). IR (NaCl pl.) = 3100 cm^{-1} (arom. C-H), 2900 cm^{-1} (alkyl C-H str.). ^{1}H NMR ($CDCl_3$) = 4.12 (18H, s, Fc–H), 3.56 (4H, s, $FcCH_2S$), 2.66 (4H, s, SCH_2CH_2S), 2.62 (4H, s, $SCH_2CH_2SCH_2$). EIMS = *m/e* 550 (M^+). Analysis. Found: C, 56.90; H, 5.90. $C_{26}H_{30}FeS_3$ calc.: C, 56.73; H, 5.45%.

2,6,19,23-Tetrathia[7.7]ferrocenophane (8)

The usual procedure was used starting from 1,1′-bis(hydroxymethyl)ferrocene (**7**) and 1,3-propanethiol under high dilution conditions. The product was recrystallized from dichloromethane and hexane, yield 0.10 g (15%). M.p. = 180°C (decomp.). IR (KBr) = 3050 cm^{-1} (Fc–H str.), 2900 cm^{-1} (alkyl C-H str.). FABMS = *m/e* 636 (M^+). Analysis. Found: C, 55.80; H, 5.70. $C_{30}H_{36}Fe_2S_4$ calc.: C, 56.60; H, 5.66%.

2,11,24,33-Tetrathia-2,6-bis(methylthio)pyridyl-ferrocenophane (9)

The usual procedure was used but under high dilution conditions. The 1,1′-bis(hydroxymethyl)ferrocene (**7**) and 2,6-bis(mercaptomethyl)pyridine were each dissolved in dichloromethane (2 × 50 ml) and the solutions were simultaneously added dropwise with stirring to a solution of trifluoroacetic acid in dichloromethane (3 drops in 100 ml). After the addition, the mixture was refluxed with vigorous stirring for 24 h. The yellow solid formed was purified by column chromatography on alumina (dichloromethane), yield 0.04 g (3%). M.p. = 150–152°C. IR (KBr) = 3050 cm^{-1} (Fc–H str.), 2900 cm^{-1} (alkyl C-H), 1580, 1560 cm^{-1} (C=N py ring str.), ^{1}H NMR ($CDCl_3$) = 7.4 (6H, m, py-H), 4.15 (16H, m, Fc-H), 3.84 (16H, s, alkyl CH_2). FABMS = *m/e* 762 (M^+). Analysis. Found: C, 59.10; H, 5.30; N, 3.10. $C_{38}H_{36}Fe_2N_2S_4$ calc.: C, 59.84; H, 4.99; N, 3.60%.

2,5,8-Trithia-[9]-ferrocenophane (10) and 2,5,8,21,24,27-hexathia-[9.9]-ferrocenophane (11)

The procedure used for **9** was employed. Column chromatography (silica gel : dichloromethane) gave first the dimer **11**, (0.01 g, 2%) and then the monomer **10** (0.20 g, 47%). Monomer **10**: M.p. 159–160°C. IR (KBr) = 3100 cm^{-1} (Fc–H str.), 2900 cm^{-1} (alkyl CH_2). ^1H NMR ($CDCl_3$ = 4.20 (8H, m, AA'BB', Fc–H J = 1.8 Hz), 3.61 (4H, s, $FcCH_2S$), 2.71 (8H, s, SCH_2CH_2S). FABMS = m/e 364 (M^+).

2,11,24,33-Tetrathia-2,6-bis(methylthio)pyridyl-ferrocenophane copper(II) dichloride [$9 \cdot Cu_2Cl_2$]Cl_2

To a solution of 2,11,24,33-tetrathia-2,6-bis(methylthio)pyridylferrocenophane (**9**) (0.05 g, 0.66 mmol) in THF (10 ml) was added a solution of copper(II) dichloride dihydrate (0.022 g, 0.13 mmol) in THF (15 ml). There was immediate colour change from yellow to dark green. The precipitate formed was filtered off and dried, yield 0.01 g (20%). M.p. = 200°C (decomp.). IR (KBr) = 3100 (Fc–H str.), 2925 cm^{-1} (alkyl CH), 1600, 1577 cm^{-1} (py C=N str.). FABMS m/e = 890 (M – 2Cl), 762 (lig.). Analysis. Found: C, 48.2; H, 3.9; N, 2.47. $C_{38}H_{36}Cl_4Cu_2Fe_2N_2S_4$ calc.: C, 47.5; H, 3.96; N, 2.92%.

