

Heteroferrocene: The Synthesis of Bis[(3*a*,4,5,6,6*a*- η)-1,3,4,5,6-pentamethylcyclopenta[*d*]imidazo-2-thionyl]iron(II)

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The synthesis of bis[(3*a*,4,5,6,6*a*- η)-1,3,4,5,6-pentamethylcyclopenta[*d*]imidazo-2-thionyl]iron(II) is reported. Structural determination of the unusual hetero-substituted metallocene by X-ray crystallographic analysis is described. Preliminary electrochemical studies reveal that oxidation and reduction potentials for the subject ferrocene lie midway between those of ferrocene and decamethylferrocene.

Relatively little is reported regarding the chemistry of ferrocenes containing fused heterocyclic rings.¹ Ferrocenes containing atoms with good donor abilities have attracted strong interest, since these complexing moieties are able to act as ligands toward transition metals. Ferrocenes with electron releasing substituents are reported to be relatively unstable.^{1,2} Aminoferrocene is stable only as its *N*-acetyl derivatives¹ and 1,1'-diaminoferrocene is characterized solely on the basis of its reaction products.² There are only a few examples of heteroferrocenes, but they too lack great thermal stability.³ Imidazole-2-thiones and imidazol-2-ylidenes show coordination chemistry in which they act as σ -donors for many transition metals and main-group elements.⁴ The σ -ligation of imidazole moieties offer an interesting compliment to the cyclopentadienyl π -bonding observed in metallocenes. Our interest in imidazole-based carbenes led us to consider the fusion of a metallocene with an imidazole. We herein report a synthetic strategy that produces these fused metallocenes in three steps. A ferrocenyl-fused imidazole-2-thione is characterized and its crystal structure is reported.

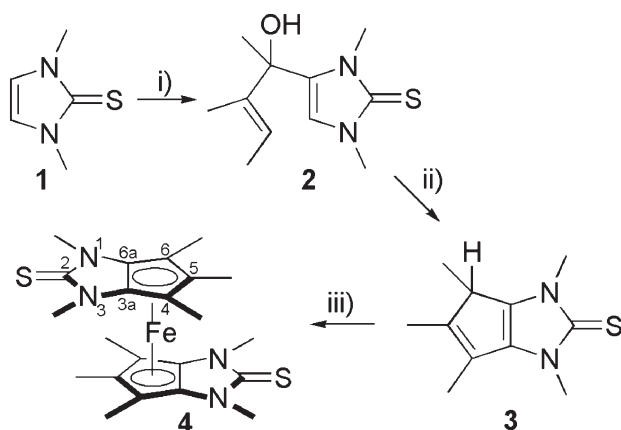
The title compound is obtained from the readily available 1,3-dimethylimidazole-2-thione.⁵ Deprotonation of thione **1** with 1 equiv. of *n*-butyl lithium followed by treatment with 3-

methyl-3-penten-2-one affords alcohol **2** in 80% yield. Nazarov-type cyclization⁶ of **2** produces the cyclopentadienyliimidazolethione **3**. Deprotonation of **3** and addition of anhydrous iron(II) chloride yields the target ferrocene **4** (Scheme 1).

Ferrocene **4** is an orange solid melting over 380 °C with solubility in range of polar organic solvents (e.g. methylene chloride, chloroform, and tetrahydrofuran).⁷ The solubility in benzene and toluene is, however, only slight. Under a nitrogen atmosphere **4** is stable for months, but slowly decomposes on prolonged exposure to air. The ¹H NMR spectrum of **4** in CDCl₃ shows 3 singlets at δ 3.65, 1.97, and 1.62. The imidazole ¹³C² center resonates at δ 176.72 ppm (about 14 ppm downfield of the same position in 1,3-dimethylimidazole-2-thione).⁵

Crystals suitable for X-ray diffraction studies were grown by diffusion of hexane into a saturated chloroform solution of **4**. Ferrocene **4** crystallizes in the monoclinic space group *C2/c*.⁸ The iron center resides on a 2-fold axis so that half of the molecule comprises the asymmetric unit. The KANVAS⁹ drawing in Figure 1 depicts the solid-state structure of **4**. Each fused ring is distinctly planar with no ring atom deviating from the best plane by more than 4.74 pm and an average deviation of 2.43 pm. The two bicyclic rings are parallel and adopt an antiperiplanar orientation. Selected bond distances and angles are presented in Table 1. The average $r_{(\text{Fe}-\text{C})}$ (205.8 pm) is comparable to the distances found in Cp₂Fe [204(2) pm]¹⁰ and (Me₅Cp)₂Fe [205.0(2) pm].¹¹

A comparative cyclic voltammetry study (Figure 2) was done for ferrocene, decamethylferrocene, and **4**.¹² The data are recorded in Table 2. The oxidation and reduction potentials for the subject ferrocene lie midway between those of ferrocene



Scheme 1. Synthesis of **4**. Reagents and conditions: (i) 1. *n*-BuLi, THF; 2. 3-Methyl-3-penten-2-one; (ii) TsOH, dichloromethane; (iii) 1. *n*-BuLi, THF; 2. FeCl₂.

