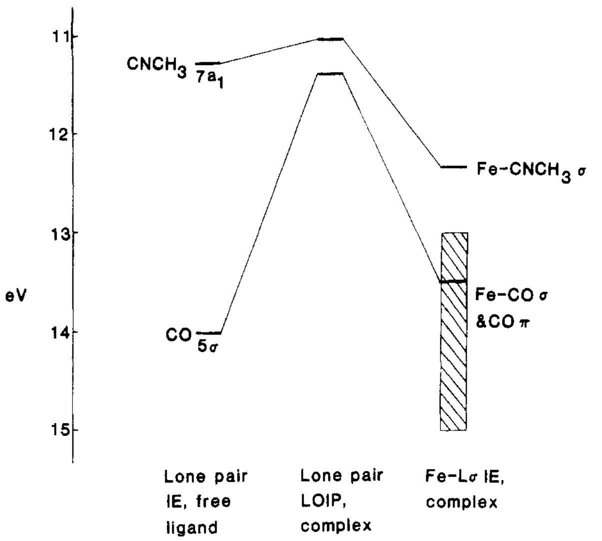

Figure 6. High-lying occupied σ orbital interactions in $Fe(CO)_4CNCH_3$.

and carbon monoxide, a ligand generally thought of as a weak σ donor.

Experimental Section

Methyl, *tert*-butyl, and phenyl isocyanide were prepared by standard methods.[23,24] Trimethylsilyl cyanide was prepared by the reaction of $(CH_3)_3SiBr$ and AgCN.[25] The iron tetracarbonyl complexes were prepared by sealed tube reactions of $Fe(CO)_5$ with the appropriate isocyanides (or cyanide).[26-28] Tetracarbonyl(methyl isocyanide)iron was purified by fractional condensation on the vacuum line, with the desired product collected in a 0 °C trap. The other products were purified by sublimation, and the melting points and infrared spectra of all of the products agreed with the literature.[29]

X-ray photoelectron spectra were obtained by using a GCA/McPherson ESCA-36 spectrometer with a Mg anode. Spectra were calibrated by using the N_2 1s (409.93 eV), Ne 1s (870.31 eV), and Ne 2s (48.47 eV) lines by a method described previously.[30] Samples were introduced through a large diameter (1.5-cm) inlet system with the flow regulated by cooling of the external sample reservoir.

He I excited spectra were recorded on a Perkin-Elmer PS-18 spectrometer using a heated inlet probe system. The ionization energy scale was calibrated by reference to peaks of admixed inert gases (Xe, Ar, He).

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Registry No. $Fe(CO)_4CNCH_3$, 14741-64-1; $Fe(CO)_4CNC(CH_3)_3$, 56448-44-3; $Fe(CO)_4CNCSi(CH_3)_3$, 19333-12-1; $Fe(CO)_4CNC_6H_5$, 17595-21-0.

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Bridged Ferrocenes. 12.[1] Metalation and Subsequent Reactions of Ferrocene Derivatives with Two or Three Trimethylene Bridges

Manny Hillman* and Joyce D. Austin

Chemical Sciences Division, Department of Energy and Environment, Brookhaven National Laboratory, Upton, New York 11973

Åke Kvick

Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973

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Reaction of 1,1′,2,2′-bis(trimethylene)ferrocene, I, 1,1′,3,3′-bis(trimethylene)ferrocene, II, and 1,1′,2,2′,4,4′-tris(trimethylene)ferrocene, III, with *n*-butyllithium (*n*-BuLi) and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) or potassium *tert*-butoxide (KO-*t*-Bu) gave metal derivatives which were converted to the corresponding mono- and dicarboxylic acids and their methyl esters and in the case of III to the 3,3′-dibromo derivative. With a few modifications due to the peculiarities of the individual compounds, the explanation for the selectivity of the metalation reactions is essentially that given[2] for the metalation of 1,1′-trimethyleneferrocene, IV. The crystal structure of the dibromide was determined.

