Metallocene Basicity. VII. Protonation of Ring Substituted Ferrocenophanes*†

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The protonation of a series of eleven alkyl and dialkylferrocenophanes has been examined using ^1H NMR. In trifluoroboric acid, the protonated species are found to be long-lived on the NMR time scale and stable to decomposition. In many cases the conformations of the protonated species could be determined. In all cases, it was found that only one conformation was observed in solution indicating a strong structural preference presumedly driven by the steric demands of the ring substituents and the bridges. Several examples of spin–spin coupling between the iron–hydrogen and the ring hydrogens are reported.

Introduction

NMR studies of the metal-protonated species formed by ferrocenes in strong acids have resulted in the evolution of a model for the geometries of the protonated species in which the molecular conformation is a compromise between the ring tilting of the protonated ferrocene moiety and the steric demands of the substituents [1–4]. We have recently reported on our studies of the protonation of a series of simple [n]ferrocenophanes and have described the conformations of the resulting species [4]. The simple [n]ferrocenophanes were found to have the conformations illustrated in Fig. 1, in which the position of the bridge relative to the ring-tilted moiety is determined by bridge length.

The generous gift of a series of acetyl substituted ferrocenophanes by the U.S. Air Force Seiler Research Laboratory [5] and the additional gift of a sample of [3]ferrocenophane-3,3′-dicarboxylic acid dimethyl ester [6] by Dr. Manny Hillman of the Brookhaven National Laboratory has made it possible to examine the steric consequences of ring substitution in protonated ferrocenophanes. Regrettably, in many cases the spectra are very complex and absolute assignments of the conformations cannot be made, but where good assignments can be made, the conformations fit the expected patterns.

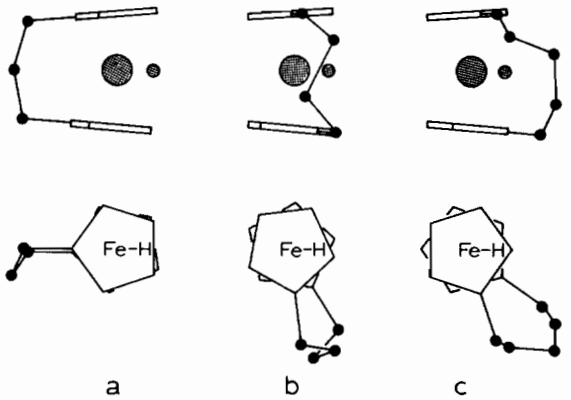

Fig. 1. Equilibrium conformations of protonated [n]ferrocenophanes [1]. The side-on and top views are based on Dreiding stereomodels of the protonated species and on the conformations established by NMR spectroscopy.

Results and Discussion

Ethylferrocenophanes

As noted above, the conformations of simple bridged ferrocenophanes in trifluoroboric acid, HBF_3OH, have been determined and are illustrated in Fig. 1. The introduction of substituents onto the rings in known positions relative to the bridge offers an opportunity to examine the forces controlling the conformations since in several cases two distinct conformations could arise upon protonation. Figure 2 illustrates this point for 2-ethyl[4]ferrocenophane. When [4]ferrocenophane is protonated the resulting species is long-lived on the NMR time scale. The four carbon bridge assumes a position to the side of the tilted ferrocene moiety such that the ring protons on

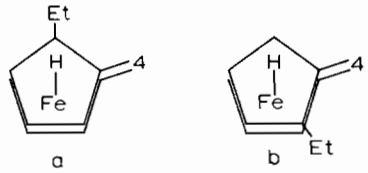

Fig. 2. Possible conformations of 2-ethyl[4]ferrocenophane.

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one side of the bridge are in a different magnetic environment than those on the other side. These environments correspond to the open face of the molecule and the region of closest interannular approach, respectively.

Previous studies [1, 4] using deuterium labeled compounds have demonstrated that ring protons occupying the region of closest interannular approach tend to be strongly shielded relative to those ring protons in the region of the open face. By extrapolation, ring substituted ethyl groups in the open face would be expected to have a different chemical shift than an ethyl group in the region of closest interannular approach. Examination of the number of ethyl group resonances should give an indication of whether one or both of the possible molecular conformations is present in the acid, and in simple cases, an examination of the ring resonance patterns should permit an exact conformational assignment to be made.

