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Formation and Characterization of 1,2-Diiodoferrocene and Related Derivatives[1]

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Iodoferrocene was mercurated and the 2-mercurated isomer, isolated as bis(2-iodoferrocenyl)mercury, was chemically characterized by conversion to the intramolecular anhydride, 1,2-ferrocenedicarboxylic anhydride. Iodination of bis(2-iodoferrocenyl)mercury gave 1,2-diiodoferrocene in essentially quantitative yield. Treatment of bis(2-iodoferrocenyl)mercury with deuterium chloride gave iodoferrocene-2-d_1. Mercuration of ferrocene was shown to produce 1,2-bischloromercuriferrocene in addition to the two major products, chloromercuriferrocene and 1,1′-bischloromercuriferrocene.

Although many 1,2-disubstituted ferrocenes are now known,[2] only 1,2-dichloroferrocene has been synthesized and reported in the 1,2-dihaloferrocene series.[3] This synthesis was accomplished by metalating chloroferrocene with *n*-butyllithium and then treating the intermediate with tri-*n*-butyl borate at −70°. After hydrolysis, the resulting boronic acid upon treatment with cupric chloride yielded 1,2-dichloroferrocene. Hedberg and Rosenberg[4] have very recently also reported that the lithiation of chloroferrocene, followed by reaction with hexachloroethane, affords 1,2-dichloroferrocene. Earlier, Huffman, Keith, and Ashbury[5] showed that lithiation of chloroferrocene followed by carbonation gave, by analogy with similar known substitutions of halobenzenes, 2-chloroferrocenecarboxylic acid. Unequivocal demonstration that the lithiation of chloroferrocene occurs in the 2 position has been recently provided by the studies of Slocum, *et al.*[6] On the other hand, bromoferrocene[7] and iodoferrocene[8] cannot be metalated as can chloroferrocene, since treatment with *n*-butyllithium gives the halogen–lithium interchange product, ferrocenyllithium.

Nefedov[9] has reported that the mercuration of haloferrocenes produces 1,3- and 1,1′-disubstituted ferrocenes. For example, mercuration of iodoferrocene (1) was indicated to produce 3-chloromercuriiodoferrocene (2) and 1-chloromercuri-1′-iodoferrocene (3). Iodination of the mercurials 2 and 3 then presumably produced 1,3-diiodoferrocene and 1,1′-diiodoferrocene, respectively.

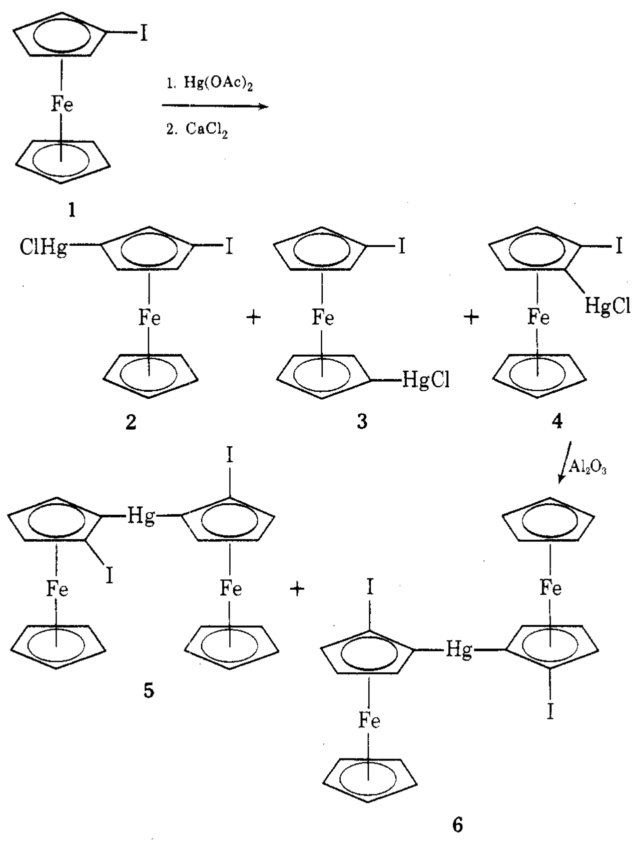
A number of investigators[10-12] have shown that the mercuration of ferrocene produces chloromercuriferrocene, 1,1′-bischloromercuriferrocene, and other unidentified mercurials. Nefedov[9,13] suggested that the mercuration of ferrocene with mercuric acetate followed by treatment with potassium bromide produced, besides bromomercuriferrocene and 1,1′-bisbromomercuriferrocene, 1,3-bisbromomercuriferrocene.