Introduction

The lithiation of ferrocene,[3] V (compounds I through XIV are illustrated in Figure 1; XV is in Figure 2), and[2] of IV with *n*-BuLi and TMEDA were found to give dilithio derivatives with the two lithium atoms situated on the corresponding positions of each cyclopentadienyl ring. In the case of V, this was determined[3] by means of a crystal structure of a related dilithio derivative; for IV the products from further reactions of the dilithio derivatives were

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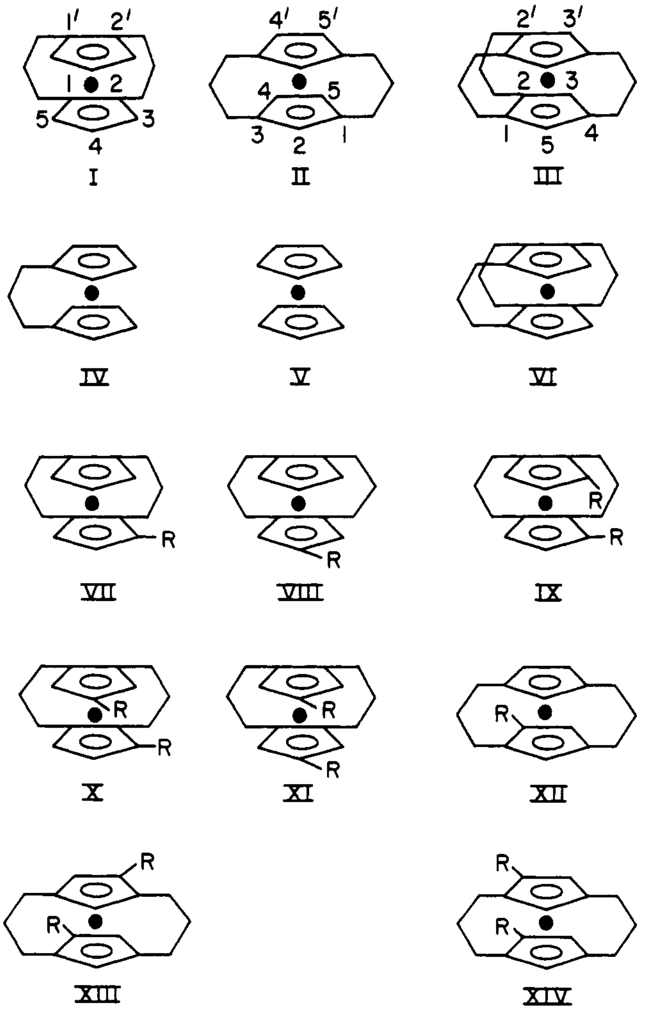

Figure 1. Schematic structures of I through XIV. The filled circles are the iron atoms.

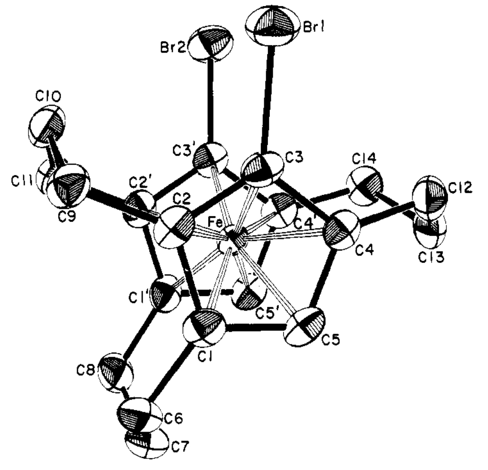

Figure 2. ORTEP diagram of XV. The 50% thermal ellipsoids are shown.

characterized. In IV, predominant substitution of the 2,2'- or the 3,3'-positions were observed. Metalation of IV with *n*-BuLi and KO-*t*-Bu, on the other hand, gave only the 3,3' derivative and a very small quantity of a differently disubstituted product which was not fully characterized.

In view of the success of this reaction with IV, it was of interest to determine the reaction course with compounds containing more than one trimethylene bridge. The compounds available with two or three trimethylene bridges were I, II, and III. The isomeric tris(trimethylene) derivative VI had been prepared[4] in quantities two small to be used for other investigations, and derivatives with four or five trimethylene bridges are unknown. Indeed, one of the inducements to engage in this study was the possibility of an alternative route to a tetrakis(trimethylene)-bridged ferrocene. A 3,3'-dicarboxylic acid of III may be elaborated to a diacetic ester which under treatment with strong base may give a β-keto trimethylene bridge as has been accomplished with ferrocene.[5] The possibility of formation of a fourth trimethylene bridge under alkaline conditions is encouraging since it has been shown[6] that the attempt to form a fourth trimethylene bridge under the usual acid conditions causes a rearrangement among the bridges.

