

Synthesis of New [1ⁿ]Metallophenanes

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Vilsmeier formylation of the trimetallic species $\{(C_5Me_4H)Fe(C_5Me_4)CH_2C_5H_4\}_2Fe$ (**1**) gives $\{(C_5Me_4CHO)Fe(C_5Me_4)CH_2C_5H_4\}_2Fe$ (**2**) and a triformylated product **3**, the structure of which has been established by a ¹H:¹H NOESY experiment. **2** can be converted, by three additional steps, to the new [1⁴]ferrocenophane, $(C_5H_4CH_2C_5Me_4)_4Fe_4$ (**8**), in which ferrocene and permethylated ferrocene units alternate. The methodology also permits the synthesis of heteronuclear species comprising two permethylated ferrocenylene units, a ferrocenylene unit, and a heterometalocenylene; thus, $\{(C_5H_4CH_2C_5Me_4)_4Fe_3Co\}^+PF_6^-$ (**10**) has been characterized.

Introduction

[1ⁿ]Metallophenanes are oligomeric species comprising more than one metallocene unit linked by *n* single-atom bridges (ferrocenophane nomenclature has been discussed in a review by Mueller-Westerhoff).¹ [1²]Ferrocenophane, more often known as [1.1]ferrocenophane, was first reported by Watts as the product of reduction of the diketone, $[(C_5H_4)_2C=O]_2Fe_2$.^{2,3} Examples of [1.1]ferrocenophanes with heteroatom bridges, $[(C_5H_4)_2X]_2Fe$, with X = SiMe₂,^{4–6} SnMe₂,^{7,8} SnⁿBu₂,^{7,8} SnⁿBu,⁹ and PbPh₂,¹⁰ have also been reported. Aspects of carbon-bridged [1.1]metallophenanes that have attracted interest include the isomerism and conformational flexibility possible in [1.1]ferrocenophane derivatives,^{1,11–18} the unusually stable carbanions formed by the deprotonation of [1.1]ferrocenophanes,^{19–22} the stable

carbocations formed by hydride abstraction from the bridges of [1.1]ferrocenophanes and ruthenocenophanes,^{1,23,24} the utility of [1.1]ferrocenophanes as hydrogen generation catalysts,^{25–28} the unusual reversible oxidation of [1.1]ruthenocenophane,²⁹ and metal–metal interactions^{30–34} in mono- and dioxidized [1.1]ferrocenophanes.^{29–34}

Although many studies have been concerned with [1.1]ferrocenophanes, relatively few [1ⁿ]metallophenanes with *n* > 2 have been studied. Previously synthesized [1⁴]metallophenanes have all involved unsubstituted cyclopentadienyl rings bridged by CH₂ groups. The first example was $[(C_5H_4)_2CH_2]_4Fe_4$; this was formed along with the corresponding [1²], [1³], and [1⁵] species from the reaction of $(LiC_5H_4)_2CH_2$ with anhydrous iron(II) chloride.³⁵ These [1ⁿ]ferrocenophanes were formed in an overall yield of ca. 18%, with the [1²], [1³], [1⁴], and [1⁵] species occurring in an approximate ratio of 1:2:3:4. An alternative strategy has been used by Mueller-Westerhoff's group; the reaction of 1,1'-bis(cyclopentadienylmethyl)ferrocene or 1,1'-bis(cyclopentadienylmethyl)ruthenocene dianions with metal ha-

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lides yields $[1^n]$ metallocenophanes with even n only. Thus, the reaction of the bis(cyclopentadienylmethyl)ferrocene dianion with $\text{FeCl}_2 \cdot 1.5\text{THF}$ gave, with careful control of the reaction conditions, a 40% yield of $[1^2]$ -ferrocenophane and a 2.1% yield of $[1^4]$ ferrocenophane.³⁶ $[(\text{C}_5\text{H}_4)_2\text{CH}_2]_4\text{Ru}_4$,³⁷ $[(\text{C}_5\text{H}_4)_2\text{CH}_2]_4\text{Ru}_2\text{Fe}_2$,³⁷ and $\{[(\text{C}_5\text{H}_4)_2\text{CH}_2]_4\text{Fe}_2\text{Co}_2\}^{2+}(\text{PF}_6^-)_2$,¹ have been obtained in analogous reactions. Most of the $[1^n]$ metallocenophanes have been characterized by NMR spectroscopy, elemental analysis, and mass spectrometry. The disordered crystal structure of the diiron–dicobalt dicationic species has also been described briefly in a review.¹ This paper describes a third route to $[1^4]$ metallocenophanes: a trimetallocene functionalized at each terminal ferrocene with a cyclopentadienyl group reacts with metal salts to give $[1^n]$ metallocenophanes where n is a multiple of 4.