Results and Discussion

In an attempt to prepare 1,3-diiodoferrocene for some additional studies, Nefedov's work was repeated. However, his structural assignment has been found to be in error. Contrary to a previous report[14] that 2-chloromercuriiodobenzene symmetrized on alumina, Nefedov assigned the mercuration product that symmetrized on chromatography on alumina as 3-chloromercuriiodoferrocene (2).[9,15] Nefedov then iodinated the symmetrized product and obtained a material which he assigned as 1,3-diiodoferrocene. The structure of the product was supposedly proved by heating it with cuprous iodide and phenylmagnesium iodide to yield 1,3-diphenylferrocene having a melting point of 107° and exhibiting an infrared absorption at 905 cm^{-1}. The melting point of this derived diphenylferrocene without a mixture melting point determination with authentic 1,3-diphenylferrocene proves nothing, since 1,2-diphenylferrocene melts at 109–110° [18] and 1,3-diphenylferrocene melts at 107°.[18] Moreover, the fact that the infrared spectrum of the product shows a band at 905 cm^{-1} as does 1,1′,3,3′-tetraphenylferrocene[19] does not in itself prove a 1,3 disposition without a comparison of additional bands.[18]

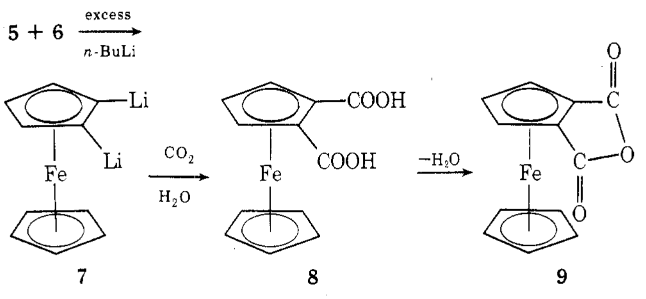
In our work, iodoferrocene (1) was mercurated in the manner of Nefedov and worked up similarly, except that the alumina for chromatography was of activity 3.[20] As the *x*-chloromercuriiodoferrocenes (2–4) passed through the column, 2-chloromercuriiodoferrocene (4) selectively symmetrized and was eluted as a pale yellow solution of bis(2-iodoferrocenyl)mercury (5, 6).

The melting point of the product obtained was the same as that reported by Nefedov.[9] The calculated nmr spectra (see Table I for chemical shift values of several monosubstituted ferrocenes) for bis(2-iodoferrocenyl)mercury and for bis(3-iodoferrocenyl)mercury indicate that these two possible homoannular positional isomers cannot be readily distinguished by nmr spectroscopy (see Table II). Further, the triplet resonance observed in the spectra of the product falls essentially under the two singlets, and hence no coupling constant values can be obtained which could be used in structural assignments. However, since bis(2-iodoferrocenyl)mercury isolated in this work has been shown to consist of a single positional isomer (*vide infra*), the two singlets observed therefore must represent the two possible stereoisomers—meso compound 6 and *dl* com-



pound **5**. A similar set of stereoisomers results from the symmetrization of 2-chloromercuriacetylferrocene.[17]

A reaction between bis(2-iodoferrocenyl)mercury (**5**, **6**) and excess *n*-butyllithium gave 1,2-dilithioferrocene (**7**), and subsequent carbonation of this intermediate followed by hydrolysis gave a 52% yield of 1,2-ferrocenedicarboxylic acid (**8**). The infrared spectrum and the melting point of 1,2-ferrocenedicarboxylic acid (**8**) agree with literature data reported by Richards and Curphey.[21] Moreover, the nmr spectrum of the product in acetone shows a singlet (δ 4.40) for the five protons of the unsubstituted cyclopentadienyl ring, as well as a predicted[22] low-field doublet (δ 5.23) for the 3 and 5 protons and a higher field triplet (δ 4.88) for the 4 proton. The additivity of chemical shifts is shown for all compounds in Table II. The observed coupling constant of 2.8 Hz is also consistent with a 1,2 disposition of the carboxyl groups in the product.[23]



Subsequent dehydration of the diacid **8** produced 1,2-ferrocenedicarboxylic anhydride (**9**). Since the melting point of this compound and the reported melting point[21] of **9** differed by nearly 20°, the product was analyzed further to be certain that it was an intramolecular anhydride. A total elemental analysis indicated a formulation consistent with **9**. The mass spectrum gives a parent ion peak at *m/e* 256, and the nmr spectrum shows singlet, triplet, and doublet resonances of area intensities 5:1:2, respectively. The nmr spectrum shows the expected[22] deshielded 3,5 protons downfield as the doublet and the less deshielded 4 proton as a triplet just below the singlet.