Bis(2,11-dithia-2,6-methylbenzeneferrocenophane) copper(II) tetrafluoroborate [$12_2 \cdot Cu$](BF_4)$_2$

To a solution of 2,11-dithia-2,6-methylbenzeneferrocenophane (0.080 g, 0.11 mmol) in dry dichloromethane (10 ml) was added a solution of copper(II) tetrafluoroborate hexahydrate (0.037 g, 0.11 mmol) in ethanol (1 ml). There was an immediate colour change from yellow to light green and formation of a fine precipitate. The solution was stirred for 15 min and the product then filtered off and washed with ethanol and dichloromethane. An olive green solid was produced, yield 0.06 g (28%). M.p. 150°C (decomp.). IR (KBr) = 3100 cm^{-1} (arom. C–H str.), 2900 cm^{-1} (alkyl C–H str.), 1040 cm^{-1} (BF_4^-). FABMS = m/e 914 (M – BF_4), 444 (L + Cu). Analysis. Found: C, 46.00; H, 4.10. $C_{40}H_{40}B_2CuF_8Fe_2S_4$ calc.: C, 46.42; H, 4.26%.

2,6-Bis(methylferrocene(methylthio)pyridinenickel(II) dichloride [$2 \cdot NiCl_2$] $\cdot H_2O$

To a solution of nickel(II) chloride hexahydrate (0.10 g, 0.42 mmol) in methanol (0.71 ml) was added a solution of 2,6-bis(methylferrocene)methylthio) pyridine (0.10 g, 0.18 mmol) in ethylacetate/methanol (50:50 v/v), 2.5 ml). The mixture was kept open to the air for 20 min, during which a green solid separated. The solid was washed with cold methanol and dried, yield 0.02 g (16%). M.p. = 124–126°C. IR (KBr) = 3450 cm^{-1} (H_2O broad), 3100 cm^{-1} (Fc–H), 2950 cm^{-1} (alkyl CH_2), 1600 and 1558 cm^{-1} (py C=N str.). FABMS = m/e 695 (M^+), 660 (M – Cl). Analysis. Found: C, 48.25; H, 4.7; N, 1.6. $C_{29}H_{31}Cl_2NNiOS_2 \cdot H_2O$ calc.: C, 48.80; H, 4.35; N, 1.96%.

Crystal data: $C_{30}H_{36}S_4Fe_2$ (**8**), M = 636.54, monoclinic, space group $P2_1/c$. a = 16.202(2), b = 9.159(2), c = 9.518(1) Å, β = 102.85(3)°, U = 1376.97 Å^3, Z = 4, D = 1.535 g cm^{-3}, crystal size 0.3 × 0.3 × 0.6 mm, Mo-K_α (λ = 0.71069 Å), T = 298 K, $F(000)$ = 664, μ = 12.97 cm^{-1}.

Data collection: 2414 unique reflections were recorded on a CAD4 diffractometer measuring to θ = 25. The structure was solved by Patterson and Fourier

Table 1a

Fractional atomic co-ordinates ($\times 10^4$) for $C_{30}H_{36}S_4Fe_2$ (**8**)

	x	y	z
Fe(1)	8518.3(4)	−125(1)	7443(1)
S(1)	6398(1)	−1994(1)	5839(1)
S(2)	3582(1)	−3608(1)	3233(1)
C(1)	8416(3)	−2294(5)	6932(5)
C(2)	9269(3)	−1913(6)	7374(6)
C(3)	9445(3)	−808(6)	6464(6)
C(4)	8691(3)	−505(5)	5419(5)
C(5)	8043(3)	−1427(4)	5700(4)
C(6)	2341(3)	−503(5)	1401(5)
C(7)	1519(3)	−361(5)	481(5)
C(8)	979(3)	−1334(5)	977(5)
C(9)	1458(3)	−2059(5)	2196(5)
C(10)	2298(2)	−1553(4)	2465(4)
C(11)	2988(3)	−2056(5)	3680(5)
C(12)	4334(3)	−2702(6)	2389(5)
C(13)	5043(3)	−1904(5)	3425(5)
C(14)	5590(3)	−2913(5)	4502(5)
C(15)	7165(3)	−1527(6)	4789(5)

methods. The positional and anisotropic vibrational parameters of all non-hydrogen atoms were refined. Hydrogen atom parameters were refined isotropically.