Experimental Section

Operations involving oxygen- or water-sensitive materials were carried out under nitrogen or *in vacuo* using standard Schlenk techniques or a Vacuum Atmospheres glovebox. Where necessary, solvents were dried by reflux over either sodium–potassium alloy (diethyl ether), potassium (THF), sodium (toluene), or P_2O_5 (dichloromethane). These solvents were distilled under nitrogen and stored under nitrogen over activated type 4 Å molecular sieves. These solvents, and others when appropriate, were deoxygenated prior to use by passage of a stream of nitrogen through the solvent.

The following materials were used as supplied by Aldrich without further purification: phosphorus oxychloride (99%), DMF (99%), pyrrolidine (99%), anhydrous cobalt(II) bromide (99%), and ammonium hexafluorophosphate (95%). Lithium aluminum hydride (Aldrich, 95%) was purified by extraction into dry diethyl ether, followed by filtration, solvent removal, and drying *in vacuo*. $\text{FeCl}_2 \cdot 1.5\text{THF}$ was prepared by Soxhlet extraction of anhydrous FeCl_2 , prepared by dehydration of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ at 200 °C *in vacuo*, into THF. Compound **1** was prepared as previously described.³⁸

Elemental analyses were performed by the analytical department of the Inorganic Chemistry Laboratory, Oxford. NMR spectra were recorded by using a Bruker AM 300 or a Varian Unity Plus 500 spectrometer. ^1H spectra were referenced *via* residual protio solvent and ^{13}C spectra *via* the solvent signal; chemical shifts (δ) are quoted in parts per million relative to Me_4Si at 0 ppm. Methyl, methylene, methine, and quaternary signals in ^1H -decoupled ^{13}C spectra were distinguished by running either additional ^1H -coupled spectra or DEPT spectra. The FAB mass spectrum of **8** was recorded by the EPSRC Mass Spectrometry Service, University of Wales, Swansea, with a VG Autospec instrument using cesium ion bombardment at 25 kV onto a 3-nitrobenzyl alcohol matrix of the sample. Cyclic voltammograms were recorded by using platinum working, tungsten auxiliary, and silver pseudoreference electrodes. Measurements were made under argon on deoxygenated dry dichloromethane solutions *ca.* 5×10^{-4} M in sample and 0.1 M in $^n\text{Bu}_4\text{N}^+\text{PF}_6^-$. Potentials were referenced to the ferrocinium/ferrocene couple at 0 V by the addition of ferrocene to the cell. The reversibility of redox processes was judged by comparison with the behavior of the ferrocinium/ferrocene couple under the same conditions. Fourier transform infrared spectra were recorded on strong dichloromethane solutions between KBr plates using a Perkin-Elmer FT 1710 spectrometer.

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Preparation of the Formylated Species 2 and 3. POCl_3 (6.04 mL, 65.2 mmol) was syringed into an ampule containing a degassed solution of 3.22 g (3.99 mmol) of **1** in 60 mL of CHCl_3 and 3.7 mL (48 mmol) of DMF; a purple solution resulted. The ampule was evacuated and heated to 60 °C for 30 min. Upon cooling, the ampule was opened and its contents were added to a mixture of 500 mL of water and 400 mL of CH_2Cl_2 . After stirring for 40 min, the mixture was transferred to a separating funnel. The aqueous layer was extracted with an additional 2×200 mL of CH_2Cl_2 . The combined CH_2Cl_2 layers were dried on MgSO_4 and filtered before removal of the solvent *in vacuo* to yield 3.18 g (3.61 mmol, 90%) of an air-stable orange solid, shown by ^1H NMR spectroscopy to be essentially pure **2**. An analytically pure sample was obtained by recrystallization from a hot benzene/hexane mixture. ^1H NMR (C_6D_6): δ 1.46 (s, 12H, CH_3), 1.58 (s, 12H, CH_3), 1.62 (s, 12H, CH_3), 2.05 (s, 12H, CH_3), 3.41 (s, 4H, CH_2), 3.94 (m, 4H, C_5H_4), 4.04 (m, 4H, C_5H_4), 10.29 (s, 2H, CHO). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 9.1 (CH_3), 9.4 (CH_3), 9.7 (CH_3), 10.2 (CH_3), 25.9 (CH_2), 68.4 (C_5H_4 CH), 69.7 (C_5H_4 CH), 72.1 (q), 79.9 (q), 81.0 (q), 82.9 (q), 84.9 (q), 85.5 (q), 88.8 (q), 194.5 (CHO). Selected IR data: 1649 cm^{-1} . Anal. Found (Calcd): C, 69.91 (69.62); H, 7.32 (7.24).

