Novel multidentate ferrocene ligands and their tungsten complexes†

Nicholas J. Long,* Jeff Martin, Andrew J. P. White and David J. Williams

*Department of Chemistry, Imperial College of Science, Technology and Medicine,
South Kensington, London, UK SW7 2AY*

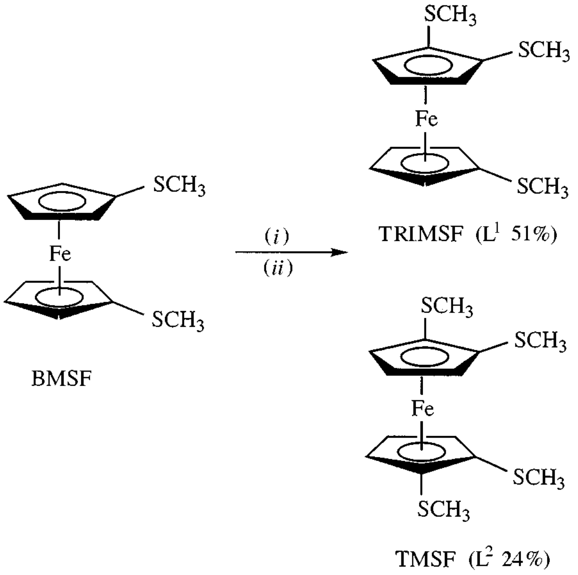
Two new multiply methylthio-substituted ferrocene ligands 1,1′,2-tris- and 1,1′,2,2′-tetrakis-(methylthio)ferrocene have been prepared by a simple, single-step procedure; substitution of the ferrocenyl rings occurs in an adjacent fashion leading to versatile, multidentate ligand behaviour as demonstrated by their reaction with a tungsten carbonyl centre.

Ferrocene-containing complexes‡,[1] are currently undergoing something of a renaissance due to their increasing role in the rapidly growing area of materials science.[2] 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. By linking these donor heteroatoms, or by the incorporation of a pre-formed 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[3] 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.[4]

To date, there have been very few examples of multiple substitution of the metallocene ring to incorporate more than two donor heteroatoms and those that are known generally feature nitrogen and phosphorus atoms. This communication reports the synthesis of two novel, multidentate methylthio-substituted ferrocenes, 1,1′,2-tris(methylthio)ferrocene (TRIMSF) L^1 and 1,1′,2,2′-tetrakis(methylthio)ferrocene (TMSF) L^2, and their versatility as ligands is demonstrated by the synthesis and structural characterisation of two tungsten carbonyl complexes, tetracarbonyl[1,1′,2-tris(methylthio)ferrocene]tungsten **1** and tricarbonyl[1,1′,2,2′-tetrakis(methylthio)ferrocene]tungsten **2**.

The ligands L^1 and L^2 are easily prepared by lithiation of 1,1′-bis(methylthio)ferrocene (BMSF)[5] using *tert*-butyllithium ($LiBu^t$) in hexane, followed by addition of dimethyl disulfide (Scheme 1).§ The oily, orange-brown products are separated from unreacted starting material and other multiply-substituted ferrocenes by column chromatography on neutral grade II alumina using hexane as eluent. Using a ratio of 1 ($LiBu^t$):1 (BMSF), the products can be isolated in reasonable yields, L^1 (51%) and L^2 (24%) [with unreacted starting material (25%)] but using ratios of *ca.* 1.5 ($LiBu^t$):1 (BMSF) and above leads to further substitution and incorporation of 5, 6 or 7 methylthio groups. The addition of the initial SMe group onto the cyclopentadienyl ring seems to catalyse the reaction (as use of $LiBu^t$ in lithiations of unsubstituted ferrocene normally effects only mono-lithiation) and it is impossible to limit the substitution using stoichiometric amounts of reagents. The splitting patterns observed in the ^1H NMR spectrum of each ligand indicate the arrangement of the substituted SMe groups, with two adjacent to each other on one ring and one on the other in L^1 and two adjacent groups on each cyclopentadienyl ring in L^2. Steric constraints would lead to the suggestion of 1,1′ and 3,3′ substitution but there is evidence for regioselective lithiation of substituted ferrocenes and simple π arene systems with N-, P- or O-containing substituents.[6–8] This has been attributed to an intramolecular co-ordination between the lithium atom and the lone pair of electrons on the substituent. These points indicate the possibility of substituting all the cyclopentadienyl protons to form deca-substituted (methylthio)ferrocene and thus the analogous 'superferrocenophanes'.[9]

