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THE SYNTHESIS OF μ-(η^5,η^5-4,5-DIHYDRO-*as*-INDECENYL)BIS(η^5-CYCLOPENTADIENYLIRON)

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Summary

μ-(η^5,η^5-4,5-Dihydro-*as*-indecenyl)bis(η^5-cyclopentadienyliron) (I) was synthesized from 2-[(dimethylamino)methyl]biferrocene via 2-[(dimethylamino)methyl]biferrocene methiodide. The latter was converted to 2-(cyanomethyl)biferrocene, which was subjected to base hydrolysis to give (2-biferrocenyl)acetic acid. The acid was cyclized with trifluoroacetic anhydride to [4-μ-(η^5,η^5-*as*-indecenyl)bis(η^5-cyclopentadienyliron)]trifluoroacetate ester. Hydrolysis of the latter followed by reduction gave compound I.

Introduction

As one part of an investigation of the electron exchange properties of the mixed valent monocations of biferrocene and bis(fulvalene)diiron [1], we desired a substituted biferrocene with a rigid configuration about the fulvalene bridge. A material satisfying these requirements has been obtained by introducing an ethylene bridge between the 2,2′ positions of the η^5,η^5-fulvalene ligand. We report here the synthesis of μ-(η^5,η^5-4,5-dihydro-*as*-indecenyl)bis(η^5-cyclopentadienyliron) (I).

Experimental

General procedures and starting materials

With the exception of the quaternization of 2-[(dimethylamino)methyl]biferrocene, all reactions were performed under a nitrogen atmosphere. Except where compounds are specifically listed as unstable, product isolation and recrystallization were conducted in air. Except where stated otherwise, ether and hydrocarbon solvents were distilled under nitrogen from sodium benzophenone ketyl. Alcohols, distilled water and wet diethyl ether were purged with nitrogen for 1 h prior to use. Chromatography columns were prepared as hexane slurries and were treated with nitrogen-purged, reagent grade hexanes before use. All solvents used in chromatography were nitrogen purged, reagent grade solvents.

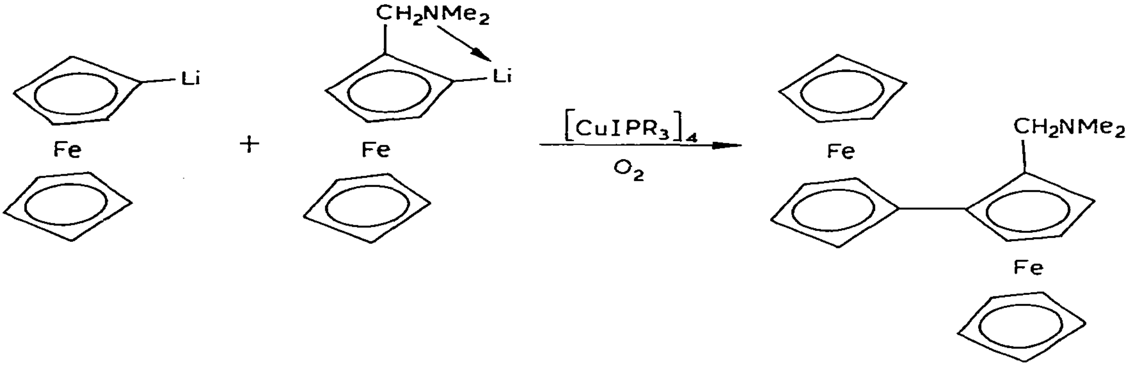
2-Lithio[(dimethylamino)methyl]ferrocene [2] and tetrakis[iodo(tri-n-butylphosphine)copper(I)] [3] were prepared by literature methods. Lithioferrocene was prepared from chloromercuriferrocene [4] and was isolated using the procedure developed by Rausch et al. [2]. Prepared in this manner, lithioferrocene contains one equivalent of lithium chloride. Titration with acid yields an equivalent weight of 230 g/mol of base. The lithium reagents routinely were stored and handled in a nitrogen-filled Vacuum Atmospheres Dry Box.