In an analogous reaction using 3.52 mL (34.9 mmol) of POCl_3 , 1.900 g (2.36 mmol) of **1**, 35 mL of CHCl_3 , and 2.0 mL (26 mmol) of DMF, the reaction was held at 60 °C for 4.5 h. After an analogous workup, the orange product was shown by ^1H NMR to be a mixture of compounds. These were separated by column chromatography under nitrogen. The products were absorbed onto silica gel (Fluka Type 60739) by addition of the silica gel to a CH_2Cl_2 solution of the mixture, followed by removal of the solvent *in vacuo*. The resulting solids were transferred to the top of a column (30 \times 4.5 cm) of silica gel (Fluka Type 60739) packed in petroleum ether (bp 40–60 °C). A 4:1 toluene/THF mixture eluted three orange bands. Removal of the solvent from the first fraction gave 320 mg of an orange powder that was shown by ^1H NMR spectroscopy to be the diformylated species **2** (0.37 mmol, 16%). The second fraction also yielded an orange solid; this was identified as the triformylated product **3**. The yield was 603 mg (0.68 mmol, 29%). The third fraction was an oily reddish solid and was not identified. An analytically pure sample of **3** was obtained by recrystallization from hot toluene. ^1H NMR (C_6D_6): δ 1.48–2.06 (overlapping CH_3 groups: 48H), 3.23 (m, 2H, CH_2), 3.30 (d, 1H, CH_2), 3.32 (d, 1H, CH_2), 3.80 (m, 1H, C_5H_4), 3.84 (m, 1H, C_5H_4), 3.99 (m, 1H, C_5H_4), 4.02 (m, 1H, C_5H_4), 4.21 (m, 1H, C_5H_3), 4.47 (m, 1H, C_5H_3), 4.63 (m, 1H, C_5H_3), 9.84 (s, 1H, $\text{C}_5\text{H}_3\text{CHO}$), 10.26 (s, 1H, $\text{C}_5\text{Me}_4\text{CHO}$), 10.29 (s, 1H, $\text{C}_5\text{Me}_4\text{CHO}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 9.0–10.4 (overlapping CH_3 groups), 25.2 (CH_2), 25.7 (CH_2), 69.5 ($\text{C}_5\text{H}_n\text{CH}$), 70.0 ($\text{C}_5\text{H}_n\text{CH}$), 70.3 ($\text{C}_5\text{H}_n\text{CH}$), 70.4 ($\text{C}_5\text{H}_n\text{CH}$), 70.8 ($\text{C}_5\text{H}_n\text{CH}$), 70.9 ($\text{C}_5\text{H}_n\text{CH}$), 74.2 ($\text{C}_5\text{H}_n\text{CH}$), 77.5–93.8 (overlapping quaternary signals), 192.2 (CHO), 194.6 (CHO), 194.9 (CHO). Selected IR data: 1651, 1662 cm^{-1} . Anal. Found (Calcd): C, 68.72 (68.78); H, 6.99 (7.02).

Preparation of the Difulvene 4. A degassed solution of excess cyclopentadiene (*ca.* 10 mL, *ca.* 0.1 mol) and KOH (*ca.* 8 g) in 100 mL of methanol was added to a degassed solution of **2** (3.01 g, 3.5 mmol) in 200 mL of THF. Pyrrolidine (5 mL) was added and the reaction mixture was then stirred under nitrogen for 15 h. The mixture was then transferred to a separating funnel, together with 500 mL of water and 300 mL of diethyl ether. The layers were separated and the aqueous layer was back-extracted with 2×200 mL of diethyl ether. The combined ethereal extracts were then washed with 2×300 mL of saturated aqueous NaCl. The organic layer was dried over MgSO_4 , filtered, and evaporated to dryness *in vacuo* to yield a red-purple oil. Repeated addition of petroleum ether (bp 40–60 °C), followed by evaporation to dryness, caused the oil to solidify to give an essentially quantitative yield of the air-stable, intensely red-purple difulvene **4** (pure by NMR spectroscopy). ^1H NMR (C_6D_6): δ 1.49 (s, 12H, CH_3), 1.70 (s,