Table I
Chemical Shift Values for Several Monosubstituted Ferrocenes[a]

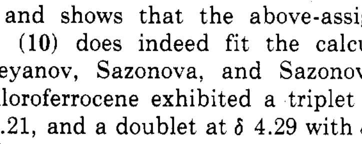
FcX	$\sigma_{1,5}$	$\sigma_{2,4}$
X = I[b]	0.23	−0.03
X = COOH[c]	0.62	0.27
X = –Hg–[b,d]	0.10	0.20
X = HgCl[e]	−0.10	0.10

[a] Values are determined by calculating the difference in chemical shift in parts per million between appropriate protons on the substituted ferrocene *vs.* the protons on ferrocene itself in the same solvent. A positive number indicates deshielded protons and a negative number indicates shielded protons relative to protons in ferrocene. [b] Taken in 5–10% solutions in $CDCl_3$. [c] Taken in saturated acetone solution. [d] Values calculated from the spectrum of *meso*-bis(2-acetylferrocenyl)mercury.[17] [e] Taken in dimethyl sulfoxide solution.

The infrared spectrum of this anhydride is identical with that of Richards and Curphey.[21] The structure of **9** is therefore confirmed, and the 1,2 disposition of bis(2-iodoferrocenyl)mercury (**5**, **6**) is unequivocally established.

Other attempts to chemically characterize the 1,2 disposition of substituents in **5** and **6** included (1) heating 1,2-diiodoferrocene (**10**) derived from **5** and **6** with phenylmagnesium iodide and cuprous iodide, which led to a very small amount of a compound that was not 1,2-diphenylferrocene by a mixture melting point determination with authentic 1,2-diphenylferrocene, and not 1,3-diphenylferrocene by a mixture melting point determination with authentic 1,3-diphenylferrocene;[24] (2) heating 1,2-diiodoferrocene with excess cuprous cyanide at 160°, which resulted in no reaction after 2 hr; (3) heating 1,2-diiodoferrocene and excess cuprous cyanide in *N*-methyl-2-pyrrolidone at 155° for 3 hr, which gave only tar.

Iodination of bis(2-iodoferrocenyl)mercury (**5**, **6**) by the method of Nefedov[9] gave 1,2-diiodoferrocene (**10**) in essentially quantitative yield. The nmr spectrum of 1,2-diiodoferrocene (**10**) shows an AX_2 pattern for the substituted-ring protons with a doublet at δ 4.51 and a triplet at δ 4.22 in $CDCl_3$ solution. Table II lists the calculated values for 1,2-diiodoferrocene (**10**) and 1,3-diiodoferrocene (*vide infra*) and shows that the above-assigned 1,2-diiodoferrocene (**10**) does indeed fit the calculated spectrum. Nesmeyanov, Sazonova, and Sazonova[3] reported that 1,2-dichloroferrocene exhibited a triplet at δ 3.90, a singlet at δ 4.21, and a doublet at δ 4.29 with $J_{3,4}$ and $J_{3,5}$ = 2.3 Hz. The nmr data obtained on the diiodoferrocene obtained in our studies again substantiates a 1,2-disubstituted homoannular isomer, and the 1,3 assignment as originally proposed by Nefedov[9] must again be assumed to be incorrect.



10

The other monomercurated products **2** and **3** isolated from the mercuration of iodoferrocene were obtained as an inseparable mixture, and iodination of this mixture produced diiodoferrocenes. The nmr spectrum of the iodination product shows it to be a mixture of 1,3- and 1,1′-diiodoferrocenes. The spectrum exhibits the expected two triplets for 1,1′-diiodoferrocene (see Table II). In addition, a low field triplet, a higher field doublet, and a singlet are also present. This is the resonance pattern expected for

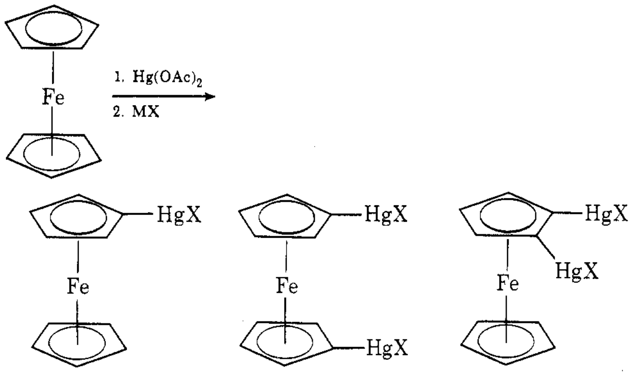
Table II
Calculated and Observed Nmr Spectra of Disubstituted Ferrocenes^a