Table I. Crystal Data

mol formula	$C_{19}H_{20}FeBr_2$
mol wt	651.14
space group	$P2_1/c$
a, pm	867.1 (2)
b, pm	1215.8 (2)
c, pm	1524.1 (2)
β, deg	97.03 (1)
V, nm^3	1.5948
Z	4
ρ_{calcd}, g/cm^3	1.930
abs coeff, cm^{-1}	58.94
2θ range, deg	2-52
reflctns collected	5126
reflctns used ($I > 3\sigma$)	2159
parameters refined	279
scan width	$0.90 + 0.35 \tan \theta$
$R(F) = \Sigma \lvert F_o - F_c \rvert / \Sigma \lvert F_o \rvert$	0.032
$R_w(F) = \Sigma \lvert F_o - F_c \rvert w^{1/2} / \Sigma \lvert F_o \rvert w^{1/2}$; $w = 1/(\sigma^2(F) + 0.0005F^2)$	0.034
max shift/error (non-H)	0.09
max shift/error (H)	0.13
res elec dens, e nm^{-3}	600

Results

I was lithiated with *n*-BuLi and TMEDA to give less than 10% conversion to the lithio derivatives. The products isolated after treatment of the metallo derivatives with CO_2 followed by esterification of the acids with methanol were the 3- and 4-monoesters VII and VIII, respectively, and the 3,3'-, 3,4'-, and 4,4'-diesters IX, X, and XI, respectively. When KO-*t*-Bu is used, the same products were obtained, IX in lower relative yield and X in greater relative yield.

II was lithiated with *n*-BuLi and TMEDA to give the 4-monoester XII and the 4,4'-diester XIII. A small quantity of the 2-monoester may have been detected in an NMR spectrum. No 2,2'-diester was detected. With KO-*t*-Bu, the 4,5'-diester XIV was also obtained.

III was lithiated with *n*-BuLi and TMEDA to give less than 10% conversion to the lithio derivatives. The acids obtained were not further examined. With KO-*t*-Bu, the conversion was about 50%. The diester appeared to hydrolyze readily and was not characterized. Instead, the dibromide XV was formed from the dimetallo derivative using $BrCF_2CF_2Br$. No monobromide derivative was detected. X-ray crystallography demonstrated that the product was the 3,3'-dibromide.

The results of the crystal structure determination are summarized in several tables and in one figure. The crystal data are in Table I; the atomic positions for all of the atoms are in Table II; and the ORTEP diagram of the molecule is in Figure 2. The thermal factors, bond distances, bond

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Table II. Fractional Coordinates[a]

atom	*x*	*y*	*z*
Br1	79 432 (6)	70 164 (4)	37 577 (4)
Br2	60 202 (6)	43 770 (4)	42 582 (3)
Fe	80 091 (6)	46 677 (4)	23 810 (4)
C1	84 406 (49)	55 784 (33)	13 504 (30)
C2	75 356 (50)	61 773 (33)	19 260 (29)
C3	84 604 (49)	62 109 (31)	27 729 (29)
C4	98 739 (46)	55 847 (31)	27 649 (29)
C5	98 549 (48)	52 428 (33)	18 614 (31)
C1′	68 380 (48)	34 294 (32)	17 570 (30)
C2′	59 138 (44)	39 956 (31)	23 377 (29)
C3′	67 593 (46)	39 049 (33)	32 058 (27)
C4′	82 284 (46)	33 627 (30)	31 783 (28)
C5′	81 956 (47)	30 326 (31)	22 728 (30)
C6	79 105 (54)	51 969 (41)	4 216 (30)
C7	78 184 (60)	39 565 (43)	2 963 (31)
C8	65 501 (55)	33 699 (41)	7 603 (32)
C9	58 527 (53)	65 421 (31)	17 349 (31)
C10	47 056 (50)	59 321 (36)	22 515 (31)
C11	44 778 (49)	46 909 (36)	20 809 (31)
C12	109 496 (49)	51 974 (36)	35 412 (32)
C13	110 479 (52)	39 293 (39)	36 427 (32)
C14	95 908 (51)	33 302 (37)	38 879 (31)
H5	1 064 (5)	474 (3)	168 (3)
H5′	897 (4)	266 (3)	207 (3)
H6A	858 (5)	552 (3)	−1 (3)
H6B	702 (7)	551 (4)	19 (4)
H7A	888 (5)	365 (3)	55 (3)
H7B	763 (5)	376 (3)	−33 (3)
H8A	566 (5)	373 (3)	58 (3)
H8B	643 (5)	255 (4)	48 (3)
H9A	561 (5)	649 (3)	115 (3)
H9B	581 (4)	738 (3)	187 (3)
H10A	506 (4)	603 (3)	292 (2)
H10B	366 (5)	627 (4)	209 (3)
H11A	418 (4)	454 (3)	144 (3)
H11B	374 (6)	445 (4)	247 (4)
H12A	1197 (5)	547 (3)	352 (3)
H12B	1058 (5)	547 (3)	409 (3)
H13A	1192 (4)	381 (3)	411 (3)
H13B	1136 (5)	363 (3)	308 (3)
H14A	992 (5)	253 (3)	405 (3)
H14B	932 (5)	362 (3)	443 (3)