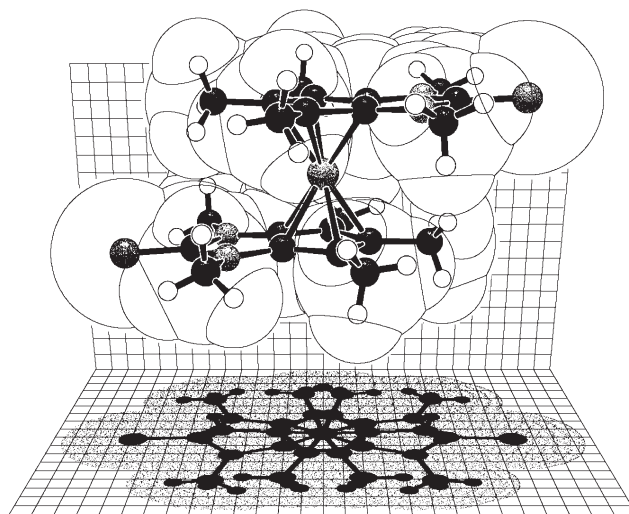
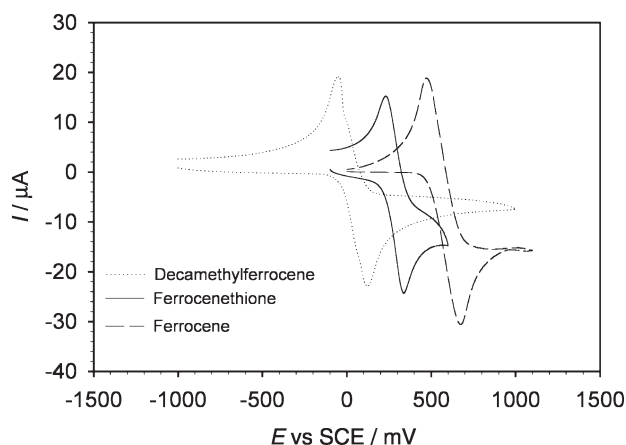


Figure 1. KANVAS⁹ depiction of bis(imidazolyl)ferrocene **4**.

Table 1. Selected bond lengths (pm) and Angles (deg) in **4**

Distance	4	Angle	4
Fe–C	205.8	C ² –N ¹⁽³⁾ –C ^{6a(3a)}	108.96(15), 108.92(15)
C ² –S ¹	167.7(19)	N ¹⁽³⁾ –C ^{6a(3a)} –C ^{3a(6a)}	106.89(15), 106.96(15)
C ² –N ¹⁽³⁾	136.9(2)	C ⁶⁽⁴⁾ –C ^{6a(3a)} –C ^{3a(6a)}	109.79(16), 110.14(15)
N ¹⁽³⁾ –C ^{6a(3a)}	140.2(2)	C ^{6a(3a)} –C ⁶⁽⁴⁾ –C ⁵	105.04(16), 104.83(16)
C ^{3a} –C ^{6a}	140.3(3)	C ⁴ –C ⁵ –C ⁶	110.18(16)
C ^{3a(6a)} –C ⁴⁽⁶⁾	142.7(2)	N ¹ –C ² –N ³	108.25(16)
C ⁴⁽⁶⁾ –C ⁵	145.0(3), 144.9(3)		

**Figure 2.** Comparative cyclic voltammetry studies on **4** and reference compounds.**Table 2.** Cyclic voltammometry data on ferrocene systems

Compound	E_{pa}/V	E_{pc}/V	E_0^1/V
Cp ₂ Fe	0.674	0.472	0.573
Ferrocene 4	0.336	0.232	0.284
Cp [*] ₂ Fe	0.123	–0.053	0.035

and decamethylferrocene. These data suggest that the thiourea moiety is approximately electro-neutral in its effect of the cyclopentadienyl group so that the redox potentials roughly track the number of methyl substituents on the Cp-ring.

This new imidazole-2-thione fused metallocene not only provides entry into imidazole thione complexes bearing a metallocene moiety, but also offers an opportunity for elaboration of the structure into a class of metallocene-fused imidazole-2-ylidenes. In future reports we will elaborate on this novel class of carbenes and their metal complexes.

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- Analytical Data for **4**. mp > 380 °C ¹H NMR (360 MHz, CDCl₃): δ 3.65, (s, 12H), 1.97 (s, 12H) 1.62 (s, 6H). ¹³C NMR (90 MHz, CDCl₃): δ 176.75, 96.96, 78.54, 60.79, 32.85, 9.92, 9.72. Anal. Calcd for C₂₂H₃₀FeN₄S₂: C, 56.165; H, 6.427; N, 11.908%. Found: C, 56.35; H, 6.49; N, 11.64%.
- Selected crystallographic data of **4**: *a* = 1781.36(4), *b* = 870.90(2), *c* = 1509.68(3) pm, β = 113.7600(10)°, *V* = 214358(8) pm³, *D*_{calcd} = 1.458 mg/m³, monoclinic, *C*2/*c*, *Z* = 4, μ(Mo) = 0.92 mm^{–1}, Mo Kα radiation, 1678 reflections (*I* > 4σ(*I*)) *R*₁ = 0.0301 and *wR*₂ = 0.0831. GOF = 1.09 Further details of the crystal structure have been deposited with the Cambridge Crystallographic Data Centre (CCDC deposition number 269184).
- This drawing was made with the KANVAS computer graphics program. This program is based on the program SCHAKAL of E. Keller (Kristallographisches Institute der Universität Freiburg, Germany), which was modified by A. J. Arduengo, III (The University of Alabama), to produce the back and shadowed planes. The planes bear a 50-pm grid, and the lighting source is at infinity so that shadow size is meaningful.
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- Cyclic voltammograms were measured in CH₂Cl₂ at 20 °C containing 0.1 mol dm^{–3} *n*-Bu₄NBF₄ as a supporting electrolyte using a Pt electrode; scan rate was 200 mV s^{–1}.