Compd	Triplet resonances		Doublet resonances		J, Hz	
	Calcd	Found	Calcd	Found	Exptl	Found
Bis(2-iodoferrocenyl)mercury	4.35^b	4.23^c	4.61^b 4.25^b	4.60^c 3.97^c	2–3	
Bis(3-iodoferrocenyl)mercury	4.51^b		4.61^b 4.25		1–1.5	
1,2-Ferrocenedicarboxylic acid^d	4.70	4.89	5.05	5.23	2–3	2.8
1,3-Ferrocenedicarboxylic acid^d	5.40		5.05		1–1.5	
1,1′-Diiodoferrocene^e	4.41 4.15	4.38 4.16				
1,2-Diiodoferrocene^e	4.12	4.22	4.38	4.51	2–3	2.5
1,3-Diiodoferrocene^e	4.64	4.67	4.38	4.32	1–1.5	1.2
1,2-Bischloromercuriferrocene^f	4.38	4.48	4.18	4.25	2–3	2.2
1,3-Bischloromercuriferrocene^f	3.98		4.18		1–1.5	

[a] All values are given in δ parts per million; see Table I for chemical shift values used in the calculated nmr spectra. [b] Values were calculated for $CDCl_3$ solutions. [c] Values obtained in o-$C_6H_4Cl_2$ solutions. [d] Values are for acetone solutions. [e] Values are for $CDCl_3$ solutions. [f] Values are for dimethyl sulfoxide solutions.

1,3-diiodoferrocene, since the proton positioned between the two iodo substituents should produce a triplet, and that triplet should be doubly deshielded and therefore appear furthest downfield. The doublet represents the 4 and 5 protons, which are not as deshielded, since these protons are adjacent to only one iodo group. The observed coupling constant of *ca.* 1.2 Hz (representing $J_{2,4}$ and $J_{2,5}$) is also indicative of a 1,3-disubstituted ferrocene.[23]

The mercuration of ferrocene gives as major products the previously reported products, halomercuriferrocene (11) and 1,1′-bishalomercuriferrocene (12).[10-13] Nefedov and Nefedova[13] reported that in addition to the above two products there is also formed a small amount of 1,3-bishalomercuriferrocene. They identified this product on the basis of the derived haloferrocene, prepared by the mercuration of monohaloferrocenes. However, since Nefedov's 1,3-dihaloferrocenes have now been proved to be 1,2-dihaloferrocenes, it then follows that his previously assigned 1,3-bishalomercuriferrocenes are in fact 1,2-bishalomercuriferrocenes. Repetition of the work of Nefedov and Nefedova[13] gave a product (**13**, X = Cl) which on iodination yielded a diiodoferrocene that has an identical nmr spectrum in benzene solution with that of authentic 1,2-diiodoferrocene in the same solvent. The nmr spectrum of 1,2-diiodoferrocene prepared in this manner also exhibited a weak extra singlet at δ 3.96 which may have been due to iodoferrocene formed during the iodination, or may have resulted from chloromercuriferrocene (**11**, X = Cl) being present as an impurity. Likewise, lithiation of 1,2-bischloromercuriferrocene (**13**, X = Cl) followed by carbonation and acidification gave a mixture of acids, ferrocenecarboxylic acid and 1,2-ferrocenedicarboxylic acid (**8**), as shown by an nmr spectrum of the products.

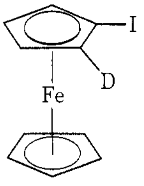


11 **12** **13**

The nmr spectrum of 1,2-bischloromercuriferrocene (**13**, X = Cl) in dimethyl sulfoxide solution shows a downfield triplet, an upfield doublet, and a singlet at still higher field at δ 4.53, 4.30, and 4.23, respectively. This is the expected order for the triplet and doublet resonances, since the nmr spectrum of 1-acetyl-2-chloromercuriferrocene shows that a chloromercuri group tends to shield protons α to this group to a greater extent than protons β to it.[25,26]

In benzene as the solvent, the nmr spectrum of iodoferrocene exhibits triplet resonances at δ 3.84 and 4.29, and a singlet at δ 4.02. The triplet at δ 4.29 can be assigned to the 2 and 5 protons due to the deshielding by the iodine atom. The 3 and 4 protons then appear at δ 3.84. Similarly, in carbon tetrachloride solution, the 2,5 protons appear at δ 4.33, the 3,4 protons at δ 4.05, and the singlet at δ 4.10.[27]

Since the 1,2 disposition of bis(2-iodoferrocenyl)mercury (**5**, **6**) has now been proved, the deuteration of this mercurial was carried out and yielded iodoferrocene-*2-d*$_1$ (**14**).