[a] The fractional coordinates of the non-hydrogen atoms are multiplied by 10^5. The fractional coordinates of the hydrogen atoms are multiplied by 10^3.

angles, the least-squares planes, and the calculated and observed structure factors are provided as supplementary material.

Discussion

It has been shown,[2,7] at least for derivatives of IV, that the order of elution of isomers from a chromatographic column is dependent on the positions of substitution: isomers with polar substituents in the 2,2′- and/or 5,5′-positions elute first followed by isomers with substituents in the 3,3′- and/or 4,4′-positions. Similar results may be expected for the derivatives of I and II. Preliminary assignments were made accordingly. The Roman numerals used to designate the products are in the order of elution.

These structural assignments were confirmed by NMR spectroscopy. The number of substituents was determined by the ratio of the ring to methyl hydrogens.

VII is expected to have five different ring-proton signals, those for the 4- and 5-protons being doublets with ortho coupling (*J* = ~2.4 Hz), the signal for the 4′-proton a triplet with ortho coupling, and the 3′- and 5′-protons giving doublets of doublets (often appearing as triplets) with ortho and meta (*J* = ~1.2 Hz) coupling. In $DCCl_3$, three distinct ring-proton peaks were observed with the ratio of 1:1:1. These could be assigned to 4-, 4′-, and 5-protons, respectively (all assignments are given in the order downfield to upfield). The other ring-proton resonances were incompletely resolved from the methyl protons. In C_6D_6, four distinct ring-proton peaks were observed with the ratio of 1:1:2:1, agreeing with the number of protons expected. The first two could easily be assigned to the 4- and 4′-protons, while the third was due to either the 3′- or the 5′- and the 5-protons. The fourth was due to either the 3′- or the 5′-protons. Thus the structure of VII was confirmed.

VIII is expected to have three different ring-proton signals, a singlet for the 3,5-protons, a triplet with ortho coupling for the 4′-protons, and a doublet with ortho coupling for the 3′,5′-protons. In $DCCl_3$, only two peaks were observed in the ratio of 2:3, accounting for the right number of protons. In C_6D_6, these were resolved into three peaks in the ratio of 2:1:2 and the expected singlet, triplet, and doublet of VIII.

IX is expected to have two different ring-proton signals, both doublets with ortho coupling. The same spectrum, but with different chemical shifts is expected for the 3,5′-isomer. Since no products have been observed or are expected with the substituents as far removed from each other as in the 3,5′-isomer, the assignment of IX was given to the 3,3′-isomer. That the structure was that of the achiral isomer, as assigned, was confirmed by using a chiral shift reagent.

X is expected to have four different ring-proton signals, those for the 4- and 5-protons as doublets with ortho coupling and those for the 3′- and 5′-protons as doublets with meta coupling. This was also confirmed.

XI was found to have a single ring-proton signal, as expected, and all of the possible disubstituted carbomethoxy derivatives of I with one substituent on each ring have been accounted for. The derivatives with two substituents on the same ring are expected to have three and four different ring-proton signals, respectively. No products with such NMR spectra were detected.