As a preliminary study into the binding properties of these ligands they were treated with $[W(CO)_4(nbd)]$ (nbd = bicyclo-[2.2.1]hepta-2,5-diene or 2,5-norbornadiene),[10] a soft zero-valent metal species featuring the labile bidentate norbornadiene group which can be displaced in the presence of strong chelating ligands. Clearly, bidentate co-ordination is required from the ligands and it was intriguing to predict the position of



Scheme 1 The syntheses of L^1 and L^2. (*i*) $LiBu^t$–hexane, 0.5 h stirring; (*ii*) S_2Me_2, 2 h stirring

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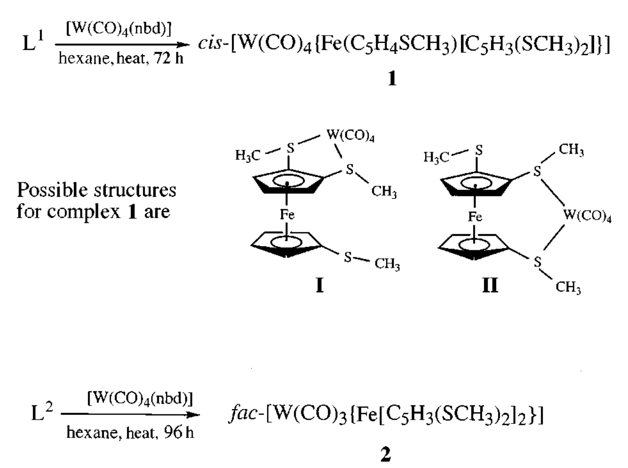
† We dedicate this paper to the memory of Professor Sir Geoffrey Wilkinson and are permanently indebted to his legacy and remarkable contributions to organometallic and in particular, metallocene chemistry.

‡ The π-complexed sandwich structure of ferrocene was first recognised by Wilkinson *et al.*[1]

§ Data for L^1: yield 51% (0.18 mmol scale); ^1H NMR ($CDCl_3$) δ 2.30 (s, 9 H, SCH_3), 4.18 (t), 4.34 (t) {4 H, C_5H_4}, 4.26 (t), 4.35 (d) {3 H, C_5H_3}; FAB mass spectrum *m/z* 324 $[M]^+$ (100%), 309 $[M - CH_3]^+$, 277 $[M - SCH_3]$ and 230 $[M - 2(SCH_3)]$.

Data for L^2: yield 24% (0.18 mmol scale); ^1H NMR ($CDCl_3$) δ 2.32 (s, 6 H, SCH_3), 4.20 (t, 1 H, C_5H_3), 4.34 (d, 2 H, C_5H_3); FAB mass spectrum *m/z* 370 $[M]^+$ (100%), 355 $[M - CH_3]^+$, 323 $[M - SCH_3]$ and 276 $[M - 2(SCH_3)]$.



Scheme 2 The syntheses of complexes **1** and **2**

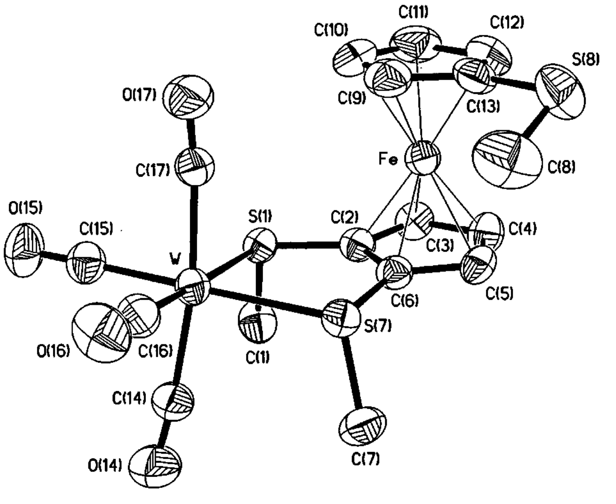


Fig. 1 The molecular structure of complex **1** (50% ellipsoids). Selected bond lengths (Å) and angles (°): W–S(1) 2.561(2), W–S(7) 2.570(2), W–C(14) 2.012(7), W–C(15) 1.964(7), W–C(16) 1.965(7), W–C(17) 2.029(7), Fe···[C(2) to C(6)] 1.639(7), Fe···[C(9) to C(13)] 1.660(7); S(1)–W–S(7) 82.88(6), W–S(1)–C(1) 109.4(2), W–S(1)–C(2) 103.8(2), C(1)–S(1)–C(2) 99.7(3), W–S(7)–C(7) 109.3(2), W–S(7)–C(6) 103.6(2), C(7)–S(7)–C(6) 99.2(3)