The final R factor was 0.038 for 1775 reflections having $F > 3\sigma(F)$. The fractional coordinates are listed in Table 1, bond lengths and angles in Tables 2 and 3. Additional material is available from the Cambridge Crystallographic Data Centre.

Table 1b

Anisotropic temperature factors ($\text{Å}^2 \times 10^3$) for $C_{30}H_{36}S_4Fe_2$ (**8**)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe(1)	30.1(3)	29.5(3)	28.6(3)	−2.1(3)	8.2(2)	0.6(3)
S(1)	41(1)	66(1)	33(1)	−5(1)	8(1)	−14(1)
S(2)	40(1)	31(1)	60(1)	−6(1)	−1(1)	4(1)
C(1)	44(3)	35(3)	40(3)	−1(2)	16(2)	5(2)
C(2)	44(3)	45(3)	48(3)	0(3)	3(2)	14(2)
C(3)	36(3)	58(3)	56(3)	−15(3)	14(2)	−1(3)
C(4)	48(3)	43(3)	42(3)	−1(2)	22(2)	−1(2)
C(5)	37(2)	32(2)	29(2)	−7(2)	12(2)	3(2)
C(6)	46(3)	31(3)	45(3)	−2(2)	25(2)	−4(2)
C(7)	75(4)	38(3)	29(2)	0(2)	11(2)	11(3)
C(8)	44(3)	43(3)	44(3)	−7(2)	−2(2)	−1(2)
C(9)	37(2)	35(3)	40(3)	4(2)	10(2)	−3(2)
C(10)	31(2)	26(2)	31(2)	1(2)	11(2)	−4(2)
C(11)	34(2)	41(3)	42(3)	−2(2)	7(2)	2(2)
C(12)	42(3)	48(3)	38(3)	−9(2)	3(2)	13(2)
C(13)	38(3)	35(3)	40(3)	−3(2)	10(2)	2(2)
C(14)	38(3)	36(3)	40(3)	3(2)	3(2)	−4(2)
C(15)	44(3)	38(3)	30(2)	−4(2)	7(2)	−4(2)

The temperature factor exponent takes the form: $-2\pi^2(U_{11}\cdot h^2\cdot a^{*2} + \ldots + 2U_{12}\cdot h\cdot k\cdot a^*\cdot b^*)$.

Table 1c

Hydrogen fractional atomic co-ordinates (×10) and isotropic temperature factors (Å^2 ×10^3) for $C_{30}H_{36}S_4Fe_2$ (**8**)

	x	*y*	*z*	*U*
H(1)	8131(22)	−2938(41)	7351(38)	34(11)
H(2)	9593(27)	−2239(48)	8144(45)	43(14)
H(3)	9907(30)	−257(52)	6654(49)	56(16)
H(4)	8538(33)	219(56)	4791(54)	53(19)
H(6)	2798(24)	−21(43)	1382(39)	32(11)
H(7)	1424(28)	332(49)	−312(50)	68(15)
H(8)	419(27)	−1402(47)	667(46)	45(14)
H(9)	1245(28)	−2734(50)	2705(45)	35(15)
H(111)	3391(25)	−1234(43)	4013(42)	46(12)
H(112)	2752(25)	−2367(44)	4451(41)	57(13)
H(121)	4056(27)	−2055(50)	1696(47)	51(15)
H(122)	4624(24)	−3425(44)	1865(42)	39(11)
H(131)	5382(26)	−1374(47)	2842(45)	49(14)
H(132)	4814(25)	−1090(46)	3924(43)	44(13)
H(141)	5277(24)	−3455(44)	5126(43)	44(13)
H(142)	5820(28)	−3623(49)	3873(48)	49(15)
H(151)	7155(24)	−2263(44)	4094(41)	53(12)
H(152)	7052(31)	−550(56)	4289(52)	67(18)

Table 2a

Bond lengths (Å) for $C_{30}H_{36}S_4Fe_2$ (**8**)