Nuclear magnetic resonance spectra were recorded on a Varian Associates T-60 or a Hitachi Perkin—Elmer R-22 90 MHz spectrometer. Infrared spectra were recorded on a Perkin—Elmer 457A spectrophotometer, mass spectra (70 eV) using a Varian Associates MAT 44. Cyclic voltammetry was performed with a PAR 175 universal programmer coupled to a PAR 173 Potentiostat on 1 m*M* acetonitrile solutions containing 0.1 *M* tetra-n-butylammonium perchlorate as supporting electrolyte.

Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. Melting points were determined using a Mel-Temp apparatus using samples sealed in glass capillaries under an inert atmosphere. Melting points are not corrected.

Synthesis of 2-[(dimethylamino)methyl]biferrocene (II)

A 500 ml, 2-necked side arm flask was charged with 2.5 g (10 mmol) of lithioferrocene [4] and 2.5 g (10 mmol) of 2-lithio[(dimethylamino)methyl]ferrocene. Tetrahydrofuran (250 ml) was added and the mixture was stirred to give a dark red-brown solution. The flask was cooled to —78° C and 3.92 g (2.5 mmol) of tetrakis[iodo(tri-n-butylphosphine)copper(I)] was added via a solids/addition tube. The reaction mixture was warmed to room temperature and treated with oxygen gas, which resulted in a red-brown solution. The solvent was removed to give a dark brown solid which was extracted with benzene. The benzene was removed in vacuo and the resulting solid was taken up in 20 ml of benzene and diluted with 20 ml of hexane. The resulting solution was loaded



(II)

onto a 12 × 0.75 inch activity III alumina column. Hexane eluted 0.16 g (0.86 mmol, 8.6% recovery) of ferrocene. Hexane/benzene (1/1) eluted the second band, biferrocene, 0.29 g (0.8 mmol, 8%). Benzene/ether (4/1) eluted the third and fourth bands which were identified as 2-[(dimethylamino)methyl]biferrocene vide infra and 2,5″-bis[(dimethylamino)methyl]biferrocene, 0.25 g (0.5 mmol, 5% yield), m.p. 195—196°C (lit. [5] 203—205°C); NMR (benzene-d_6) δ 2.3 (s, 12 H), 3.2 (s, 2 H), 3.8 (s, 2 H), 4.0 (s, 10 H), 4.0-5.0 ppm (m, 6 H); molecular weight, 484 g/mol (mass spectrometry). The remaining material on the chromatography column was removed with Et_2O/methanol. This fraction consisted of two materials; the starting amine, and the other isomer of the disubstituted biferrocene, 2,2″-bis[(dimethylamino)methyl]biferrocene [5].

2-[(Dimethylamino)methyl]biferrocene was recrystallized from pentane to give air-stable red-brown crystals. Yield, 1.02 g (2.4 mmol, 24% yield), m.p. 110—111.5°C.

Analysis: Found: C, 65.17; H, 6.11; N, 3.22. $C_{23}H_{25}NFe_2$ calcd.: C, 64.67; H, 5.90; N, 3.28%.

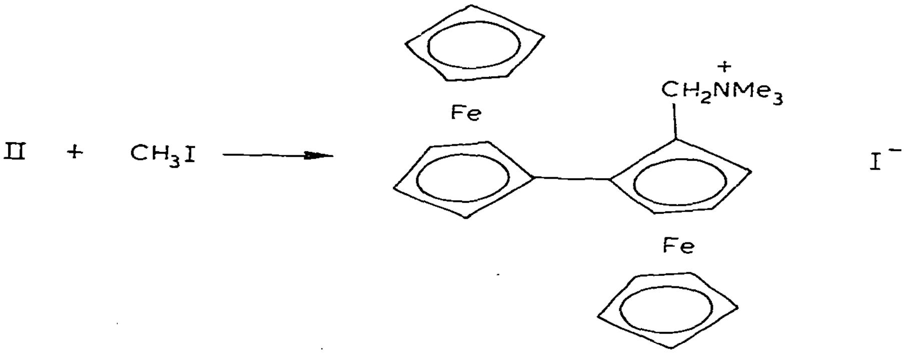
NMR (90 MHz) $CDCl_3$: δ 2.18 (s, 6H); 3.02 (d, 12 Hz, 1 H); 3.58 (d, 12 Hz, 1 H); 3.98 (s, 5 H); 4.05 (s, 5 H); 4.1—4.2 (m, 4 H); 4.35—4.45 (m, 2 H); 4.55—4.7 (m, 1 H) ppm.