NMR spectra of the ethylferrocenophanes in trifluoroboric acid were recorded with no complications. The observed chemical shifts for these compounds are presented in Table I.

The ring proton patterns of the NMR spectra of the ethylferrocenophanes in trifluoroboric acid tend to be complex. With the exception of the ring resonance region of 2-ethyl[4]ferrocenophane which appears as a narrow envelope of absorptions with only three distinct maxima, the remaining spectra show five or six distinct ring resonances. In all cases the iron–hydrogen resonance is broadened indicating probable spin–spin coupling between the iron–hydrogen and the ring protons, but the absence of distinct maxima in the iron–hydrogen signal makes it impossible to attribute any of the ring resonances to splitting caused by coupling. As the assymmetry of the protonated species must produce seven unique structural positions, the observation of five or six resonances with some accidental overlaps is not unreasonable.

An additional explanation for the complexity of the ring proton pattern would be the coexistence of two conformational isomers such as those described for 2-ethyl[4]ferrocenophane. As noted earlier, a test for the presence of two conformations would be the presence of two ethyl signals reflecting the different magnetic environments of the open face and the region of closest interannular approach. In the assymmetric diethylferrocenophanes discussed below, two ethyl signals are observed, but in all five of the monoethylferrocenophanes, only a single ethyl signal is

TABLE I. NMR Parameters for Ethyl[n]ferrocenophanes in HBF_3OH.

Compound	Ring Protons	CH_2CH_3	CH_2CH_3	Bridge Protons	Iron Protons
2-Ethyl[3]ferrocenophane	4.43 (1H, s) 4.89 (1H, s) 5.01 (2H, s) 5.18 (1H, s) 5.29 (1H, s) 5.42 (1H, s)	2.8–2.0 (8H, m)	1.27 (3H, t) J = 8.0 Hz	2.8–2.0 (8H, m)	–1.33 (1H, s)
3-Ethyl[3]ferrocenophane	4.36 (1H, s) 4.75 (1H, s) 4.92 (1H, s) 5.17 (1H, s) 4.26 (2H, s) 4.43 (1H, s)	2.50 (8H, m)	1.27 (3H, t) J = 7.5 Hz	2.50 (8H, m)	–1.10 (1H, s)
2-Ethyl[4]ferrocenophane	4.97 (1H, s) 5.13 (5H, m) 5.30 (1H, s)	2.63 (2H, q) J = 7.0 Hz	1.42 (3H, t) J = 7.0 Hz	2.93 (4H, s)[a] 2.17 (4H, s)[b]	–2.29 (1H, s)
3-Ethyl[4]ferrocenophane	4.98 (2H, s) 5.25 (3H, s) 5.44 (1H, s) 5.60 (1H, s)	2.47 (2H, q) J = 7.0 Hz	1.38 (3H, t) J = 7.0 Hz	2.90 (4H, s)[a] 2.10 (4H, s)[b]	–2.19 (1H, s)
3-Ethyl[5]ferrocenophane	4.72 (1H, s) 5.17 (1H, s) 5.32 (1H, s) 5.50 (3H, s) 5.65 (1H, s)	2.47 (2H, q) J = 7.0 Hz	1.37 (3H, t) J = 7.0 Hz	2.60 (4H, s)[a] 1.83 (6H, s)[b]	–1.91 (1H, s)

[a]Ring adjacent methylenes in 4 and 5 carbon bridges. [b]Central methylenes in 4 and 5 carbon bridges.

observed, demonstrating that only a single conformer is formed. As steric crowding is known to force many groups out of the region of closest interannular approach, it appears likely that the prefered conformation will be that in which the ethyl group occupies the open face of the tilted species, *i.e.* similar to that shown in Fig. 2a.

Dialkyl[3]ferrocenophanes

Protonations of the disubstituted ferrocenophanes in trifluoroboric acid was accomplished with no evidence of oxidation, decomposition of rearrangement as indicated for the ethylferrocenophanes. Chemical shift data and probable proton assignments are given in Table II.