12H, CH₃), 1.71 (s, 12H, CH₃), 1.88 (s, 12H, CH₃), 3.29 (s, 4H, CH₂), 3.91 (m, 4H, C₅H₄), 3.96 (m, 4H, C₅H₄), 6.50–6.60 (m, 8H, fulvene ring CHs), 7.13 (s, 2H, fulvene bridge CH). ¹³C{¹H} NMR (C₆D₆): δ 9.4 (CH₃), 9.6 (CH₃), 10.1 (CH₃), 11.6 (CH₃), 25.7 (CH₂), 68.3 (FeC₅H₄CH), 69.6 (FeC₅H₄CH), 78.8 (q), 79.3 (q), 80.5 (q), 80.8 (q), 83.4 (q), 84.6 (q), 89.0 (q), 122.4 (fulvene CH), 126.0 (fulvene CH), 128.9 (fulvene CH), 132.3 (fulvene CH), 139.7 (fulvene CH), 144.1 (fulvene q). Selected IR data: 1613, 2906, 2966, 3051 cm⁻¹.

Preparation of the Dilithium Salt 6. A solution of 260 mg (6.85 mmol) of LiAlH₄ in 100 mL of dry diethyl ether was added dropwise under nitrogen to a solution of 3.10 g (3.23 mmol) of **4** in 270 mL of diethyl ether. The purple color of the solution slowly faded and a purple precipitate, assumed to be the monolithium salt **5**, appeared. The purple precipitate was gradually replaced with a yellow solid; after 40 h the reaction appeared to be complete: the solids were yellow and the supernatant was pale yellow. The solids were collected on a sintered glass frit and washed with 3 × 100 mL of dry diethyl ether before drying *in vacuo* to yield 2.37 g (2.43 mmol, 75%, assuming no solvent is incorporated into the solid) of **6** as an air-sensitive orange-yellow powder.

Preparation of the Diprotonated Dilithium Salt 7. A mixture of 5 mL of methanol and 20 mL of diethyl ether was added, under nitrogen, to 20 mg of **6**; the solid reacted instantly and dissolved to give an orange solution. The solution was transferred to a separating funnel and washed with 50 mL of water and 2 × 50 mL of aqueous NaCl. The ether solution was dried over MgSO₄ and filtered; solvent removal afforded an air-stable orange solid, which was extracted into C₆D₆ and investigated by NMR spectroscopy. ¹H and ¹³C spectra were consistent with the identity of the solid as the doubly protonated dilithium salt **7**. ¹H NMR (C₆D₆): isomeric mixture δ 1.63 (s, 12H, CH₃), 1.74 (s, *ca.* 6H, CH₃), 1.75 (s, *ca.* 6H, CH₃), 1.77 (s, *ca.* 6H, CH₃), 1.81 (s, *ca.* 6H, CH₃), 1.87 (s, 12H, CH₃), 2.71 (apparent s, *ca.* 2H, C₅H₅CH₂), 2.74 (apparent s, *ca.* 2H, C₅H₅CH₂), 3.35 (s, *ca.* 2H, C₅H₅CH₂C₅Me₄), 3.38 (s, *ca.* 2H, C₅H₅CH₂C₅Me₄), 3.47 (s, 4H, FeC₅H₄CH₂C₅Me₄), 3.97 (m, 4H, FeC₅H₄), 4.07 (m, 4H, FeC₅H₄), 5.88 (m, *ca.* 1H, C₅H₅CH), 6.14 (m, *ca.* 1H, C₅H₅CH), 6.15 (m, *ca.* 1H, C₅H₅CH), 6.30 (m, *ca.* 1H, C₅H₅CH), 6.41 (m, *ca.* 1H, C₅H₅CH), 6.52 (m, *ca.* 1H, C₅H₅CH). ¹³C{¹H} NMR (C₆D₆): isomeric mixture δ 9.7 (CH₃), 9.9 (CH₃), 10.0 (CH₃), 10.1 (CH₃), 10.5 (CH₃), 26.2 (CH₂), 26.4 (CH₂), 27.2 (CH₂), 41.2 (CH₂), 43.3 (CH₂), 68.2 (CH), 69.7 (CH), 78.0 (q), 78.4 (q), 78.5 (q), 79.1 (q), 79.2 (q), 81.4 (q), 82.2 (q), 83.6 (q), 89.5 (q), 126.2 (C₅H₅CH), 127.0 (C₅H₅CH), 130.7 (C₅H₅CH), 132.6 (C₅H₅CH), 133.8 (C₅H₅CH), 136.0 (C₅H₅CH), 146.8 (C₅H₅ q), 149.2 (C₅H₅ q).