IR ($CHCl_3$): 3090 s, 3000 m, 2970 (sh), 2940 s, 2860 m, 2820 s, 2770 s, 1465 (sh), 1455 s, 1405 m, 1370 w, 1350 m, 1290 m, 1255 (sh), 1245 m, 1170 m, 1150 w, 1125 m, 1105 s, 1070 m, 1030 m, 1020 s, 1000 s, 980 w, 945 w, 875 w, 845 (sh), 820 s cm^{-1}.

Mass spectrometry: parent ion, m/e 427.

Quaternization of 2-[(dimethylamino)methyl]biferrocene with iodomethane (III)

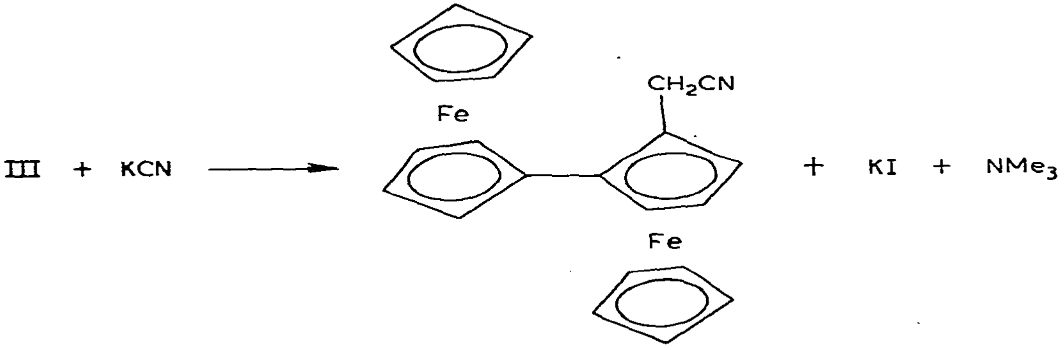
2-[(Dimethylamino)methyl]biferrocene (0.50 g, 1.2 mmol) was taken up in 10 ml of benzene and 1 ml of iodomethane was added. This mixture was stirred for 30 min and the resulting yellow precipitate was collected by filtration and air dried to give 0.67 g (1.2 mmol, 100%) of the methiodide salt of 2-[(dimethylamino)methyl]biferrocene. This material was used without further purification.



(III)

Preparation of 2-(cyanomethyl)biferrocene (IV)

A flask was charged with 0.67 g (1.2 mmol) of 2-[(dimethylamino)methyl]biferrocene methiodide and 0.44 g (7.0 mmol) of potassium cyanide. Distilled water, 20 ml, was added to the flask and the contents of the flask were heated to reflux. After 2 h an orange oil had formed. The contents of the flask were cooled to room temperature and the solidified product was collected by filtration, dissolved in diethyl ether and dried with $MgSO_4$. The solvent was removed under reduced pressure to yield an air-stable red-brown product. Recrystallization from hot hexane gave 0.38 g (0.88 mmol, 73%) of red-brown crystals of 2-(cyanomethyl)biferrocene. Another recrystallization gave an analytically pure sample, m.p. 111—112.5°C.