C(1)–Fe(1)	2.043(6)	C(2)–Fe(1)	2.049(7)
C(3)–Fe(1)	2.034(7)	C(4)–Fe(1)	2.037(6)
C(5)–Fe(1)	2.049(6)	C(14)–S(1)	1.816(6)
C(15)–S(1)	1.811(6)	C(11)–S(2)	1.820(6)
C(12)–S(2)	1.804(7)	C(2)–C(1)	1.396(7)
C(5)–C(1)	1.434(6)	C(3)–C(2)	1.402(8)
C(4)–C(3)	1.421(7)	C(5)–C(4)	1.418(6)
C(15)–C(5)	1.495(6)	C(7)–C(6)	1.427(7)
C(10)–C(6)	1.409(6)	C(8)–C(7)	1.402(7)
C(9)–C(8)	1.410(7)	C(10)–C(9)	1.407(6)
C(11)–C(10)	1.491(6)	C(13)–C(12)	1.523(8)
C(14)–C(13)	1.513(8)		

Table 2b

Hydrogen bond lengths (Å) for $C_{30}H_{36}S_4Fe_2$ (**8**)

H(1)–C(1)	0.896(35)	H(2)–C(2)	0.855(40)
H(3)–C(3)	0.887(45)	H(4)–C(4)	0.890(48)
H(6)–C(6)	0.867(38)	H(7)–C(7)	0.972(44)
H(8)–C(8)	0.892(40)	H(9)–C(9)	0.899(41)
H(111)–C(11)	1.001(39)	H(112)–C(11)	0.944(38)
H(121)–C(12)	0.926(43)	H(122)–C(12)	1.006(38)
H(131)–C(13)	0.991(42)	H(132)–C(13)	0.999(41)
H(141)–C(14)	0.996(40)	H(142)–C(14)	1.009(45)
H(151)–C(15)	0.941(39)	H(152)–C(15)	1.011(49)

Table 3a

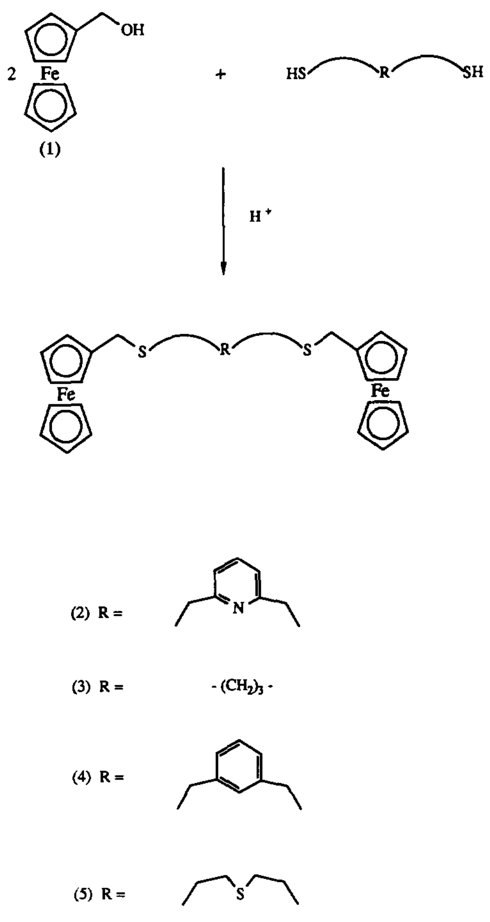
Bond angles (°) for $C_{30}H_{36}S_4Fe_2$ (**8**)

C(2)-Fe(1)-C(1)	39.9(2)	C(3)-Fe(1)-C(1)	67.7(3)
C(3)-Fe(1)-C(2)	40.2(2)	C(4)-Fe(1)-C(1)	68.3(3)
C(4)-Fe(1)-C(2)	68.0(3)	C(4)-Fe(1)-C(3)	40.9(2)
C(5)-Fe(1)-C(1)	41.0(2)	C(5)-Fe(1)-C(2)	68.2(3)
C(5)-Fe(1)-C(3)	68.5(3)	C(5)-Fe(1)-C(4)	40.6(2)
C(15)-S(1)-C(14)	101.4(3)	C(12)-S(2)-C(11)	100.9(3)
C(2)-C(1)-Fe(1)	70.3(4)	C(5)-C(1)-Fe(1)	69.7(3)
C(5)-C(1)-C(2)	108.5(5)	C(1)-C(2)-Fe(1)	69.8(4)
C(3)-C(2)-Fe(1)	69.3(4)	C(3)-C(2)-C(1)	108.6(5)
C(2)-C(3)-Fe(1)	70.5(4)	C(4)-C(3)-Fe(1)	69.7(4)
C(4)-C(3)-C(2)	108.2(5)	C(3)-C(4)-Fe(1)	69.4(4)
C(5)-C(4)-Fe(1)	70.2(3)	C(5)-C(4)-C(3)	108.0(5)
C(1)-C(5)-Fe(1)	69.2(3)	C(4)-C(5)-Fe(1)	69.2(3)
C(4)-C(5)-C(1)	106.8(5)	C(15)-C(5)-Fe(1)	130.0(4)
C(15)-C(5)-C(1)	127.9(5)	C(15)-C(5)-C(4)	125.2(5)
C(10)-C(6)-C(7)	108.4(5)	C(8)-C(7)-C(6)	107.6(5)
C(9)-C(8)-C(7)	107.8(5)	C(10)-C(9)-C(8)	109.1(5)
C(9)-C(10)-C(6)	107.1(5)	C(11)-C(10)-C(6)	128.3(5)
C(11)-C(10)-C(9)	124.6(5)	C(10)-C(11)-S(2)	113.9(4)
C(13)-C(12)-S(2)	114.8(4)	C(14)-C(13)-C(12)	112.9(5)
C(13)-C(14)-S(1)	114.5(4)	C(5)-C(15)-S(1)	112.1(4)