14

The nmr spectrum of **14** (benzene solution) is instructive as to proton assignments in iodoferrocene. The signal at δ 4.28 which is observed as a triplet integrates for 1.3 protons relative to the 5-proton singlet at δ 4.01, representing the unsubstituted cyclopentadienyl ring. The signal at δ 4.28 represents the 5 proton in **14** as well as 2,5 protons in iodoferrocene, a small amount of which is believed to be present. The 3,4 protons appear as a doublet at δ 3.83 and integrate for approximately two protons. These results therefore confirm the above proton assignments in the nmr spectrum of iodoferrocene.

Experimental Section

Nmr spectra were recorded on a Varian A-60 spectrometer in 5–10% solutions wherever possible. Ir spectra were taken on a Beckman IR-10 spectrometer and were calibrated using the 1601-cm^{-1} band of polystyrene. Mass spectra were recorded on an A. E. I. MS-9 spectrometer by Dr. Alan Siegel at Carnegie-Mellon University, Pittsburgh, Pa.

The alumina of activity grade 3 used throughout this work was made by shaking 1000 g of neutral, activated CAMAG alumina (Alfa Inorganics, Inc.) with 60 ml of water. All columns were packed dry. The dimensions of the column were not considered important as long as the stated amount of alumina was used and the column was packed evenly. Melting points were taken on a Mel-Temp apparatus and are uncorrected. Dry ethyl ether was distilled from lithium aluminum hydride. All microanalyses were carried out by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts. Skellysolve B is the fraction of hydrocarbons boiling between 40 and 60°.

Mercuration of Iodoferrocene. The method given below is a modification of the procedure of Nefedov.[9] In a 2-l., three-necked flask under nitrogen were placed 49.2 g (0.16 mol) of iodoferrocene (**1**) and 120 ml of benzene. A solution of 51.2 g (0.16 mol) of mercuric acetate in 800 ml of methanol was added with stirring over 5 min. The reaction mixture was stirred at room temperature for 20 min, poured into a cold solution of 80 g (0.72 mol) of calcium chloride in 800 ml of methanol, and stirred for 1 min. This mixture was then poured into 2 l. of cold water and the precipitate was suction filtered, washed with 400 ml of cold water, and dried in air. The residue was stirred at room temperature with 500 ml of Skellysolve B for 6 hr and filtered, and the residue was again stirred with 500 ml of Skellysolve B for 6 hr and filtered. The Skellysolve B filtrates were combined and set aside. The residue was then stirred for 6 hr with a mixture of 250 ml of Skellysolve B and 250 ml of benzene, and filtered. The filtrate was saved and the residue was reextracted four more times as above with the 1:1 Skellysolve B–benzene mixture. The final residue, which amounted to 38.4 g, was not further investigated.

The Skellysolve B extracts were placed on a column of 450 g of alumina. Iodoferrocene (15.0 g, 30%) was eluted with Skellysolve B, leaving two bands on the column. Then 500 ml of the 1:1 Skellysolve B–benzene extract was placed on the same column. Elution with about 2 l. of a 1:1 Skellysolve B–benzene mixture removed a pale yellow solution from the column, although no formal band was visible. This solution contained bis(2-iodoferrocenyl)mercury (**5, 6**) resulting from symmetrization of 1-chloromercuri-2-iodoferrocene (**4**) on the column. When the solution became almost colorless, chloroform was used to remove the last band from the column.

The other 2 l. of Skellysolve B–benzene extracts was placed on another column of 1000 g of alumina. The bis(2-iodoferrocenyl-mercury (**5, 6**) was eluted with about 7 l. of 1:1 Skellysolve B–benzene and the last band was eluted with about 2 l. of chloroform.

The solvent was evaporated from the combined eluate containing bis(2-iodoferrocenyl)mercury and the residue was crystallized from a mixture of 50 ml of Skellysolve B and 50 ml of benzene to yield 4.10 g of yellow crystals, mp 175–177° (lit.[9] mp 175°). A second crop (1.38 g), mp 172–174°, was obtained to give a total of 5.48 g (8%) of bis(2-iodoferrocenyl)mercury (**5, 6**), nmr (o-dichlorobenzene) singlets at δ 4.26 and 4.30 and triplet at δ 4.23 (12 H, unsubstituted cyclopentadienyl ring protons of the *dl* and meso compounds and 4-protons), doublet of doublets at δ 3.97 (2 H, 3-protons) and doublet of doublets at δ 4.60 (2 H, 5-protons).