(IV)

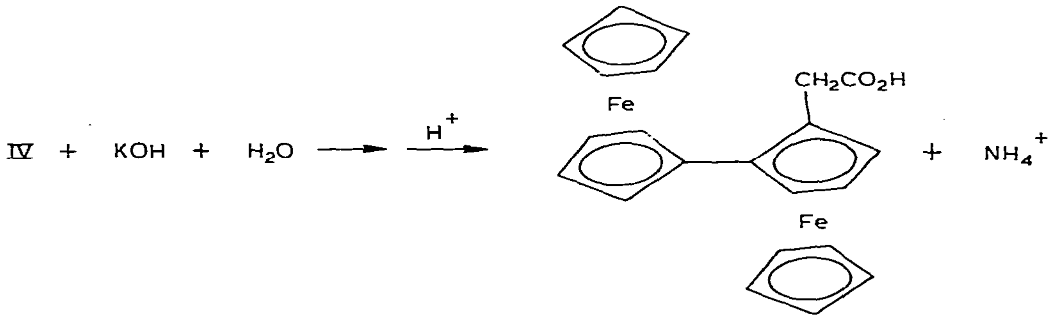
Analysis: Found: C, 65.26; H, 4.87. $C_{22}H_{19}NFe_2$ calcd.: C, 64.59; H, 4.68%.

NMR (benzene-d_6): δ 3.0 (d, 2 Hz, 2 H); 3.98 (s, 5 H); 4.02 (s, 5 H); 4.1 (m); 4.2 (m) ppm.

IR ($CHCl_3$): 3090 m, 3000 m, 2250 m, 1410 m, 1130 w, 1105 s, 1070 w, 1020 m, 1000 s, 870 w, 820 s, 750 (br) s cm^{-1}.

Preparation of (2-biferrocenyl)acetic acid (V)

To 2-(cyanomethyl)biferrocene (0.40 g, 1.0 mmol) and 0.50 g (10 mmol) of potassium hydroxide was added 12 ml of 1-propanol/water (1/1, v/v) and the contents of the flask were heated to reflux. After 30 h the solution was acidified with dilute HCl and was extracted with ether until the ether extracts were



(V)

colorless. The combined ether extracts were shaken with dilute aqueous KOH. The organic phase was collected and dried with $MgSO_4$. The ether was removed under reduced pressure to recover the unreacted starting material and (2-biferfocenyl) acetamide. The aqueous layer was neutralized and extracted with diethyl ether until the ether extracts were colorless. The combined ether extracts were dried with $MgSO_4$ and the ether was removed to give 0.26 g (0.6 mmol, 60%) of (2-biferrocenyl)acetic acid. This material was recrystallized twice by slow evaporation of solvent from its ether/hexane solution to give an analytically pure product, m.p. 170—171°C.

Analysis: Found: C, 61.76; H, 4.65. $C_{22}H_{20}O_2Fe_2$ calcd.: C, 61.72; H, 4.71%.

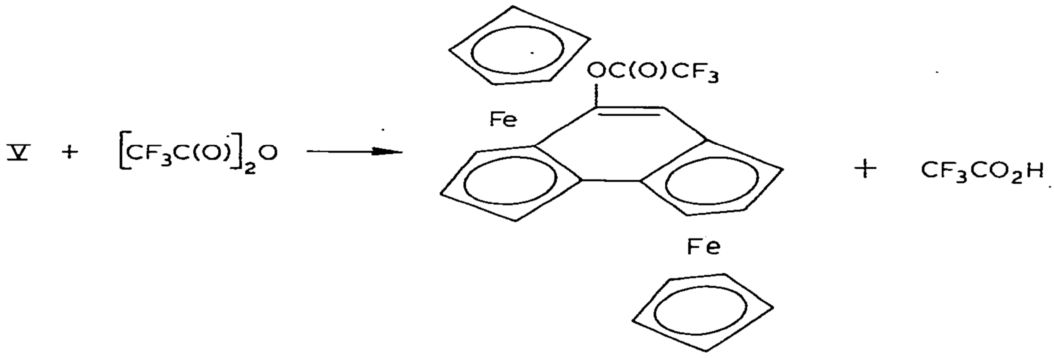
NMR ($CDCl_3$): δ 3.6 (s, 2 H); 3.97 (s, 5 H); 4.02 (s, 5 H); 4.1 (m, 4 H); 4.3 (m, 3 H) ppm.