It is possible that a very small amount of a 2-carbomethoxy derivative of II was observed in an NMR spectrum, but this product could not be confirmed.

XII, the 4-carbomethoxy derivative of II, is expected to have five different ring-proton signals, that for the 2-proton being a doublet with meta coupling, that for the 5-proton a doublet with meta coupling, the one for the 2′-proton a triplet with meta coupling, and those for the 4′- and 5′-protons doublets of doublets with ortho and meta coupling (often appearing as triplets). These were observed.

From the rules for order of elution, it would not be possible to tell the difference between XIII and XIV. The greater polarity expected for XIV suggests that it should be eluted after XIII. Furthermore, XIII and XIV are expected to have the same NMR spectra but with differing chemical shifts for the signals for the two different pairs of ring protons, both doublets with meta coupling. XIII is expected to have a narrower bridge-proton band, and a preliminary assignment was made accordingly. This assignment was confirmed by the use of a chiral shift reagent. XIII is chiral, and a complex ring-proton spectrum resulted on addition of the shift reagent, indicative of the formation of two distinct shift complexes. XIV is not chiral, and only small shifts in the positions of the ring-proton peaks were observed on addition of the reagent.

XV cannot be differentiated from the other dibromo derivatives of III by means of the NMR spectra since all three candidates are expected to have single ring-proton

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(7) Lundgren, J. O.; Kvick, A., unpublished results.

signals. A chiral shift reagent may possibly distinguish the 3,5′-isomer from the other two but could not differentiate the other two from each other. It was necessary to resort to X-ray crystallography to determine the structure as the 3,3′-isomer (Figure 2).

The reaction of IV with *n*-BuLi and TMEDA results in substitution of the corresponding positions adjacent to the bridge, the 2,2′-positions, and those not adjacent to the bridge, the 3,3′-positions. Very little, if any, disubstitution occurred at the noncorresponding positions, e.g., the 2,3′-positions. This is readily explained by the formation of a bridging complex between the ferrocene, the *n*-BuLi, and the TMEDA.[3] The reaction of IV with *n*-BuLi and KO-*t*-Bu, on the other hand, does not give any of the 2,2′-substituted product and does give some of a product with substitution on noncorresponding positions, possibly 2 and 3′. Since the corresponding positions are preferred even when KO-*t*-Bu is used, a bridging complex is also suggested, but one that is larger than the one formed with TMEDA. Reaction adjacent to a bridge is inhibited, and reaction at noncorresponding positions is possible.

Reactions of I and III using TMEDA do not proceed as well as those of ferrocene, II, or IV or when using KO-*t*-Bu. Conversions are less than 10%. This may be due to any or all of several effects: lowered lability of the ring protons because of the influence of the alkyl-type substituents, steric crowding by the bridges (the 2-position of II is substituted in very low yield if at all), and increased distance required for spanning the rings because of the tilting of the rings (II is more flexible than I and can achieve a more parallel ring configuration). The use of the stronger and apparently larger base KO-*t*-Bu overcomes these effects (except for the crowding) to some extent. Neither base is as effective with II as with the others. This is evident by the relatively large yields of monosubstituted products.

The metalation reactions with I, II, and III appear to follow similar courses as with IV. When TMEDA is used, the major disubstituted products have substitution at the corresponding positions, with small amounts of substitution at noncorresponding postions. Similarly, with KO-*t*-Bu, the major products involve substitution at the corresponding positions, but larger amounts of disubstitution at noncorresponding positions are obtained.

With KO-*t*-Bu, IV does not give products with substitution next to the bridges, though I and II do, but in low yield. The formation of these products is apparently due to decreased competition from the formation of the alternative products. The exceptional crowding of the 2,2′-positions of II, however, does not allow substitution even when TMEDA is used. In III, there is no alternative, and, although very little reaction was observed with TMEDA, KO-*t*-Bu did give a reasonable (50%) conversion to a disubstituted product.

No evidence has been found for products with substitution at nonvicinal noncorresponding positions, e.g., the 2,4′- and the 2,5′-derivatives of IV, and the 3,5′-derivatives of III. This indicates that the bridging complex is not long enough to span that distance competitively and that stepwise metalation is not an alternative course of the reaction.