this co-ordination *i.e.* between the sulfur atoms on the same cyclopentadienyl ring (**I**) or between one sulfur on one ring and one sulfur on another (**II**) (Scheme 2). Complex **1** was formed by treating $[W(CO)_4(nbd)]$ in refluxing hexane with an equal amount of L^1 and the reaction monitored by IR spectroscopy.¶ A shift to lower wavenumber in the C≡O stretching frequencies indicated metal co-ordination and initial ^1H NMR spectroscopic studies indicated that the bidentate co-ordination arises from the two sulfur atoms on the same ring, *i.e.* the symmetry in **I** is manifest by the relatively simple splitting patterns of the *four* independent cyclopentadienyl ring proton environments; if **II** had been favoured, *five* different signals would be expected for the cyclopentadienyl ring protons. The X-ray analysis of complex **1**|| confirms the bidentate chelation of the tungsten atom by the sulfur atoms of the disubstituted C_5 ring (Fig. 1). The geometry at tungsten is slightly distorted octahedral with angles in the ranges 82.9(1) to 96.8(2) and 171.1(3) to 176.8(2)°. The two W–S bonds are normal at 2.561(2) and 2.570(2) Å, and the two equatorial W–C bonds are *ca.* 0.05 Å shorter than their axial counterparts. The two methyls on the co-ordinated sulfur atoms are in a *syn* relationship, and this geometry is accompanied by a *ca.* 12° out-of-plane fold of the equatorial co-ordination plane relative to the SC_5H_3S plane, thereby moving the tungsten atom towards the iron centre (W···Fe 4.54 Å). The two C_5 rings are eclipsed and inclined by *ca.* 4° relative to each other.

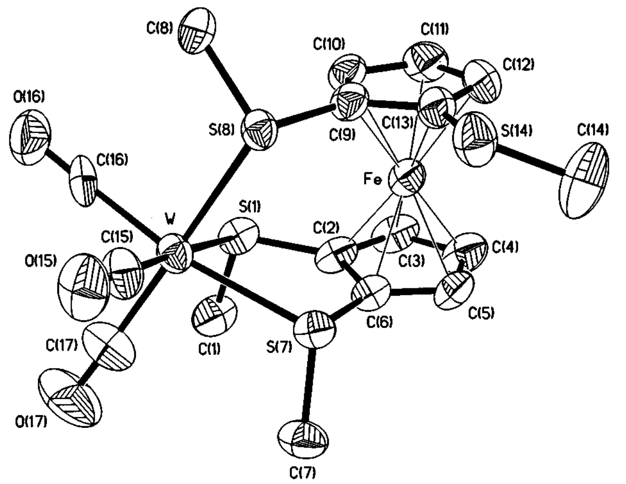


Fig. 2 One of the two crystallographically independent molecules present in the crystals of complex **2** (50% ellipsoids). Selected bond lengths (Å) and angles (°) [the values in parentheses are for the second independent molecule]: W–S(1) 2.580(2) [2.583(2)], W–S(7) 2.577(2) [2.577(2)], W–S(8) 2.563(2) [2.564(2)], W–C(15) 1.931(10) [1.950(9)], W–C(16) 1.938(9) [1.945(9)], W–C(17) 1.968(10) [1.954(10)], Fe···[C(2) to C(6)] 1.64(1) [1.64(1)], Fe···[C(9) to C(13)] 1.64(1) [1.65(1)]; S(1)–W–S(7) 82.25(7) [82.18(7)], S(1)–W–S(8) 94.47(7) [92.39(7)], S(7)–W–S(8) 79.76(7) [81.31(7)], W–S(1)–C(1) 109.6(4) [108.6(4)], W–S(1)–C(2) 103.6(3) [103.3(3)], C(1)–S(1)–C(2) 99.6(4) [99.4(4)], W–S(7)–C(7) 110.0(3) [110.3(3)], W–S(7)–C(6) 102.8(3) [102.8(3)], C(7)–S(7)–C(6) 101.1(4) [100.1(4)], W–S(8)–C(8) 109.5(3) [110.1(3)], W–S(8)–C(9) 116.7(3) [118.0(3)], C(8)–S(8)–C(9) 100.3(4) [100.9(4)]

In an analogous reaction, 2 equivalents of $[W(CO)_4(nbd)]$ were reacted with 1 equivalent of L^2 in refluxing hexane (Scheme 2). After a longer reaction time than in the formation of **1**, a small amount of a yellow-orange crystalline material **2** was obtained and analysed by X-ray crystallography|| (though there was not enough material to complete full physical analysis). The X-ray study of compound **2** shows the tetrasubstituted chalcogenide ferrocenyl ligand L^2 adopting a tridentate chelating (*fac*) role rather than bridging to a second metal centre (Fig. 2). There are two crystallographically independent molecules of **2** in the asymmetric unit which have essentially the same geometry. The geometry at tungsten is distorted octahedral with angles in the ranges 79.8(1) [81.3(1)] to 100.1(4) [98.5(3)] and 170.3(3) [172.8(3)] to 177.3(3)° [176.0(3)°] (the numbers in parentheses refer to the other independent mole-