Table 3b

Hydrogen bond angles (°) for $C_{30}H_{36}S_4Fe_2$ (**8**)

H(1)-C(1)-Fe(1)	123.8(23)	H(1)-C(1)-C(2)	127.2(23)
H(1)-C(1)-C(5)	124.3(23)	H(2)-C(2)-Fe(1)	120.5(30)
H(2)-C(2)-C(1)	123.3(30)	H(2)-C(2)-C(3)	127.6(30)
H(3)-C(3)-Fe(1)	114.0(31)	H(3)-C(3)-C(2)	124.3(30)
H(3)-C(3)-C(4)	125.9(31)	H(4)-C(4)-Fe(1)	115.6(33)
H(4)-C(4)-C(3)	133.1(33)	H(4)-C(4)-C(5)	117.5(34)
H(6)-C(6)-C(7)	128.8(25)	H(6)-C(6)-C(10)	122.7(26)
H(7)-C(7)-C(6)	120.1(27)	H(7)-C(7)-C(8)	132.3(26)
H(8)-C(8)-C(7)	126.7(29)	H(8)-C(8)-C(9)	124.9(29)
H(9)-C(9)-C(8)	124.1(29)	H(9)-C(9)-C(10)	126.8(29)
H(111)-C(11)-S(2)	108.6(22)	H(111)-C(11)-C(10)	109.7(22)
H(112)-C(11)-S(2)	105.8(25)	H(112)-C(11)-C(10)	109.5(24)
H(112)-C(11)-H(111)	109.2(33)	H(121)-C(12)-S(2)	109.9(27)
H(121)-C(12)-C(13)	109.4(27)	H(122)-C(12)-S(2)	110.7(22)
H(122)-C(12)-C(13)	105.6(22)	H(122)-C(12)-H(121)	105.9(34)
H(131)-C(13)-C(12)	107.7(24)	H(131)-C(13)-C(14)	111.4(24)
H(132)-C(13)-C(12)	111.1(23)	H(132)-C(13)-C(14)	110.9(23)
H(132)-C(13)-H(131)	102.2(33)	H(141)-C(14)-S(1)	101.4(23)
H(141)-C(14)-C(13)	114.1(23)	H(142)-C(14)-S(1)	114.3(25)
H(142)-C(14)-C(13)	103.3(25)	H(142)-C(14)-H(141)	109.7(33)
H(151)-C(15)-S(1)	108.2(24)	H(151)-C(15)-C(5)	108.5(24)
H(152)-C(15)-S(1)	113.2(28)	H(152)-C(15)-C(5)	105.5(28)
H(152)-C(15)-H(151)	109.3(34)		