The ring proton region of 3,4-diethyl[3]ferrocenophane consists of four resonances whose relative areas are 1:1:2:2. The separation of the downfield doublet is 4.5 Hz, identical to that of the well defined iron-hydrogen triplet. The simplicity of the ring proton pattern indicates that the protonated species retains the mirror plane of the parent compound, with the iron-hydrogen bond lying in this plane. This conformation is further supported by the sharp trimethylene bridge singlet and the superimposition of the ethyl resonances. The probable conformation of this species is shown in Fig. 3a.

Assignment of the ring protons to the NMR resonances can be made from the assumed conformation. It has been previously shown that ring protons in the open face tend to appear at lower field than do those protons closer to the region of closest interannular approach. In the present case, the downfield doublet would be assigned to the ring protons on positions 3'- and 4'-, which also have the same relative orientation to the iron–hydrogen bond. The two, two proton singlets in the ring proton region differ significantly in width, with the upfield signal being narrower than the midrange signal. We have assigned the upfield resonance to the 2- and 5-ring protons, reasoning that they cannot be broadened by coupling to adjacent ring hydrogens as is possible for the 2'- and 5'-hydrogens. Furthermore, the 2- and 5-hydrogens are positioned between two alkyl groups which should increase their chemical shift relative to the protons at 2'- and 5'- which have only one adjacent alkyl group.

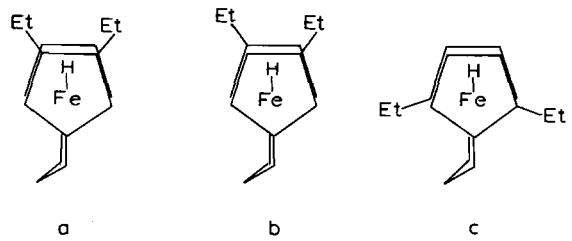

Fig. 3. Probable conformations of protonated symmetric diethyl[3]ferrocenophanes.

TABLE II. NMR Parameters for Dialkyl[3]ferrocenophanes in HBF_3OH.

Compound	Ring Protons	CH_2CH_3	CH_2CH_3	Bridge Protons	Iron Protons
3,4-Diethyl[3]ferrocenophane	H_2, H_5 4.83 (2H, s) $H_{2'}$, $H_{5'}$ 4.90 (2H, s) $H_{3'}$, $H_{4'}$ 5.03 (2H, d, J = 4.5 Hz)	2.60 (4H, q) J = 7.0 Hz	1.35 (6H, t) J = 7.0 Hz	2.43 (6H, s)	−0.83 (1H, t) J = 4.5 Hz
3,4'-Diethyl[3]ferrocenophane	H_2, $H_{5'}$ 4.77 (2H, s) $H_{2'}$, H_5 5.00 (2H, s) $H_{3'}$, H_4 5.08 (2H, d, J = 5.5 Hz)	2.57 (4H, q) J = 7.5 Hz	1.45 (6H, t) J = 7.5 Hz	2.43 (6H, s)	−1.31 (1H, t) J = 5.5 Hz
2.5'-Diethyl[3]ferrocenophane	H_2, H_5 4.52 (2H, s) H_3, H_3, 5.10 (4H,d) H_4, $H_{4'}$ 5.10 (4H, d, J = 4.0 Hz)	2.40 (4H, q) J = 7.0 Hz	1.30 (6H, t) J = 7.0 Hz	2.56 (6H, s)	−1.57 (1H, t) (broad)
2,4'-Diethyl[3]ferrocenophane	4.06 (1H, s) 4.60 (1H, s) 5.19 (2H, s) 5.44 (1H, d, J = 7.0 Hz) 4.54 (1H, d, J = 7.0 Hz)	2.38 (4H, q) J = 7.0 Hz	1.30 (3H, t) J = 7.0 Hz 1.13 (3H, t) J = 7.0 Hz	3.0–2.0 (6H, m)	−1.20 (1H, t) J = 7.0 Hz
2,3'-Diethyl[3]ferrocenophane	4.57 (1H, s) 4.64 (1H, s) 5.2–4.8 (4H, m)	2.40 (2H, q) J = 7.5 Hz 2.48 (2H, q) J = 7.0 Hz	1.30 (3H, t) J = 7.5 Hz 1.44 (3H, t) J = 7.0 Hz	3.0–2.0 (6H, m)	−1.40 (1H, m)
3,3'-Dimethyl[3]ferrocenophane	H_2, $H_{2'}$ 4.12 (2H, s) H_5, $H_{5'}$ 5.63 (2H, s) H_4, $H_{4'}$ 5.80 (2H, d, J = 11.0 Hz)		1.87 (6H, s)	2.1–2.9 (6H, m)	−1.17 (1H, t) J = 11.0 Hz