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¶ Data for complex **1**: yield 26% (0.26 mmol scale) (Found: C, 33.13; H, 2.39. $C_{17}H_{16}FeO_4S_3W$ requires C, 32.92; H, 2.60%); IR (CH_2Cl_2) 2020, 1892 and 1859 cm^{-1} [ν(CO)]; ^1H NMR ($CDCl_3$) δ 2.35 (s, 3 H, SCH_3), 2.86 (s, 6 H, $WSCH_3$), 4.33 (t, 2 H, C_5H_4), 4.46 (t, 2 H, C_5H_4), 4.57 (d, 2 H, C_5H_3), 4.82 (t, 1 H, C_5H_3); FAB mass spectrum *m/z* 620 $[M]^+$ (90%), 592 $[M - CO]^+$ and 536 $[M - 3CO]$.

|| Crystal data for complex **1**: $C_{17}H_{16}FeO_4S_3W$, $M = 620.2$, monoclinic, space group $P2_1/n$ (no. 14), $a = 11.037(2)$, $b = 13.406(2)$, $c = 13.565(2)$ Å, $\beta = 95.76(1)°$, $U = 1997.0(6)$ Å^3, $Z = 4$, $D_c = 2.063$ g cm^{-3}, μ(Mo-Kα) = 68.2 cm^{-1}, λ = 0.710 73 Å, $F(000) = 1192$. An orange prismatic block of dimensions 0.77 × 0.43 × 0.23 mm was used. *Crystal data* for complex **2**: $C_{17}H_{18}FeO_3S_4W$, $M = 638.3$, triclinic, space group $P1$ (no. 2), $a = 10.241(1)$, $b = 10.658(1)$, $c = 19.535(1)$ Å, $\alpha = 86.63(1)$, $\beta = 89.46(1)$, $\gamma = 72.38(1)°$, $U = 2028.7(3)$ Å^3, $Z = 4$ (there are two crystallographically independent molecules in the asymmetric unit), $D_c = 2.090$ g cm^{-3}, μ(Mo-Kα) = 68.1 cm^{-1}, λ = 0.710 73 Å, $F(000) = 1232$. An orange-red block of dimensions 0.35 × 0.30 × 0.23 mm was used. Data for both structures were measured at room temperature on a Siemens P4/PC diffractometer with Mo-Kα radiation (graphite monochromator) using ω scans. The structures were solved by direct methods and the heavy atom method for **1** and **2** respectively, and the non-hydrogen atoms were refined anisotropically using full-matrix least squares based on F^2 giving $R1 = 0.038$ (0.039), $wR2 = 0.098$ (0.087) for 3101 (5567) independent, observed, absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 50°$] and 236 (470) parameters for **1** (**2**) respectively. CCDC reference number 186/625.

cule). The two equatorial W–S bond lengths are the same for both independent molecules at 2.577(2) [2.577(2)] and 2.580(2) Å [2.583(2) Å], but are slightly longer than the corresponding axial distance of 2.563(2) Å [2.564(2) Å]. Although in one molecule the pattern of W–C distances is the same as observed in complex **1** with the two equatorial lengths being *ca*. 0.03 Å shorter than their axial counterpart, in the other there are no significant differences. The two methyls on the co-ordinated sulfur atoms of the bidentate SC_5H_3S ring are again in a *syn* relationship, this being accompanied by a *ca*. 25° [23°] out-of-plane fold of the equatorial co-ordination plane relative to the bidentate SC_5H_3S plane, thereby moving the tungsten atom further towards the iron centre (W $\cdots$ Fe 4.21 Å [4.24 Å] *cf*. 4.54 Å in **1**). Whereas in complex **1** the ferrocenyl unit adopts an eclipsed conformation, here in **2** the geometry is partially staggered and the two rings are inclined by *ca*. 5° [5°], *cf*. 4° in **1**. The unexpected co-ordination of just one tungsten centre presumably results from the prolonged reaction time and the loss of a carbonyl ligand to give the energetically favourable facial tricarbonyl species through binding of three sulfur atoms.

Full synthetic details of the ligands and complexes and further metal co-ordination studies will be reported subsequently but this communication shows the potential of these type of multidentate chalcogenide ferrocenyl ligands and leads to on-going studies into the incorporation of mixtures of donor heteroatoms such as S/Se, P/S and S/N around the metallocene nucleus.

Acknowledgements

We wish to thank EPSRC for an Earmarked studentship (to J. M.).

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Received 2nd *May* 1997; *Communication* 7/03030D