Experimental Section

I–III were prepared according to the literature[4] procedures. ^{1}H NMR spectra were obtained on a Varian CFT-20 spectrometer equipped with a dual 80-MHz proton and 20-MHz carbon probe. The NMR data are given in parts per million (intensity, multiplicity, coupling constant, position). Tris[3-((heptafluoropropyl)hydroxymethylene)-*d*-camphorato]europium(III) was used as a chiral shift reagent. All NMR spectra were obtained in $DCCl_3$ unless otherwise noted. Absorption grade alumina (Fischer) and silica gel (Baker) were used for the chromatography. Hexane was dried over CaH_2. Elemental analyses were obtained from Schwarzkopf Microanalytical Laboratory, and mass spectra were obtained from Dr. Charles Iden of the State University of New York at Stony Brook.

The general procedures for the reaction of I, II, and III with *n*-BuLi and TMEDA or KO-*t*-BU and the subsequent reactions with CO_2 or $C_2F_4Br_2$ were the same as previously reported.[2] All preparations were carried out under N_2. After the reaction of the metallo derivative was complete, a N_2 atmosphere was not used further.

Reaction of I Using TMEDA. From 1.01 g (3.79 mmoles) of I, 9.1 mmoles of nBuLi, 1.37 mL (9.1 mmoles) of TMEDA and CO_2, 83.4 mg of a mixture of acids were obtained, and 847 mg of I were recovered. The mixture of acids from two preparations (159 mg) was esterified with methanol to give 141 mg of a mixture of esters. The esters were chromatographed on silica gel using benzene and mixtures of benzene and ethyl acetate to give 15 mg of VI, 27 mg of VIII, 20 mg of IX, 4 mg of X, and 58 mg of XI. The separation of IX and X on the silica-gel column was incomplete and the relative yields were determined by NMR spectroscopy. IX and X were separated on a thick-layer silica-gel plate using 2% of ethyl acetate in benzene.

Reaction of I Using KO-*t*-Bu. From 1.02 g (3.82 mmol) of I, 9.17 mmol of *n*-BuLi, 1.05 g (9.38 mmol) of KO-*t*-Bu, and CO_2, 870 mg of a mixture of acids was obtained, and 305 mg of I was recovered. The acids were esterified with methanol to give 846 mg of a mixture of esters. Chromatography of the esters as above gave 39 mg of VII, 78 mg of VIII, 18 mg of IX, 145 mg of X, and 438 mg of XI.

VII was recrystallized from hexane to give orange-yellow crystals: mp 84.5–85.5 °C; ^{1}H NMR ($DCCl_3$) δ 4.67 (H, d, J = 2.6 Hz, 4), 4.22 (H, t, J = 2.4 Hz, 4′), 4.04 (H, d, J = 2.6 Hz, 5), 3.78–3.83 (2 H, m, 3′, 5′), 3.71 (3 H, s, CH_3), 0.7–2.6 (12 H, CH_2); ^{1}H NMR (C_6H_6) δ 4.92 (H, d, J = 2.6 Hz, 4), 4.22 (H, t, J = 2.6 Hz, 4′), 3.81–3.84 (2 H, m, 3′ (or 5′), 5), 3.62–3.65 (H, m, 5′(or 3′)), 3.48 (3 H, s, CH_3), 1.17–2.94 (6 H, m, CH_2). Anal. Calcd for $C_{18}H_{20}O_2Fe$: C, 66.69; H, 6.22. Found: C, 67.18; H, 6.44; M^+, 324. VIII was recrystallized from hexane to give orange crystals: mp 111.5–112 °C; ^{1}H NMR ($DCCl_3$) δ 4.50 (2 H, s, 3,5), 4.08 (3 H, m, 3′,4′,5′), 3.71 (3 H, s, CH_3), 1.24–2.23 (6 H, m, CH_2); ^{1}H NMR (C_6H_6) δ 4.66 (2 H, s, 3,5), 4.12 (H, t, J = 2.4 Hz, 4′), 3.91 (2 H, d, J = 2.4 Hz, 3′,5′), 3.54 (3 H, s, CH_3), 0.77–1.95 (6 H, m, CH_3). Anal. Calcd for $C_{18}H_{20}O_2Fe$: C, 66.69; H, 6.22. Found: C, 67.20; H, 6.38; M^+, 324. IX was recrystallized from hexane/benzene to give reddish crystals: mp 208–209 °C; ^{1}H NMR δ 4.83 (2 H, d, J = 2.7 Hz, 4,4′), 3.99 (2 H, d, J = 2.7 Hz, 5,5′), 3.71 (6 H, s, CH_3), 0.7–2.6 (6 H, m, CH_2); ^{1}H NMR with the chiral shift reagent δ 4.94 (2 H, 4,4′), 4.02 (2 H, 5,5′), 3.84 (6 H, s, CH_3). Anal. Calcd for $C_{20}H_{22}O_4Fe$: C, 62.85; H, 5.80. Found: C, 63.05; H, 5.77. X was recrystallized from hexane/benzene to give yellow-orange plates: mp 157–158 °C; ^{1}H NMR δ 4.67 (H, d, J = 2.7 Hz, 4), 4.51 (H, d, J = 1.3 Hz, 3′), 4.34 (H, d, J = 1.2 Hz, 5′), 4.25 (H, d, J = 2.7 Hz, 5), 3.74 (3 H, s, CH_3), 3.73 (3 H, s, CH_3), 0.7–2.6 (6 H, m, CH_2). Anal. Calcd for $C_{20}H_{22}O_4Fe$: C, 62.85; H, 5.80. Found: C, 63.25; H, 5.84. XI was recrystallized from benzene to give reddish crystals: mp 260–261 °C; ^{1}H NMR δ 4.67 (4 H, s, 3,3′,5,5′), 3.73 (6 H, s, CH_3), 1.2–2.3 (6 H, m, CH_2). Anal. Calcd for $C_{20}H_{22}O_4Fe$: C, 62.85; H, 5.80. Found: C, 62.79; H, 5.84.