The solvent was removed from the last band to be eluted to produce 11.4 g (17%) of a powder. A 0.40-g sample of this product was iodinated in the manner of 1,2-diiodoferrocene, as described below, and the product was purified in a similar manner: nmr ($CDCl_3$) triplet at δ 4.16, singlet at δ 4.20, triplet at δ 4.38, doublet at δ 4.32, triplet at δ 4.67; nmr (C_6H_6) triplets at δ 3.82 (4 H, β protons on 1,1′-diiodoferrocene) and 4.18 (4 H, α protons on 1,1′-diiodoferrocene), singlet at δ 3.97 (5 H, unsubstituted ring protons of 1,3-diiodoferrocene), doublet at δ 4.10 (1.6 H, 4- and 5-protons of 1,3-diiodoferrocene), triplet at δ 4.45 (0.8 H, 2-proton of 1,3-diiodoferrocene). The integration of the nmr spectrum in benzene indicates that there is 55% of 1,1′-diiodoferrocene and 45% of 1,3-diiodoferrocene present.

All attempts to separate the yellow powder into pure samples of 1′-chloromercuri- (**3**) and 3-chloromercuri-1-iodoferrocene (**2**) *via* chromatography on an alumina column treated with sodium cyanide[17] failed to give any separation.

Three runs with 12.3 g of iodoferrocene, one run with 21.8 g of iodoferrocene, and two runs with 24.6 g of iodoferrocene produced essentially the same percentage yields of products as described above.

1,2-Ferrocenedicarboxylic Acid (8). Bis(2-iodoferrocenyl)mercury (**5, 6**, 0.52 g, 0.63 mmol), 20 ml of dry benzene, and 45 ml of dry ethyl ether were stirred under nitrogen for 10 min. Subsequently there was added 2.2 ml (5.0 mmol) of 2.25 *M* *n*-butyllithium in hexane. This mixture was stirred for 10 min, poured onto crushed Dry Ice, and allowed to warm to room temperature. Water (100 ml) was added and the ether layer was removed and discarded. The water layer was acidified with dilute hydrochloric acid and extracted four times with 50-ml portions of chloroform. The extracts were combined and dried over sodium sulfate and the solvent was evaporated. The residue was crystallized from chloroform to yield 0.18 g (52%) of 1,2-ferrocenedicarboxylic acid (**8**); mp (air) 205–207° dec; mp (sealed under nitrogen) 195–198° with foaming (lit.[21] mp 206–206.5° dec); nmr (acetone) singlet at δ 4.40 (5 H, unsubstituted cyclopentadienyl ring protons), triplet at δ 4.89 (1 H, 4-proton), doublet at δ 5.23 (2 H, 3,5-protons, J = 2.8 Hz); ir (KBr) 2900 (broad, -COOH), 1690 (-COOH), 1600 cm^{-1}.

Two other runs with 0.75 and 0.45 g of bis(2-iodoferrocenyl)-mercury gave 60 and 30% yields, respectively, of 1,2-ferrocenedicarboxylic acid. 1,2-Ferrocenedicarboxylic acid and its solutions should be protected from light, since photochemical decomposition takes place in a short time.

1,2-Ferrocenedicarboxylic Anhydride (9). 1,2-Ferrocenedicarboxylic acid (**8**, 0.09 g, 0.35 mmol) was dissolved in 10 ml of acetone. To this solution was added a solution of 0.07 g (0.34 mmol) of *N,N*-dicyclohexylcarbodiimide dissolved in 5 ml of acetone, and the mixture was stirred for 30 min, during which time it became cloudy. The reaction mixture was filtered, 5 ml of Skellysolve B was added, and the solution was again filtered. The volume was reduced and 1,2-ferrocenedicarboxylic anhydride (**9**) was crystallized to give 0.03 g (36%) of product, mp 143–150°. This material was recrystallized from Skellysolve B–benzene three times to yield 10 mg of 1,2-ferrocenedicarboxylic anhydride (**9**): mp (sealed under nitrogen) 157–160° (lit.[21] mp 176–176.5°); nmr ($CDCl_3$) singlet at δ 4.49 (5 H, unsubstituted cyclopentadienyl ring), triplet at δ 4.89 (1 H, 4-proton), doublet at δ 5.15 (2 H, 3- and 5-protons, J = 2.4 Hz); ir ($CDCl_3$) 1834 and 1775 cm^{-1} (anhydride); mass spectrum *m/e* 256 (calcd mol wt, 256).

Anal. Calcd for $C_{12}H_8FeO_3$: C, 56.29; H, 3.15; Fe, 21.81; O, 18.75. Found: C, 56.37; H, 3.19; Fe, 21.8; O, 18.59.

Another run with 0.30 g of 1,2-ferrocenedicarboxylic acid yielded 36% of 1,2-ferrocenedicarboxylic anhydride. This product is light sensitive and should be protected from light both in solution and in the solid state.