Preparation of the [1⁴]Ferrocenophane 8. An orange-brown solution of 1.04 g (1.07 mmol) of **7** in 150 mL of dry THF was added dropwise over 30 min to a slurry of 0.41 g (1.75 mmol) of FeCl₂·1.5THF in 150 mL of dry THF. After 15 h the solvent was removed *in vacuo*; the resulting solids were extracted with toluene and filtered through a bed of Celite. Solvent removal afforded 405 mg (0.40 mmol, 30%) of **8**. An analytical sample was obtained by cooling a dichloromethane/methanol solution to -80 °C. ¹H NMR (C₆D₆): δ 1.58 (s, 24H, CH₃), 1.82 (s, 24H, CH₃), 3.62 (s, 8H, CH₂), 3.99 (m, 8H, CH), 4.11 (m, 8H, CH). ¹³C{¹H} NMR (C₆D₆): δ 9.8 (CH₃), 10.7 (CH₃), 27.0 (CH₂), 67.9 (CH), 70.1 (CH), 78.0 (q), 79.4 (q), 83.6 (q), 89.6 (q). MS (FAB): *m/z* 1016 (M⁺) (trace of 2032). Molecular mass determination (Signer method) found 1066. Anal. Found (Calcd): C, 70.51 (70.89); H, 7.15 (7.14).

Preparation of the Triiron-Cobalt [1⁴]Metallophenane 9 and Its Salt 10. An orange-brown solution of 0.623 g (0.639 mmol) of **7** in 100 mL of dry THF was added dropwise over 30 min to a solution of 155 mg (0.708 mmol) of anhydrous CoBr₂ in 100 mL of dry THF. After 10 h the solvent was removed *in vacuo*; the resulting solids were extracted with 75 mL of dry toluene and filtered through a bed of Celite to afford an orange-brown solution of **9**. A solution of 500 mg of NH₄⁺PF₆⁻ in 25 mL of dry THF was added to the solution of

9. After 48 h a purple-gray precipitate was present and the supernatant was pale brown. The solids were collected on a frit and washed with 200 mL of water, 10 mL of THF, and 100 mL of diethyl ether to yield 403 mg (0.346 mmol, 54%) of **10** as a turquoise powder, air-stable as a solid. An analytically pure sample was obtained by layering an acetonitrile solution with diethyl ether. (N.B. If the isolation of **10** is carried out in air, the product shows a paramagnetically broadened and shifted NMR ¹H spectrum; however, sharp spectra can be obtained by stirring an acetonitrile solution of this product with excess sodium dithionite.) ¹H NMR (CD₃CN): δ 1.63 (s, 12H, CH₃), 1.65 (s, 12H, CH₃), 1.82 (s, 12H, CH₃), 1.85 (s, 12H, CH₃), 3.42 (s, 4H, CH₂), 3.45 (s, 4H, CH₂), 3.99 (pseudo q, FeC₅H₄), 5.47 (pseudo q, CoC₅H₄). ¹³C{¹H} NMR (CD₃CN): δ 9.4 (CH₃, two overlapping signals), 10.4 (CH₃), 10.5 (CH₃), 24.9 (CH₂), 26.4 (CH₂), 68.2 (FeC₅H₄CH), 70.1 (FeC₅H₄CH), 78.7 (C₅Me₄ q), 79.1 (C₅Me₄ q), 80.8 (C₅Me₄ q), 81.2 (C₅Me₄ q, two overlapping signals), 81.8 (C₅Me₄ q), 84.4 (CoC₅H₄ CH), 85.1 (CoC₅H₄ CH), 89.8 (FeC₅H₄ q), 107.0 (CoC₅H₄ q). Anal. Found (Calcd): C, 61.84 (61.88); H, 6.41 (6.23).