Reaction of II Using TMEDA. From 1.00 g (3.76 mmol) of I, 9.1 mmol of *n*-BuLi, 1.36 mL (9.1 mmol) of TMEDA and CO_2, 724 mg of a mixture of acids was obtained, and 461 mg of II was recovered. The acids were esterified with methanol to give 498 mg of a mixture of esters. The esters were chromatographed on silica gel using benzene and mixtures of benzene and ethyl acetate to give 127 mg of XII, 39 mg of XIII, and 234 mg of XIV.

Reaction of II Using KO-*t*-Bu. From 1.01 g (3.80 mmol) of II, 9.11 mmol of *n*-BuLi, 1.06 g (9.47 mmol) of KO-*t*-Bu, and CO_2, 800 mg of a mixture of acids was obtained, and 329 mg of II was recovered. The acids were esterified with methanol to give 820 mg of a mixture of esters. Chromatography of the esters as above gave 301 mg of XII, 104 mg of XIII, and 229 mg of XIV.

XII was recrystallized from hexane to give yellow-orange crystals: mp 117.5–118.5 °C; ^{1}H NMR δ 4.61 (H, d, J = 1.4 Hz, 5), 4.16 (H, m, 4′ (or 5′)), 4.09 (H, d, J = 1.4 Hz, 2), 3.85 (H, m, 5′ (or 4′)), 3.78 (H, t, J = 1.4 Hz, 2′), 3.69 (3 H, s, CH_3), 1.2–2.8 (6 H, m, CH_2). Anal. Calcd for $C_{18}H_{20}O_2Fe$: C, 66.69; H, 6.22. Found: C, 66.87; H, 6.33. XIII was recrystallized from hexane to give yellow-orange crystals: mp 120–121 °C; ^{1}H NMR δ 4.51 (2 H, d, J = 1.6 Hz, 5,4′), 4.01 (2 H, d, J = 1.6 Hz, 2,2′), 3.72 (3 H, s, CH_3), 1.2–3.0 (6 H, m, CH_2); ^{1}H NMR with the chiral shift reagent δ 4.75 (2 H, d, J = 1.6 Hz, 5,4′), 4.68 (2 H, d, J = 1.6 Hz, 2,2′), 3.97, 4.05, 4.13 (6 H, CH_3). Anal. Calcd for $C_{20}H_{22}O_4Fe$: C, 62.85; H, 5.80. Found: C, 63.72; H, 5.96. M^+: calcd, 382.0866; found, 382.0869. XIV was recrystallized from benzene/hexane to give reddish crystals: mp 148–148.5 °C; ^{1}H NMR δ 4.78 (2 H, d, J = 1.6 Hz, 5,5′), 4.01 (2 H, d, J = 1.6 Hz, 2,2′), 3.68 (6 H, s, CH_3), 1.6–2.9 (6 H, m, CH_2); ^{1}H NMR with the chiral shift reagent δ 4.91 (2 H, d, J = 1.4 Hz, 5,5′), 4.08 (2 H, d, J = 1.4 Hz, 2,2′), 3.83 (6 H, s, CH_3), 1.6–3.0 (6 H, m, CH_2). Anal. Calcd for $C_{20}H_{22}O_4Fe$: C, 62.85; H, 5.80. Found: C, 62.59; H, 5.77.