1,2-Diiodoferrocene (10). The method given below is a modification of the procedure of Nefedov.[9] To a boiling solution of 1.27 g (1.55 mmol) of bis(2-iodoferrocenyl)mercury (**5, 6**) in 60 ml of 1,2-dichloroethane was added 1.5 g (5.9 mmol) of iodine in 90 ml of 1,2-dichloroethane. The mixture was heated on the steam bath for 10 min and 10 g of finely ground sodium thiosulfate was added. The purple solution was stirred until it turned yellow. The solution was decanted, the solvent was evaporated, and the residual oil was dissolved in a small amount of Skellysolve B. This extract was placed on a column of alumina and the 1,2-diiodoferrocene (**10**) was eluted with Skellysolve B. The solvent was removed by a jet of air to yield 1.33 g (98%) of **10**: mp 42–44° (lit.[9] mp 47.5°); nmr ($CDCl_3$) singlet at δ 4.19 (5 H, unsubstituted cyclopentadienyl ring), triplet at δ 4.22 (1 H, β proton), doublet at δ 4.51 (2 H, α protons); nmr (C_6H_6) singlet at δ 3.96 (5 H, triplet), 3.73 (1 H), doublet at δ 4.21 (2 H); ir (KBr) 1100 and 995 cm^{-1} (unsubstituted cyclopentadienyl ring).

Iodoferrocene-*2-d*$_1$. Into a 250-ml round-bottom flask under nitrogen were placed 100 ml of dry dioxane (freshly distilled from lithium aluminum hydride), 0.55 g (0.67 mmol) of bis(2-iodoferrocenyl)mercury (**5, 6**), and 2.0 ml (111 mmol) of deuterium oxide. To this solution was added 10.0 g (75 mmol) of anhydrous aluminum chloride. An immediate green color developed with the evolution of heat. The mixture was stirred for 1.5 hr and poured into 500 ml of water containing 20 g of sodium bisulfite. The aqueous layer was extracted with ether and the extracts were washed three times with 50-ml portions of water and evaporated. The residue was dissolved in Skellysolve B and chromatographed on 50 g of alumina, eluting with Skellysolve B. Evaporation of the solvent gave an oil, which was crystallized from a methanol–mixture. The yield of iodoferrocene-*2-d*$_1$ was 0.27 g (67%): mp 42–45°; nmr (C_6H_6) doublet at δ 3.83 (2 H, 3,4-protons), singlet at δ 4.01 (5 H, unsubstituted cyclopentadienyl ring), triplet at δ 4.28 (1.3 H, 5-protons plus some 2-protons from iodoferrocene).

Mercuration of Ferrocene. Into a 5-l. three-necked flask equipped with a mechanical stirrer, a reflux condenser, and a heated dropping funnel were placed 148.8 g (0.80 mol) of ferrocene, 1500 ml of methanol, and 1000 ml of ethyl ether. The mixture was heated to reflux and a solution of 127.5 g (0.40 mol) of mercuric acetate in 800 ml of boiling methanol was added dropwise over 1 hr. After the addition was complete, the reaction mixture was stirred for an additional 5 hr, whereupon heating was discontinued and a solution of 17.8 g (0.42 mol) of lithium chloride in 200 ml of boiling methanol was added.

The entire contents of the reaction flask was transferred to a 4-l. beaker and evaporated overnight with a gentle jet of air. The residue was then placed in a Soxhlet cup in a 3-l. Soxhlet extraction apparatus and extracted for 2 days with Skellysolve B to give, upon evaporation of the solvent, 52 g (35%) of recovered ferrocene.

The material in the Soxhlet cup was next extracted for 2 days with methylene chloride to give, after evaporation of the solvent, 155 g of crude chloromercuriferrocene. Crystallization of this material from *n*-butyl alcohol gave 105 g of a material that melted at 160–185°, and a residue (residue 1) of 30 g. The 105 g of material was extracted twice with 500-ml portions of Skellysolve B to leave 76 g (45%) of chloromercuriferrocene, mp 194–196° dec (lit.[11] mp 193–194° dec). The Skellysolve B extracts yielded 29 g of ferrocene for a total of 81 g (55%) of recovered ferrocene.

The remaining material in the Soxhlet cup was extracted for 2 days with acetone. Upon evaporation of the solvent, there resulted 25 g of material which was combined with residue 1 and the total was dissolved in 750 ml of dimethylformamide. The residue that would not dissolve was filtered and combined with the residue left in the Soxhlet cup.

The dimethylformamide filtrate was chromatographed, one-third at a time, on three columns, each containing 450 g of alumina. Elution with a mixture of dimethylformamide–chloroform–methanol (5:3:2 volume ratio) produced a colored forerun that was discarded. The first and major band was then slowly eluted with the above solvent mixture, leaving two bands on the colunn, which were eluted with a 1:1 volume mixture of dimethylformamide–methanol.