Results and Discussion

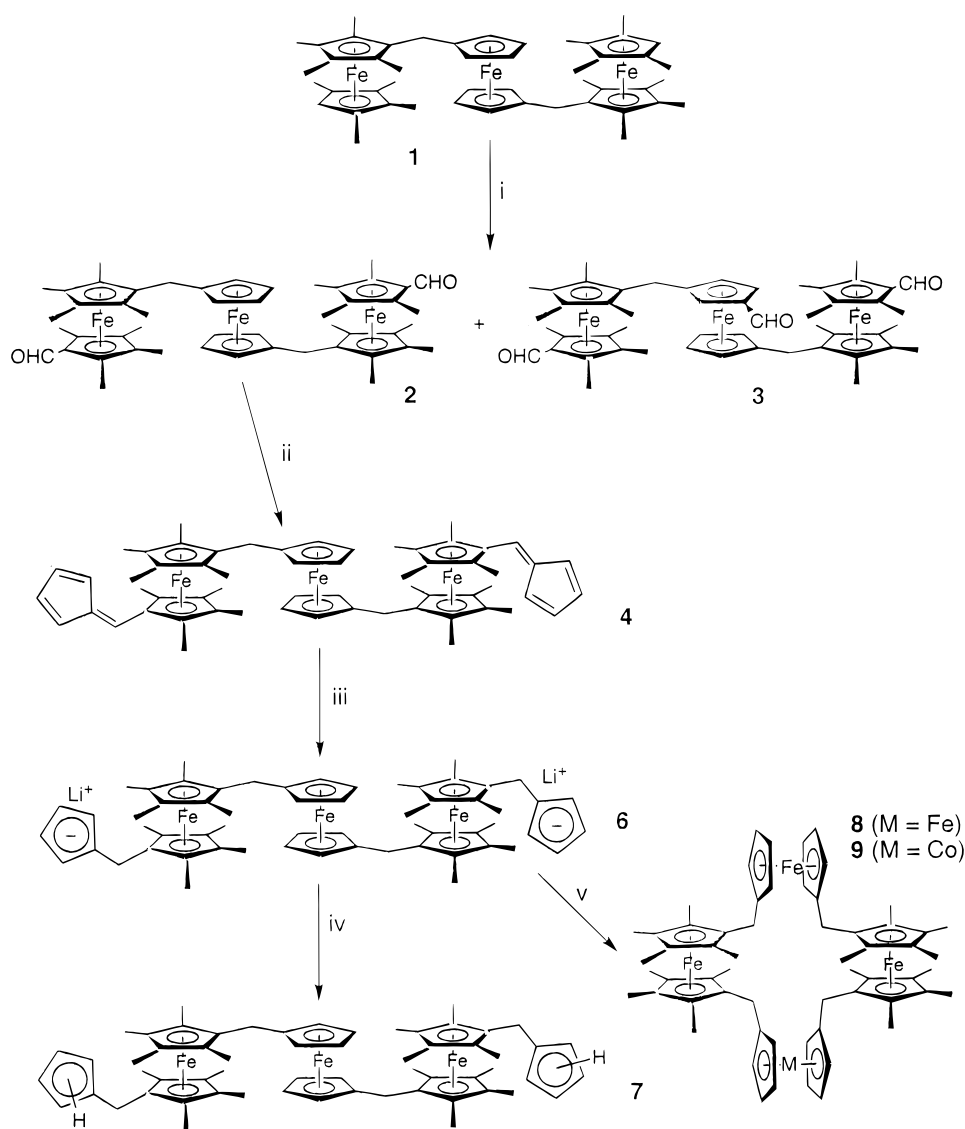
We have previously described the synthesis and structures of several trimetallic compounds composed of carbon-bridged metallocenes.^{38–40} The triiron complex **1** (Scheme 1) appeared to be a suitable candidate for functionalization and subsequent conversion to higher nuclearity complexes. The CH positions of the terminal octamethylferrocenyl units would be expected to undergo electrophilic substitution more readily than the CHs of the central ferrocenylene unit.

1 was heated with DMF and phosphorus oxychloride in chloroform. Complete and selective formylation of the terminal tetramethylated cyclopentadienyl rings was achieved by reaction for 30 min at 60 °C. The selectivity is presumably due to the much greater electron richness and, therefore, susceptibility to electrophilic attack of the methylated rings. However, longer reaction times led to a mixture of the diformylated compound **2** and a second product. These compounds could be separated by column chromatography on silica gel. Both compounds are orange-red solids, soluble in THF and in chlorinated and aromatic solvents, sparingly soluble in alcohols and diethyl ether, and insoluble in hexanes. The ¹H and ¹³C NMR spectra indicated that the second product was the triformylated species **3** shown in Scheme 1. The infrared spectrum of **3** also showed the presence of two different types of formyl group, corresponding to those bonded to the terminal and the central ferrocene units.

Two isomers of **3** may be envisaged, differing in whether the third formyl group is in a 2- or 3-position relative to the bridging CH₂ group. In principle, it should be possible to distinguish between these isomers by examination of the coupling patterns of the cyclopentadienyl resonances in the ¹H NMR spectrum of the molecule. However, coupling constants between inequivalent protons on substituted ferrocenes are often small, and in this case it was not possible to satisfactorily resolve the coupling and unambiguously identify the isomer present. The isomer was identified by a ¹H: ¹H NOESY experiment; the C₅H₃CHO formyl resonance showed cross peaks with *two* cyclopentadienyl CH

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Scheme 1^a

^a (i) DMF, POCl₃, CHCl₃; (ii) excess C₅H₆, KOH, pyrrolidine, MeOH/THF; (iii) LiAlH₄, Et₂O; (iv) MeOH, Et₂O; (v) for M = Fe, FeCl₂·1.5THF, THF; for M = Co, CoBr₂, THF.

resonances, which, together with the cross peaks between the other cyclopentadienyl resonances, unambiguously indicated a 1,3,1'-substitution pattern on the central ferrocene.