Reaction of III Using TMEDA. From 1.01 g (3.49 mmol) of III, 8.4 mmol of *n*-BuLi, 1.27 mL of TMEDA, and CO_2, 86.2 mg of a crude acid product was obtained and 911 mg of III was recovered. The acid was not treated further.

Reaction of III Using KO-*t*-Bu. From 0.77 mmol of *n*-BuLi, 100 mg (0.3 mmol) of III, 80 mg (0.8 mmol) of KO-*t*-Bu, and 0.1 mL of $C_2F_4Br_2$, 140 mg of a crude product containing approximately equal amounts of III and XV was obtained. Partial separation of IV from III was accomplished by chromatography on an alumina column with hexane. The fractions enriched in IV were recrystallized from 1:1 benzene/hexane to give yellow-orange crystals: mp 233.5–234.5 °C; ^{1}H NMR δ 3.83 (2 H, 5,5′), 1.20–2.20 (18 H, m, CH_2).

One crystal, measuring approximately 0.26 × 0.22 × 0.11 mm, mounted along the *a* axis, was used for the collection of diffraction intensity data on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 71.07 pm). The diffraction symmetry was determined to be $P2_1/c$ from preliminary film data, and this was confirmed from the systematic absences in the diffraction data. The unit cell dimensions (Table I) were determined from 25 reflections with $28° < 2\theta < 49°$. Intensities were collected by using θ–2θ scans and were corrected for Lorentz and polarization effects. Absorption corrections (μ = 58.94 cm^{-1}) were done by using the method of Gaussian grid integration, and the adequacy of the correction was confirmed.

The structure was determined by using a computing package for a PDP 11/23 computer.[7] The atomic scattering factors for iron including components for anomalous dispersion were taken from tabulations of Doyle and Turner[8] and Cromer and Liberman.[9] Those for hydrogen are from Stewart et al.[10] The other atomic scattering factors are from Cromer and Mann.[11] The iron and bromine atoms were located on Patterson maps, and the remaining atomic positions were obtained from successive difference Fourier maps. Least-squares refinement, using[12] LINEX74, of the coordinates of the non-hydrogen atoms with anisotropic thermal parameters and of the hydrogen atoms with isotropic thermal parameters was done in blocks. The final shifts in the parameters were less than 0.1 of the estimated standard deviations, except for one of the coordinates of two of the hydrogens, the largest of whose shift was 0.13 of the esd. The final $R(F)$ was 0.031 for 279 variables and 2159 reflections. The largest remaining peak was near a bromine atom and had an electron density of 600 e nm^{-3} corresponding to 10% of a typical carbon atom.

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Registry No. I, 38117-82-7; II, 12092-08-9; III, 56045-61-5; VII, 93806-07-6; [carboxylic acid], 93806-15-6; VIII, 93806-08-7; [carboxylic acid], 93841-91-9; IX, 93841-90-8; [dicarboxylic acid], 93806-16-7; X, 93806-09-8; [dicarboxylic acid], 93806-17-8; XI, 93806-10-1; [dicarboxylic acid], 93806-18-9; XII, 93806-11-2; [carboxylic acid], 93841-92-0; XIII, 93806-12-3; [dicarboxylic acid], 93841-93-1; XIV, 93806-13-4; [dicarboxylic acid], 93806-19-0; XV, 93806-14-5; $BrCF_2CF_2Br$, 124-73-2.

Supplementary Material Available: Tables of thermal factors, bond distances, bond angles, least-squares planes, and calculated and observed structure factors (17 pages). Ordering information is given on any current masthead page.

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