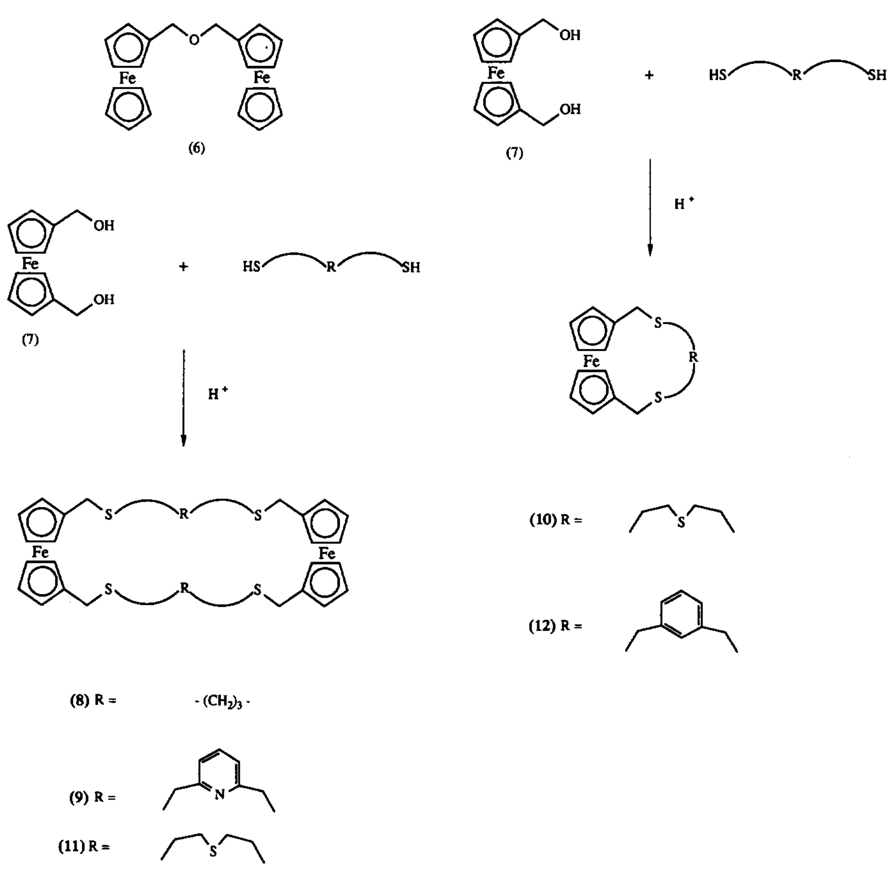
Scheme 1.

The programs used as well as sources of scattering-factor data were as reported previously [9].

Results and discussion

Syntheses

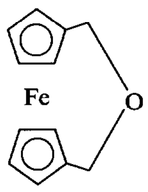
Acyclic and macrocyclic thioethers are well known to stabilize low and unusual oxidation states of catalytically active transition metals through their ability to act as π-acid ligands [10]. The attachment to or integration of ferrocene redox-active moieties into these types of systems was undertaken by use of the synthetic procedure reported by Ratajczak et al. [11]. Typically, a dichloromethane solution of two equivalents of hydroxymethylferrocene (**1**) and the appropriate bisthiol containing three drops of trifluoroacetic acid was heated under reflux for *ca.* 12 h. Upon cooling, removal of solvent, and subsequent column chromatography the acyclic products (**2–5**) were isolated in yields of 32–44% (Scheme 1). The formation of these compounds was accompanied by a competing reaction in which two



Scheme 2.

molecules of hydroxymethylferrocene underwent condensation to give the bisferrocene ether as a by-product (**6**).

The macrocyclic ligands **8–12** were prepared under high dilution conditions [12]. 1,1′-Bis(hydroxymethyl)ferrocene (**7**) and the appropriate bisthiol were each dissolved in dichloromethane and the solutions were added simultaneously to a vigorously stirred large volume of dichloromethane containing three drops of trifluoroacetic acid. Removal of solvent and column chromatographic purification gave the new macrocyclic ligands as yellow orange powders in yields of 3–47% (Scheme 2). In a reaction related to the formation of the acyclic ether (**6**) during the synthesis of the acyclic thioethers, 3-oxa-[3]-ferrocenophane (**13**) was a common



(13)

by-product in these macrocyclic ligand syntheses. All the ligands were characterized by elemental analysis, ^1H NMR spectroscopy, fast atom bombardment mass spectrometry and infra red spectroscopy (see Experimental).

X-Ray structural investigation of 2,6,19,23-tetrathia[7.7]ferrocenophane (8) [11]

Crystals of **8** suitable for X-ray diffraction were grown by slow evaporation of a dilute solution of the ligand in dichloromethane (Fig. 1). All the C–S bonds are in a *gauche* conformation, which results in the sulphur atoms adopting an exodentate orientation. Cooper *et al.* [10,13] have found that the tetrathia macrocycles **[12]**-ane-S_4 and **[14]**-ane-S_4 also have C–S linkages that without exception adopt the *gauche* conformation.