IR (Kel F): 3080 m, 3020 (sh) m, 2900 m, 1700 vs, 1405 s. (Nujol): 1705 vs, 1375 s, 1365 (sh), 1315 m, 1280 w, 1260 w, 1235 s, 1220 s, 1205 s, 1130 w, 1104 s, 1075 m, 1050 w, 1025 m, 1000 s, 925 w, 875 w, 840 (sh) w, 820 s, 805 s, 780 w, 720 w, 660 w, 490 s cm^{-1}.

(2-Biferrocenyl)acetic acid is mildly air-sensitive.

The preparation of [4-μ-(η^5, η^5-as-indecenyl)bis(η^5-cyclopentadienyliron)trifluoroacetate ester (VI)

A flask was charged with 0.20 g (0.45 mmol) of (2-biferrocenyl)acetic acid and 5 ml of methylene chloride was added. To this solution was added 1 ml (0.72 mmol) of trifluoroacetic anhydride. A green solution resulted. After 2.5 h, a saturated aqueous sodium bicarbonate solution (5 ml) was added to the reaction mixture. The organic phase was collected and the aqueous phase was extracted with 5 ml of methylene chloride. The combined organic phase was washed with 5 ml of aqueous sodium bicarbonate and dried over magnesium sulfate. The solvent was removed to give a dark red powder. All attempts to recrystallize this material resulted in partial decomposition, so the material was characterized and used without further purification.



(VI)

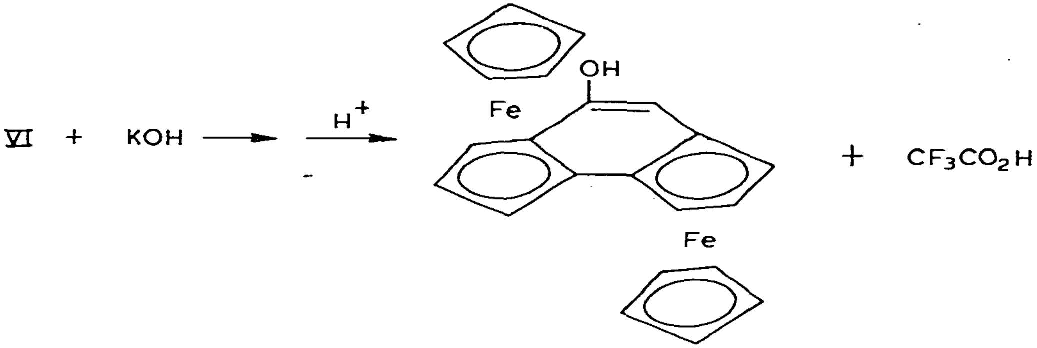
NMR (CD_2Cl_2): δ 3.8 (s, 10 H); 3.9 (q, 3 Hz, 2 H); 4.1 (s, 1 H); 4.3 (m, 2 H); 4.0 (m, 2 H) ppm.

IR (CH_2Cl_2): 3080 m, 2960 s, 2925 m, 2860 m, 1795 s, 1650 m, 1610 w, 1500 w, 1400 m, 1350 s, 1335 m, 1315 w, 1220 s, 1170 vs, 1130 vs, 1090 vs, 1010 vs, 870 s, 810 vs cm^{-1}.

No analysis was attempted. On the basis of the infrared spectrum and the conditions of the reaction, the material is identified as the trifluoroacetate enol ester.