The major band was worked up in the following manner. The volume of the solvent was tripled with water, and the organic layer was removed and evaporated to yield a total of 2.0 g (2%) of crude 1,2-bischloromercuriferrocene (**13**). The crude material was crystallized from acetone to give a yellow compound: mp 200–205° dec (sealed under nitrogen) with mercury given off at about 217°; ir (KBr) 3080, 1328, 1160, 1101, 998, 900, 806 cm^{-1}.

Anal. Calcd for $C_{10}H_8Cl_2FeHg_2$: C, 18.29; H, 1.23; Cl, 10.81; Fe, 8.51. Found: C, 18.39; H, 1.31; Cl, 10.91; Fe, 8.50.

The nmr spectrum (dimethyl sulfoxide) of 1,2-bischloromercuriferrocene (**13**) was not well defined, so the material was recrystallized from dimethyl sulfoxide to give orange crystals: mp (sealed under nitrogen) 170–172°;[28] nmr (dimethyl sulfoxide) singlet at δ 4.25 (5 H, unsubstituted cyclopentadienyl ring), doublet at δ 4.30 (2 H, α protons), triplet at δ 4.48 (1 H, β proton).

The remaining two bands were eluted together with dimethylformamide–methanol, and upon work-up as above yielded 1.5 g of material. Iodination of this material, as described for the iodination of 1,2-bischloromercuriferrocene, gave an oil which, from the nmr spectrum, proved to be 1,1′-diiodoferrocene with possibly a small impurity of 1,2- and/or 1,3-diiodoferrocene. The residue in the Soxhlet cup (*ca.* 50 g) was crystallized from dimethylformamide to yield 7 g (5%) of 1,1′-bischloromercuriferrocene (**12**), mp (sealed under nitrogen) 240° dec (lit.[11] decomposition at elevated temperatures).

Two other runs gave essentially the same results as described above.

Iodination of 1,2-Bischloromercuriferrocene (13). To 0.4 g (0.6 mmol) of crude 1,2-bischloromercuriferrocene (**13**) in 50 ml of 1,2-dichloroethane was added 0.4 g (1.6 mmol) of iodine. The reaction mixture was stirred for 10 min, after which time there was added 100 ml of a 10% solution of sodium thiosulfate. The mixture was stirred for 30 min, the layers were separated, and the organic layer was again treated with iodine and sodium thiosulfate as above. After separation of the organic layer for the second time, the solvent was evaporated and the residual oil was dissolved in a minimum of Skellysolve B and chromatographed on an alumina column. Elution with Skellysolve B and subsequent evaporation gave an oil: nmr (C_6H_6) triplet at δ 3.72 (1 H), singlet at δ 3.94 (5 H), doublet at δ 4.20 (2 H), singlet at δ 3.97 (0.3 H). This product can be assigned as 1,2-diiodoferrocene (**10**), since the nmr spectrum is in agreement with that of authentic 1,2-diiodoferrocene. The singlet at δ 3.97 is due to a small amount of iodoferrocene present.

Lithiation of 1,2-Bischloromercuriferrocene (13). Into a nitrogen-flushed flask were placed 0.05 g (0.08 mmol) of 1,2-bischloromercuriferrocene (**13**), 20 ml of anhydrous ethyl ether, and 1.0 ml (2.3 mmol) of 2.25 *M* *n*-butyllithium in hexane. The reaction mixture was stirred for 15 min at room temperature and then poured into Dry Ice. When the ether layer had warmed to room temperature, the lithium salts were extracted twice with 30-ml portions of water. The aqueous layer was separated, acidified with 3 ml of 6 *N* hydrochloric acid, and extracted twice with 50-ml portions of chloroform. The chloroform was evaporated on a rotary evaporator with aluminum foil placed around the flask to avoid photodecomposition. Attempts to recrystallize the material from chloroform only resulted in decomposition, so an nmr spectrum was taken: nmr (acetone) singlet at δ 4.18, singlet at δ 4.40, triplet at δ 4.38, triplets at δ 4.88, doublet at δ 5.23. This spectrum is in agreement with a mixture of ferrocenecarboxylic acid and 1,2-ferrocenedicarboxylic acid (**8**).

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Registry No.—**1**, 51021-52-4; **5**, 51021-54-6; **6**, 51021-55-7; **8**, 51021-53-5; **9**, 51004-02-5; **10**, 51021-51-3; **12** (X = Cl), 12145-90-3; **13** (X = Cl), 51021-49-9; **14**, 51021-50-2; ferrocene, 102-54-5; chloromercuriferrocene, 51108-07-7.

References and Notes

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