The cyclopentadienyl rings of **8** are tilted by *ca.* 1.6° so that C3, C4, C6 and C7 are closer to the iron atom than C1, C2, C8 and C9. The twist angle between rings is 26.9°, suggesting that the conformation is midway between the fully eclipsed and staggered.

Electrochemical studies

The electrochemical properties of **2–5** and **8–11** were investigated by cyclic voltammetry and coulometry with $[^nBu_4N]BF_4$ as the supporting electrolyte, and the results are shown in Table 4. All the compounds undergo reversible two electron oxidations and differential pulse voltammetry measurements gave only one wave, suggesting that oxidation of the two ferrocene moieties occurred at the same potential.

Coordination chemistry

Preliminary coordination chemical investigations of these new acyclic and macrocyclic thioether ligands with a variety of transition metals such as palladium(II), rhodium(I) and copper(II) proved disappointing. For example, in most cases polymeric complex species of limited solubility were produced when

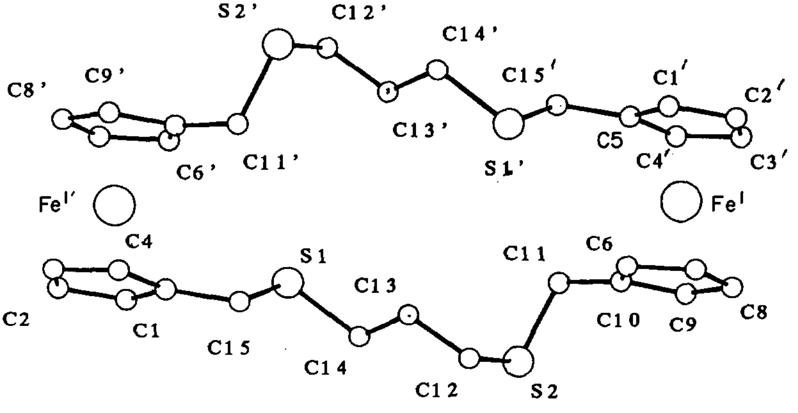


Fig. 1. Structure of **8**.

Table 4

Electrochemical data [a]

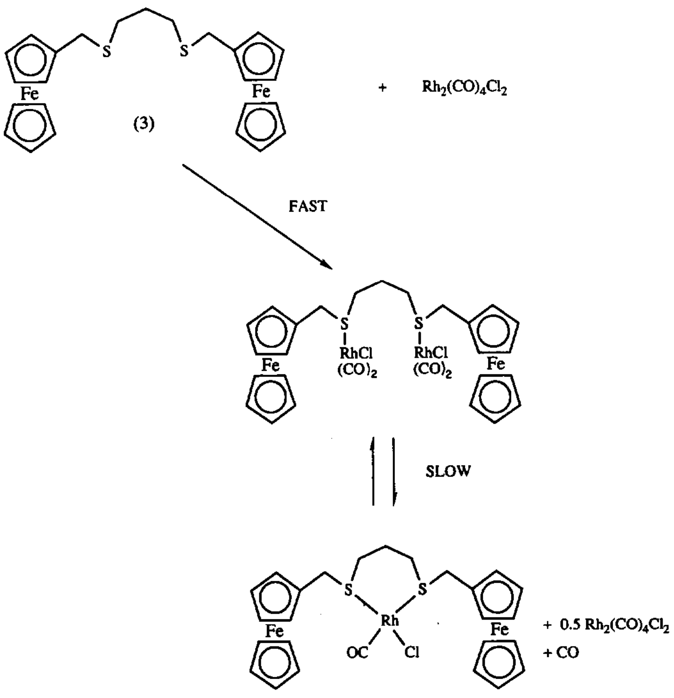
Compound	E_{pa} (V)	E_{pc} (V)
2	0.57	0.47
3	0.64	0.52
4	0.56	0.46
5	0.65	0.53
8	0.63	0.51
9	0.66	0.54
11	0.62	0.53

[a] Obtained from cyclic voltammetry studies in dichloromethane solvent containing 0.2 M $^{n}Bu_4NBF_4$ as supporting electrolyte. Solutions were *ca.* $2\times10^{-3}M$ and potentials were determined with reference to SCE.