In the previous paper in this series, we noted that the spectrum of [3]ferrocenophane appeared to require an interpretation based on coupling between four ring protons in the open face, *i.e.*, protons 3-,3′-, 4-, and 4′-, and the iron bound hydrogen. This conclusion was based on the appearance of a doublet for the downfield resonance which had been shown by labeled compounds to be assigned to the 3- and 4- protons, and an apparent multiplet for the iron-hydrogen. Recent work in our laboratory using a higher resolution spectrometer has confirmed that the iron–hydrogen resonance is a quintet with a coupling constant identical to that of the downfield resonance in the ring proton region. Furthermore, decoupling experiments have confirmed the interaction between these two resonances. The observed coupling constant between the 3- and 4- ring protons and the iron-hydrogen is 4.0 Hz. Presumedly coupling is also occurring between the iron-hydrogen and the protons at the 2- and 5- ring positions, but these coupling constants are below the limits of resolution of our instrument.

The coupling between the downfield ring resonances and the iron–hydrogen in 3,4-diethyl[3]-ferrocenophane has a coupling constant of 4.5 Hz, which suggests that the relative positions of the iron–hydrogen and ring protons are about the same as in [3]ferrocenophane.

The ring proton region of 3,4′-diethyl[3]ferrocenophane is very similar to that of the 3,4 isomer except that in this instance accidental overlap of the low field doublet with the central ring resonance gives a ring proton resonance pattern with an integration of 1:3:2. Again, the splitting of the iron–hydrogen triplet, 5.5 Hz, is close to that estimated for the downfield doublet indicating coupling between these sets of protons and suggesting that the relative orientations of these protons are similar to those found in the simple [3]ferrocenophane. Assignment of the ring hydrogens at the 2- and 5′- positions follows from the previous arguments. The probable equilibrium conformation for this species is given in Fig. 3b.

The ring proton region of protonated 2,5′-diethyl-[3]ferrocenophane contains a four proton doublet at low field and a two proton singlet at high field. The iron–hydrogen resonance in this instance is broad and poorly defined. The downfield doublet has a separation of 4.8 Hz. There are two possible interpretations of this spectrum. It is possible that coupling between the iron–hydrogen and the ring-protons in the open face is small or unresolved and that the doublet is due to the fact that the protons at positions 3- and 4′- are in slightly different environments than those at 4- and 3′-. Alternately, the protons in the open face could be in a very similar environment and the separation is due to coupling with the iron–hydrogen. Because of the strong similarities between the separation value of 4.8 Hz and the coupling constants noted above, we believe that the second interpretation is the more likely. Unfortunately, decoupling experiments were not possible to settle this question.

3,3′-Dimethyl[3]ferrocenophane fills a unique position in the series of disubstituted ferrocenophanes since neither 3,3′- nor 2,2′-diacetyl[3]ferrocenophanes were recovered by the Air Force workers. The spectrum of the protonated 3,3′-dimethyl[3]-ferrocenophane consists of a two proton doublet at lowfield and two, two proton singlets at higher field. The doublet splitting of 10.0 Hz is identical to that of the well defined iron–hydrogen triplet, and is the largest coupling constant observed in this series of compounds, although it should be noted that values of 15.0 Hz have been observed for doubly bridged ferrocenophanes [7].