We initially attempted the conversion of **2** to the difulvene **4** by using excess cyclopentadiene and ethanolic potassium hydroxide, in analogy with the preparation of 6-(octamethylferrocenyl)fulvene.³⁸ However, the low solubility of **3** in alcohols made this reaction very slow; complete reaction was only achieved after several weeks or after heating the reaction mixture. Either option led to contamination of the product with complex products probably arising from side reactions of the fulvene with cyclopentadiene or with itself. **4** could only be obtained in low yield after column chromatography. Such side reactions have previously been described for a number of fulvene systems. For example, Kovac *et al.* found that the sodium-catalyzed formation of fulvenes from arylferrocenes and cyclopentadiene in ethanol was accompanied by the formation of dimeric species

via a Diels–Alder reaction.⁴¹ Similar reactions of 1,1'-diaroylferrocenes were accompanied by the formation of oligomers; Diels–Alder adducts of fulvene and cyclopentadiene were also observed. However, clean conversion of **2** to **4** was achieved in essentially quantitative yield by the use of cyclopentadiene, potassium hydroxide, and pyrrolidine in a 2:1 THF/methanol mixture (in which **2** is readily soluble). Curiously, *both* potassium hydroxide and pyrrolidine appear to be required to catalyze this reaction: use of either cyclopentadiene/KOH or cyclopentadiene/pyrrolidine in 2:1 THF/methanol is unsuccessful. **4** is an intensely red-purple solid that is very soluble in common organic solvents, including petroleum ether.

4 was reduced to the dilithium salt **6** in good yield with 2 equiv of lithium aluminum hydride in diethyl ether. Initially a purple precipitate was formed; the purple coloration presumably indicates that this material still contains a fulvene group bearing a methylated ferrocene substituent [6-(octamethylferrocenyl)fulvene

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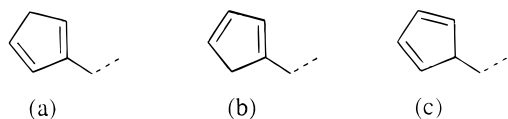


Figure 1. Isomerism in the cyclopentadiene groups of the doubly protonated dilithium salt **7**.

and **4** are both purple]. This purple precipitate, assumed to be the monolithium salt **5**, was slowly converted to the yellow dilithium salt **6**.

Although not characterized directly, **6** was characterized by treatment with methanol to yield its protonated derivative **7**. The ^1H and ^{13}C NMR spectra of **7** were complicated by isomerism in the terminal cyclopentadiene rings (Figure 1). This isomerism, arising from the positions of the double bonds in the ring relative to the CH_2 bridge, only has an effect on the chemical shifts of reasonably close nuclei: those in the ring itself, those of the CH_2 bridge, and those of the C_5Me_4 ring to which the cyclopentadiene group is bridged. The NMR evidence indicated that approximately half the terminal cyclopentadienes have the structure a shown in Figure 1 and half have the structure b, with no evidence for the presence of any with structure c.

The reaction of a dilute THF solution of the dilithium salt **6** with $\text{FeCl}_2 \cdot 1.5\text{THF}$ gave moderate yields of a yellow compound, **8**. Compound **8** is insoluble in alcohols, soluble in petroleum ether and diethyl ether, and very soluble in THF, aromatic solvents, and dichloromethane. It can be conveniently recrystallized from dichloromethane/methanol. The elemental analysis is consistent with the composition $(\text{C}_5\text{Me}_4\text{CH}_2\text{C}_5\text{H}_4)_n\text{Fe}_n$, but obviously cannot distinguish between $[1^4]$, $[1^8]$, and higher $[1^n]$ ferrocenophanes. ^1H and ^{13}C NMR spectra are extremely simple, as one would expect if the proposed cyclic structure were correct. The ^1H NMR spectrum shows two signals attributable to methyl groups, one CH_2 resonance, and two cyclopentadienyl CH resonances, with intensities in the ratio 3:3:1:1:1. The NMR data also imply that only a single species of $[1^n]$ ferrocenophane is present in significant amounts; the $[1^n]$ ferrocenophanes reported by Katz, Acton, and Martin were found to have distinguishable ^1H NMR spectra.³⁵ Evidence for the tetrametallic structure of **8** was provided by mass spectrometry and a molecular mass determination. The most intense ion in the FAB mass spectrum of **8** occurs at 1016 mass units and is attributable to $(\text{C}_5\text{Me}_4\text{CH}_2\text{C}_5\text{H}_4)_4\text{Fe}_4$; a trace of the $[1^8]$ -ferrocenophane species is also seen, but is presumably present in too low concentrations to be observed in the NMR spectra of **8**. Although, in principle, it is possible that the ion at 1016 mass units is a fragmentation product of that at 2032, this explanation seems very unlikely as no other fragments of comparable intensity are seen between 1016 and 2032, or indeed below 1016. A molecular mass determination using the Signer method,⁴² with dichloromethane as a solvent and decamethylferrocene as a reference compound, gave a value of 1066 g mol^{-1} , which is also consistent with the identity of **8** as the $[1^4]$ ferrocenophane.