Conversion to the enol or the ketone (VII)

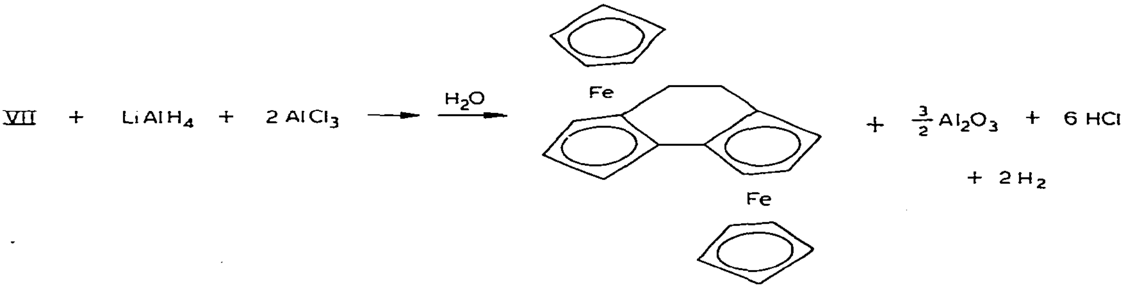
This material was hydrolyzed by refluxing in alcoholic KOH for 2 h, followed by a dilute acid workup. The product was not characterized except to note a slight change in color and decreased solubility in saturated hydrocarbons. A yield was not determined for the first step, the synthesis of the trifluoroacetate ester. The yield, for the entire reaction, conversion of the (2-biferrocenyl)acetic acid to the enol (or ketone) product is 0.1 g (0.27 mmol, 50%).



(VII)

The preparation of μ-[η^5,η^5-4,5-dihydro-as-indecenyl)bis(η^5-cyclopentadienyliron) (I)

An aluminum chloride, lithium aluminum hydride mixture was prepared by adding a diethyl ether solution (2 ml) containing 0.1 g (0.7 mmol) of aluminum chloride to a suspension of 0.013 g (0.34 mmol) of lithium aluminum hydride in 2 ml of diethyl ether. To this was added a suspension of 0.10 g (0.27 mmol) of the product from the ester hydrolysis dissolved in ether. This mixture was stirred for 1 h and then was heated to reflux for 3 h. The mixture was cooled to room temperature and wet diethyl ether was added. A brown solid precipitated which coagulated in the solution. On addition of distilled water, the solid dissolved and the solution separated into an organic and an aqueous phase. The



(I)

organic phase was collected, washed with distilled water, and dried over magnesium sulfate. The solvent was removed in vacuo and the product was stored under nitrogen.

This material was dissolved in a minimum amount of benzene and loaded onto a short silica gel chromatography column. Benzene eluted the first band which was dried in vacuo to give 0.05 g (0.13 mmol, 50%) of an orange solid. This was recrystallized from heptane/diethyl ether to obtain analytically pure μ-(η^5,η^5-4,5-dihydro-*as*-indecenyl)bis(η^5-cyclopentadienyliron), m.p. 229.5—231°C.

Benzene/ether eluted a second band which is tentatively assigned as the 4-hydroxy-5-hydro-*as*-indecenyl product on the basis of its infrared spectrum. This material was not obtained in sufficient yield to characterize further.

Analysis: Found: C, 66.15; H, 4.84. $C_{22}H_{20}Fe_2$ calcd.: C, 66.72; H, 5.09%.

NMR (benzene-d_6): δ 2.5 (d, 2 Hz, d, 4 Hz, 2 H); 3.7 (s, 2 H); 3.9 (s, 10 H); 4.0 (d, 2 Hz, 4 H); 4.2 (m, 2 H) ppm.

IR (CH_2Cl_2): 3090 m, 2960 m, 2930 m, 2900 m, 2840 w, 1400 w, 1320 w, 1105 s, 1010 s, 815 m, 810 s cm^{-1}.

Mass spectrometry: *m/e* 396 (14); 328 (10); 274 (27); 153 (26); 152 (46); 122 (11); 121 (90); 95 (12); 56 (100).

Cyclic voltammetry (CH_3CN): $E_{1/2}$ 0.23 and 0.59 V vs. SCE.

Second chromatography band. IR (CH_2Cl_2): 3580 (sh) m, 3560 m, 3090 m, 2020 w, 2920 m, 2900 (sh), 2850 (sh) m, 1720 m, 1650 m, 1470 m, 1380 m, 1105 s, 1045 m, 1000 s, 960 m, 820 s cm^{-1}.