A second unusual feature of the spectrum of protonated 3,3′-dimethyl[3]ferrocenophane is the appearance of the trimethylene bridge resonance as a broad multiplet. In the unprotonated compound, the bridge resonance is a sharp singlet, which is a common feature observed for trimethylene bridges in several [3]ferrocenophanes and protonated [3]-ferrocenophanes, thus broadening of this signal in this case suggests that either the accidental overlap of the central and ring-adjacent methylenes has been disturbed, or that the oscillation of the bridge which averages the geminal proton environments has been slowed, or hindered. Since the accidental overlap is retained in all of the protonated [3]ferrocenophanes discussed thus far, the latter explanation seems more appropriate in this case.

Models of protonated 3,3′-dimethyl[3]ferrocenophane suggest that this species can adopt two possible conformations which are shown in Fig. 4. In both conformations, the trimethylene bridge is off of the centerline of the tilted ferrocene moiety where its oscillation might be disrupted. In the conformation shown in Fig. 4a, the ring methyl groups occupy the open face of the tilted species which would appear to be favored on steric grounds, while in the second conformation, the methyl groups are to the side of the tilted moiety and a pair of hydrogens (4- and 4′-) are occupying the open face. Since the spectrum of the protonated compound shows only one sharp resonance which can be attributed to the ring methyl groups, it follows that only one of the possible conformations is actually formed in solution.

We suggest that the large coupling constant between the iron-hydrogen and two of the ring hydrogens argues in favor of the conformation shown in Fig. 4b. Coupling constants between hydrogens on adjacent carbons are known to be sensitive to the torsional angles between the carbon–hydrogen bonds, with larger coupling constants being observed for smaller torsional angles. In the conformation

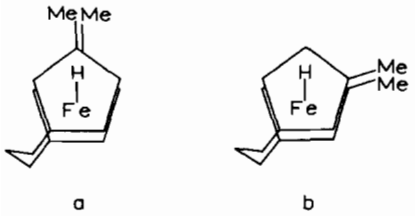

Fig. 4. Possible conformations of protonated 3,3'-dimethyl-[3]ferrocenophane.

shown in Fig. 4b, the relative torsional angle between the iron–hydrogen and the ring protons at positions 4- and 4'- is small compared with that proposed for the other protonated [3]ferrocenophanes described above, thus the larger coupling constant is reasonable.

The ring resonance region of protonated 2,4'-diethyl[3]ferrocenophane has a unique feature in the apparent two proton 'triplet' at low field. This 'triplet' has a coupling constant of 7.0 Hz, which is identical to that of the one-proton, iron-hydrogen triplet. As there is only one iron–hydrogen, it seems likely that the ring proton 'triplet' is actually due to a pair of closely spaced doublets which have overlapped. The iron–hydrogen triplet arises from a coupling of the iron–hydrogen with two magnetically dissimilar ring protons having about the same torsional angle and hence the same coupling constant with the iron–hydrogen.

The remaining ring protons in the spectrum of the protonated 2,4'-diethyl[3]ferrocenophane appear as a two proton singlet at midrange and two, one proton singlets at higher field. Further structural information is provided by the broad trimethylene bridge resonance and the two ethyl signals at slightly different chemical shifts. A conformation which reflects these spectral features is illustrated in Fig. 5.

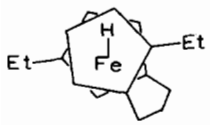

Fig. 5. Probable conformation of protonated 2,4'-diethyl-[3]ferrocenophane.

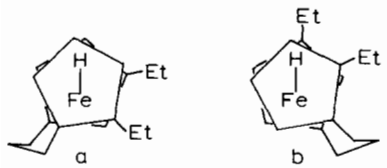

Fig. 6. Possible conformations of 2,3'-diethyl[3]ferrocenophane.

2,3'-Diethyl[3]ferrocenophane is protonated to give a species which has a very complex ring resonance pattern and iron–hydrogen resonance. Not unsurprisingly, two ethyl signals are resolved. Models indicate that two conformations are possible for the protonated species and these are illustrated in Fig. 6. The conformation shown in Fig. 6b would appear favored over that in Fig. 6a, since it avoids the steric problem of placing the 2-ethyl group in the region of closest ring approach.