The cyclic voltammogram of **8** in dichloromethane (Figure 2) shows two reversible waves in a 1:1 ratio at -460 and $+40$ mV relative to the ferrocinium/ferrocene couple. Both processes appear to be chemically revers-

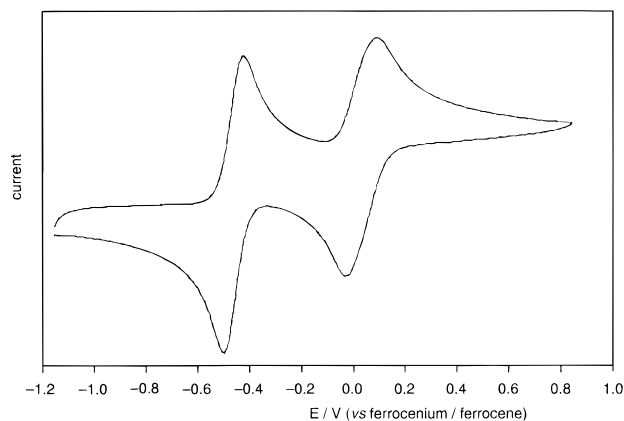


Figure 2. Cyclic voltammogram of the $[1^4]$ ferrocenophane **8** recorded in dichloromethane with a scan rate of 100 mV s^{-1} .

ible, i.e., the voltammogram does not change with time and the forward and reverse currents are equal for each wave. The wave at -460 mV corresponds to oxidation of the methylated ferrocene units and occurs at a potential similar to that of the octamethylferrocenyl units of the parent metallocene **1** (-470 mV in CH_2Cl_2)³⁸ and between those reported for octamethylferrocene (-340 ⁴³ or -400 mV in MeCN)⁴⁴ and decamethylferrocene (-530 mV in MeCN⁴⁵ or -570 mV in CH_2Cl_2).⁴⁶ The fact that the nonmethylated ferrocenes are slightly more difficult to oxidize than ferrocene itself, despite having two alkyl bridge substituents, presumably reflects the difficulty of creating a cation adjacent to two other cationic species.

Reaction of **7** with anhydrous cobalt(II) bromide under conditions similar to those used for the preparation of **8** gave a brown-orange product **9**, which was assumed to be the triiron-cobalt analogue of **8** and was not characterized directly. However, the diamagnetic turquoise cobaltocenium salt, $\{(\text{C}_5\text{Me}_4\text{CH}_2\text{C}_5\text{H}_4)_4\text{Fe}_3\text{Co}\}^+\text{PF}_6^-$ (**10**), was obtained after oxidation with ammonium hexafluorophosphate. The NMR spectra are somewhat more complex than those of **8**, consistent with the lower symmetry arising from the inequivalence of the two nonmethylated metallocenylene units. If solutions of **10** are exposed to air, ^1H NMR spectra show paramagnetic broadening and shifting. Notably, the signals attributable to the methyl groups are *ca.* 5 ppm broad and are centered at a chemical shift of *ca.* -5 ppm (in CD_3CN). The cobaltocenium and ferrocene cyclopentadienyl CH resonances are sharper and closer to their expected chemical shifts. Evidently, some aerial oxidation of the methylated ferrocenes takes place. However, sharp NMR spectra may be obtained by reduction with sodium dithionite and are fully consistent with the formation of the $[1^4]$ metallophenane cation.

Conclusions

A new route to $[1^4]$ ferrocenophanes has been demonstrated. The ferrocenophanes combine both methylated

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and nonmethylated ferrocene units, with the methylation conferring good solubility. [¹⁴C]Metallocenophanes with three ferrocene units and one other metallocene may also be produced by this approach; this has been demonstrated for the case where the fourth metallocene unit is a cobaltocene.

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