bis(benzonitrile)palladium(II) dichloride and dirhodium tetracarbonyl dichloride were used as reactants. The reaction of **3** with $Rh_2(CO)_4Cl_2$ in methanol gave an orange precipitate exhibiting in the FAB mass spectrum molecular ions with isotopic envelopes at 481 and 453, which correspond to $[Rh(\mathbf{3})CO]^+$ and $[Rh(\mathbf{3})]^+$ respectively. Elemental analysis was not conclusive, suggesting the product to be a mixture of complex species, and so the reaction was studied further by use of FTIR spectroscopy. A solution of the ligand **3** in dichloromethane was added to an equimolar dichloromethane solution of $Rh_2(CO)_4Cl_2$. After *ca.* 2 min the two carbonyl stretching bands (2035 and 2098 cm^{-1}) of the reactants had been replaced by two new bands at 2015 and 2089 cm^{-1}. After 2 h the appearance of another band at 2074 cm^{-1} was observed at the expense of some of those relating to the first product, and carbonyl stretching frequencies corresponding to the reactant $Rh_2(CO)_4Cl_2$ began to reappear. Monitoring the reaction further revealed that although the 2074 cm^{-1} absorption had increased slightly in intensity after 4 h, no change in the ratio of the absorption peaks had occurred after a further 6 or 8 h. A possible mechanism for these infrared spectroscopic changes is shown in Scheme 3. A fast initial reaction of the reactants leads to a bimetallic complex which subsequently slowly decomposes to form an equilibrium mixture of bimetallic, monometallic, and reactant complexes. Rhodium(I)-containing products of the other ligands were insoluble, and elemental analysis and FABMS studies were uninformative.

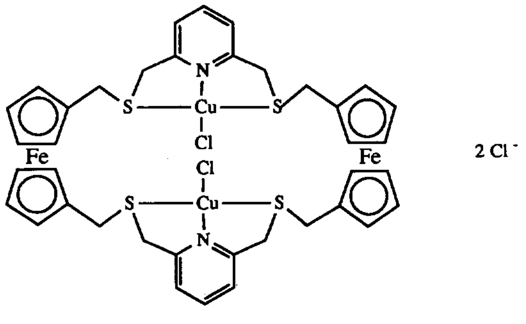
Bimetallic **14** and monometallic copper(II) complexes of macrocyclic ligands **9** and **12** were respectively isolated after the addition of copper(II) chloride dihydrate to a THF solution of **9** or copper(II) tetrafluoroborate addition to a methanol/dichloromethane solution of **12**. Both complexes exhibited limited solubility, but FABMS of the latter complex displayed a molecular ion at 760 corresponding to the $[\mathbf{12}_2CuBF_4]^+$ fragment. Room temperature magnetic susceptibility measurements gave magnetic moment values of 1.50 BM for $[\mathbf{9}\cdot Cu_2Cl_2]Cl_2$ and 2.0 BM for $[\mathbf{12}_2\cdot Cu](BF_4)_2$. The latter value is typical for Cu^{2+}, but the former suggests a degree of antiferromagnetic coupling between the two copper cations as commonly observed for bimetallic copper(II) complex systems [14].

Complexation with nickel(II) was studied only with ligand **2**. A methanolic solution of nickel(II) chloride hexahydrate was added to a solution of **2** in a 50:50 methanol:ethylacetate mixture, and after 1 h an apple-green solid had separated.



Scheme 3.

Again this nickel(II) complex was of limited solubility, but it was characterised by FABMS (isotopic cluster 697), IR spectroscopy, and elemental analysis which suggested $[2 \cdot NiCl_2] \cdot H_2O$. Room temperature magnetic susceptibility measurements gave a magnetic moment of 3.20 BM, characteristic of paramagnetic octahedral nickel(II).



(14)

Conclusions

A series of new bisferrocene redox-active acyclic and macrocyclic ligands has been prepared by reaction of hydroxymethyl ferrocene or 1,1'-bishydroxymethylferrocene with an appropriate dithiol in the presence of trifluoroacetic acid. Preliminary studies of their coordination to palladium(II) and rhodium(I) transition metals led in most cases only to polymeric species. Mono- and bi-metallic copper(II) complexes of **9** and **12**, and a nickel(II) complex of **2** have been isolated and characterized. The coordination chemistry of these ligands with organometallic species is currently being investigated.

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