Conclusions

In this paper, we have described the protonation of eleven ring substituted ferrocenophanes in trifluoroboric acid. The protonated species which are formed are stable in the acid and have lifetimes which are long on the NMR time scale. In all cases, only one conformation is formed which argues that alternate conformations must have much lower stabilities. The present studies do not rule out the formation of these alternate conformations followed by their rapid rearrangement to the more stable forms, they do, however, indicate a remarkable preference of one form over the alternatives.

Acknowledgements

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Experimental

NMR spectra were recorded on a Varian Associates A60-A NMR Spectrometer at room temperature with tetramethylsilane or tetramethylammonium tetrafluoroborate (3.33 ppm) as an internal standard. Sample preparation for protonation studies has been described elsewhere [1]. After protonation, the samples were poured into water and extracted with ethyl ether. A pale blue color was observed in the water phase in a few cases indicating that some oxidation had occurred during the recording of the spectrum or during workup. No changes in chemical shift or spectral pattern was observed to result from

TABLE III. Spectral Data for Alkyl[n]ferrocenophanes.

2-Ethyl[3]ferrocenophane
IR: 3075(s), 2900(s), 1750–1600(broad m), 1450(s), 1374(s), 1340(s), 1323(s), 1315(s), 1309(s), 1222(m), 1241(m), 1225(m), 1220(m), 1198(m), 1132(w), 1040(s), 990(m), 970(m), 959(m), 939(m), 912(s), 850(s), 800(s).
NMR: 4.1–3.8(6H, m), 3.47(1H, s), 2.22(2H, q, J = 7.3 Hz), 1.9(6H, m), 1.05(3H, t, J = 7.3 Hz).
GC/MS: Retention time, 1.4 min: 121.0(4.7), 224.0(7.6), 225.1(5.6), 237.2(4.7), 238(5.2), 239(16.7), 252.1(17.3), 254.2(100,0, M^+), 255.1(20.5). See also Vigo [8].

3-Ethyl[3]ferrocenophane
IR: 3060(s), 2940(sh), 2880(s), 2835(sh), 1650(m), 1480-(m), 1459(sh), 1435(s), 1362(m), 1320(s), 1310(s), 1256-(m), 1220(m), 1198(m), 1040(sh), 1032(s), 1009(s), 922-(m), 910(s), 840(s), 800(s).
NMR: 4.03(2H, m), 4.0–3.8(5H, m), 2.23(2H, q, J = 7.8 Hz), 1.93(6H, s), 1.13(3H, t, J = 7.8 Hz).
GC/MS: Retention time, 1.2 min: 56.0(12.9), 121.0(4.7), 134.1(4.6), 224.1(4.3), 237.1(4.6), 239.0(38.0), 240.1-(6.8), 252.1(35.4), 254.2(100.0, M^+), 255.1(20.1). See also Vigo [8].

2-Ethyl[4]ferrocenophane
IR: 3060(s), 2880(s), 2830(sh), 1670(broad m), 1460(sh), 1440(s), 1368(m), 1325(sh), 1308(m), 1222(m), 1035(s), 1019(sh), 848(sh), 830(sh), 800(s).
NMR: 4.1–3.9(6H, m), 3.72(1H, s), 2.32(2H, q, J = 7.8 Hz), 2.34(4H, m), 1.84(4H, m), 1.07(3H, t, J = 7.8 Hz).
GC/MS: Retention time, 1.8 min: 56.0(9.7), 121.0(63.6), 134.1(6.6), 237.1(6.8), 238.2(20.9), 240.1(9.6), 266.0-(16.9), 268.0(100.0, M^+), 269.0(18.5).

3-Ethyl[4]ferrocenophane
IR: 3060(m), 2940(sh), 2900(s), 2830(s), 1650(broad m), 1482(m), 1458(sh), 1440(s), 1365(m), 1310(m), 1040(m), 1030(m), 912(m), 837(m), 810(s), 800(sh).
NMR: 4.1–3.9(6H, m), 3.79(1H, m), 2.40(4H, m), 2.27(2H, q, J = 7.5 Hz), 1.80(4H, m), 1.12(3H, t, J = 7.5 Hz).
GC/MS: Retention time, 1.8 min: 56.0(15.2), 134.1(7.0), 237.1(4.2), 238.2(5.9), 239.1(10.6), 240.1(7.7), 253.1-(7.1), 264(10.2), 266.0(33.4), 268.0(100.0, M^+), 269.0-(19.0).