Results and discussion

Rockett et al. have demonstrated that 2-lithio[(dimethylamino)methyl]ferrocene reacts with cobalt(II) chloride to give a mixture of 2,2''- and 2,5''-disubstituted biferrocenes [5]. Our prior success in preparing biferrocene by the oxidative coupling of lithioferrocene on tetrakis[iodo(tri-n-butylphosphine)copper-(I)] [6] suggested the possibility of obtaining 2-[(dimethylamino)methyl]biferrocene (II) from a mixture of lithioferrocene and 2-lithio[(dimethylamino)-methyl]ferrocene. This mixture can indeed be coupled with $[CuIP(Bu)_3]_4$/oxygen to give the mono-substituted biferrocene (II) in 25% yield. Also isolated from this reaction are low yields of biferrocene and the two disubstituted biferrocenes, 2,2''- and 2,5''-bis[(dimethylamino)methyl]biferrocene.

By analogy with ferrocene chemistry [7], the monosubstituted biferrocene (II) reacts rapidly with iodomethane to give the quaternary ammonium salt III which reacts with potassium cyanide to give the nitrile IV in good yield. On the other hand, base hydrolysis of IV is much slower than hydrolysis of cyanomethylferrocene. 2-(Cyanomethyl)biferrocene reacts in a refluxing alkaline 1-propanol/water solvent mixture to give (2-biferrocenyl)acetic acid (V) in 60% yield. This slightly air-sensitive yellow solid can be handled briefly in air but best results were achieved when it was isolated and recrystallized under nitrogen.

Trifluoroacetic anhydride is reported to convert 3-ferrocenyl/propionic acid and 4-ferrocenylbutyric acid to the 1,1'- and 1,2-cyclic ketones in high yield [8]. (2-Biferrocenyl)acetic acid reacts with trifluoroacetic anhydride to give a red solid which has been tentatively identified as the enol ester VI by IR and NMR spectroscopy. The single carbonyl stretch at 1795 cm^{-1} and the strong infrared bands at 1170 and 810 cm^{-1} are characteristic of a trifluoroacetate moiety and the NMR spectrum is consistent with a substituted biferrocene. It would appear that the initial product of the reaction is the cyclic ketone which isomerizes to the enol tautomer, an aromatic alcohol, and reacts with excess trifluoroacetic anhydride to give the ester.

Attempts to purify VI were unsuccessful so the trifluoroacetate was hydrolyzed with alcoholic potassium hydroxide and the product was reduced with lithium aluminum hydride and aluminum chloride to give the ethylene-bridged biferrocene (I). μ-(η^5,η^5-4,5-Dihydro-*as*-indecenyl)bis(η^5-cyclopentadienyliron) is readily purified by chromatography on silica gel and recrystallization from heptane/diethyl ether. The IR, NMR and mass spectra are all consistent with the formulation of the compound.

Cyclic voltammetry in acetonitrile revealed two reversible, one electron oxidations at 0.23 and 0.59 V vs. SCE which is very similar to the results obtained for biferrocene [9].

A biferrocene with a rigid configuration of the metals was needed in order to assess the effects of rotation about the fulvalene bridge on the rate of electron exchange in the mixed-valent biferrocene monocation. This geometry was preferred because it gives maximum π alignment and should correspond to the maximum rate of electron exchange if exchange occurs primarily by a ligand bridge mechanism. The successful synthesis of μ-(η^5,η^5-4,5-dihydro-*as*-indecenyl)bis(η^5-cyclopentadienyliron) (I), satisfied these requirements, and thus is an important part of an investigation into the electron exchange properties of the mixed-valent monocations of biferrocene and bis(fulvalene)diiron. We are tentatively assigning the geometry of I as *trans*. An examination of molecular models shows that it is impossible to have a vigorous *cis* geometry for a biferrocene with the two five-membered rings parallel to the fulvalene ring. Thus, a *cis* geometry, which cannot be excluded from our data, would require some degree of ring tilting of the cyclopentadienyl rings.

If I has the *trans* configuration it would give the minimum rate of electron exchange if only a direct exchange mechanism is involved.

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