3-Ethyl[5]ferrocenophane
IR: 3060(m), 2940(sh), 2900(s), 2840(sh), 1640(broad m), 1480(m), 1455(sh), 1448(s), 1370(m), 910(m), 835(m), 810(m), 800(sh).
NMR: 4.2–3.8(6H, m), 3.74(1H, m), 2.50–2.10(6H, multiplet with quartet at 2.33, J = 7.7 Hz), 2.1–1.8(4H, m), 1.14(3H, t, J = 7.7 Hz).
GC/MS: Retention time, 2.8 min: 56.0(9.4), 134.1(6.6), 280.2(18.1), 282.1(100.0, M^+), 283.1(20.7).

3,4-Diethyl[3]ferrocenophane
IR: 3065(m), 2958(s), 2920(s), 2865(sh), 2845(m), 1700-1600(broad m), 1462(m), 1438(m), 1373(m), 1321(m), 1222(m), 1038(m), 1010(m), 910(m), 842(m), 810(m), 790(m).
NMR: 3.95(2H, s), 3.90–3.75(4H, m), 2.25(4H, q, J = 7.0 Hz), 1.88(6H, s), 1.09(6H, t, J = 7.0 Hz).
GC/MS: Retention time, 2.1 min: 121.0(4.3), 252.1(10.8), 253.2(14.5), 265.1(4.5), 267.2(18.4), 268.2(4.2), 280.2-(13.5), 282.1(100.0, M^+), 283.1(19.8).

3,4'-Diethyl[3]ferrocenophane
IR: 3060(m), 2945(sh), 2990(s), 2840(s), 1650(broad m), 1488(m), 1458(sh), 1435(s), 1370(m), 1320(m), 1308(m), 1255(m), 1030(m), 1010(m), 929(m), 904(m), 838(s), 818(s).
NMR: 3.90(4H, m), 2.26(4H, q, J = 7.7 Hz), 1.88(6H, s), 1.13(6H, t, J = 7.7 Hz).
GC/MS: Retention time, 2.0 min: 91.2(4.0), 134.0(4.4), 252.1(9.3), 253.1(7.2), 265.1(5.9), 267.1(25.8), 268.1-(4.8), 280.1(16.9), 282.1(100.0, M^+), 283.1(20.8). See also Vigo [8].

2,5'-Diethyl[3]ferrocenophane
IR: 3060(m), 2940(sh), 2860(s), 1730(m), 1600(m), 1460-(s), 1450(s), 1370(s), 1330(m), 1310(m), 1258(m), 1190-(m), 1058(m), 1035(s), 945(m), 870(m), 835(m), 800(s).
NMR: 3.97(4H, s), 3.40(2H, s), 2.23(4H, q, J = 7.2 Hz), 2.00(6H, s), 1.05(6H, t, J = 7.2 Hz).
GC/MS: Retention time, 2.1 min: 252.1(7.8), 253.1(7.4), 265.1(4.5), 267.2(7.4), 280.2(15.2), 282.2(100,0, M^+), 283.2(21.1). See also Vigo [8].

2,4'-Diethyl[3]ferrocenophane
IR: 3060(m), 2900(s), 2840(sh), 1722(m), 1640(m), 1600-(m), 1479(sh), 1448(s), 1438(sh), 1370(s), 1302(s), 1253-(m), 1200(m), 1053(sh), 1033(m), 910(m), 832(s), 803(s).
NMR: 4.10–3.60(6H, m), 3.40(1H, m), 2.23(4H, q, J = 7.3 Hz), 2.05–1.85(6H, m), 1.12(3H, t, J = 7.3 Hz), 1.06(3H, t, J = 7.3 Hz).
GC/MS: Retention time, 2.1 min: 55.9(9.0), 77.1(4.6), 91.1(6.6), 121.1(4.6), 121.9(4.3), 134.0(5.8), 147.1(4.0), 148.2(4.3), 160.0(5.2), 252.0(9.0), 253.1(10.1), 265.1-(4.3), 267.2(16.5), 268.1(4.9), 280.1(24.0), 282.1 (100.0, M^+), 283.2(19.1). See also Vigo [8].

2,3'-Diethyl[3]ferrocenophane
IR: 3060(m), 2950(sh), 2900(s), 2835(s), 1723(m), 1650-(broad m), 1479(sh), 1460(sh), 1446(s), 1438(s), 1368(m), 1310(m), 1258(m), 1055(m), 1033(s), 910(m), 839(s), 800(s).
NMR: 4.00–3.85(2H, m), 3.85–3.70(3H, m), 3.43(1H, m), 2.18(2H, q, J = 7.7 Hz), 2.15(2H, q, J = 7.7 Hz), 2.05–1.85(6H, m), 1.13(3H, t, J = 7.7 Hz), 1.05(3H, t, J = 7.7 Hz).
GC/MS: Retention time, 2.1 min: 134.0(4.1), 252.1(9.0), 253.1(7.6), 265.1(4.1), 267.1(16.7), 280.1(15.2), 282.1-(100.0, M^+), 283.2(18.9). See also Vigo [8].

3,3'Diemethyl[3]ferrocenophane
Mp. 108–110 °C.
IR: 3050(w), 2850(s), 1475(w), 1428(m), 1366(w), 1312-(w), 1252(m), 1193(w), 1050(sh), 1024(s), 930(s), 908(w), 852(m), 832(s), 792(s).
NMR: 4.0–3.7(6H, m), 1.88(6H, s), 1.75(6H, s).
GC/MS: Retention time, 2.1 min: 56.1(8.5), 239.1(5.5), 252.2(9.2), 254.3(100.0, M^+), 255.2(20.5).

this oxidation. TLC of the recovered materials showed no new spots to indicate that decomposition or rearrangement had occurred. In some cases, GC/MS and NMR spectra of the recovered samples were recorded and, again, there was no evidence of decomposition or rearrangement.

Substituted ferrocenophanes were used as received from the donors. Melting points of the samples were compared with published values prior to reduction to insure that the labeled samples corresponded to the literature assignments. No decomposition or rearrangement was observed in any of the samples examined. NMR spectra of the reduced compounds were recorded in deuterochloroform. IR spectra were recorded on a Perkin Elmer 467 Grating Spectrometer using the neat oils or deuterochloroform solution. Mass spectra were recorded on a Hewlett Packard Model 5990A GC/MS operating at a column temperature of 150 °C, and a block temperature of 160 °C with a flow rate of 30 ml/min.

Mixed Hydride Reduction Procedure—General Procedure

100–200 mg of acetylferrocenophane or ferrocenophane methyl ester was added slowly with nitrogen counterflow to a 50 ml Schlenk tube containing a spin bar, 0.25 g of lithium aluminum hydride and 1.0 g of aluminum chloride in 25 ml of anhydrous ethyl ether. A reflux condenser was affixed to the Schlenk tube and the mixture was refluxed with stirring. After three hours the remaining hydride was decomposed by the sequential addition of ethyl acetate, methanol and water. The ether layer was separated and washed with water, 10% sodium bicarbonate solution and again with water, then dried over magnesium sulfate. After solvent removal, the product was taken up in petroleum ether and chromatographed on a 20 cm × 1 cm silica gel column using petroleum ether as an elutant. Removal of the solvent gave 80–90% yields of the ethyl and methyl ferrocenophanes. GC/MS of the compounds prepared in this manner showed only one component. All compounds except 3,3′dimethyl[3]ferrocenophane are yellow oils, Vigo has reported several of the ethyl and diethyl[3]ferrocenophanes in his Dissertation [8] and values given there agree in all cases with those found in this research. Because of the very small quantities of the various starting materials, it was not possible to obtain analytical samples, therefore the M^+ fragment in the mass spectrum of the compounds was used to confirm the identity of the compounds. In all cases, the M^+ fragment is the base line fragment and an iron isotopic pattern is well resolved..

Spectral data for the alkylferrocenophanes are presented in Table III.

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