Metallocene Basicity. VIII. Protonation of Bridge Substituted Ferrocenophanes in Strong Acid Media*

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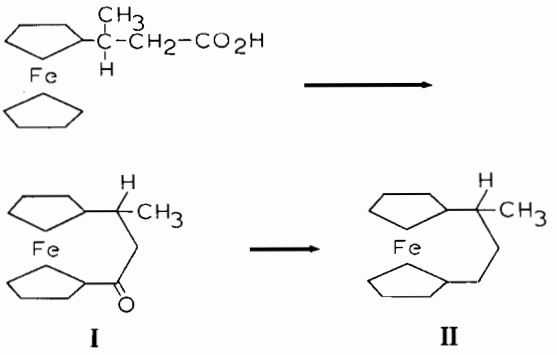
Abstract

A series of bridge substituted [3]-, [4]-, and [5]-ferrocenophanes have been prepared and characterized by ^1H NMR and mass spectroscopy. In trifluoroboric acid, HBF_3OH, solution these ferrocenophanes protonate at the iron to form long-lived species which can be studied by ^1H NMR. Analysis of the complex ^1H NMR spectra of the protonated species suggests that bridge substituents either slow or block the free oscillation of the rings and bridges. The iron–hydrogen chemical shift values have been shown to depend only on the length of the bridge and seem to be insensitive to substituents on the bridge.



Scheme 1.

Introduction

In our previous communications [2, 3], we have discussed the protonation of simple bridged ferrocenes and bridged ferrocenes with additional alkyl substituents on the rings. Spectra of the simple bridged species suggest that molecular oscillations of the rings and bridge serve to average the ring and bridge proton environments on the NMR time scale. It was of interest to examine the consequences of introducing substituents onto the bridges of ferrocenophanes since these substituents might be expected to inhibit the bridge oscillatory freedom, and perhaps that of the rings as well. As will be discussed below, the NMR spectra of these bridge substituted species are more complex than those of the unsubstituted species which may be attributable to the restriction of the ring and bridge oscillatory freedom.

Synthesis

Bridge substituted [3]ferrocenophanes are prepared by routes which are summarized in Schemes 1–3. Ring closure of ferrocenylpropionic acids with trifluoroacetic acid anhydride as a catalyst has been shown to be an effective route to [3]ferrocenophanes [4]. Using this method, 8-methyl[3]ferrocenophan-6-one (**I**) was prepared in good yield. The ketone was converted into 6-methyl[3]ferrocenophane (**II**) by reduction with mixed hydrides. [3]Ferrocenophan-6-one (**III**) was prepared by the one-step annelation procedure described by Turbitt and Watts [5]. When this procedure was applied to the preparation of 7-methyl[3]ferrocenophan-6-one (**IV**), a second compound, 1,3-bis(ferrocenyl)-2-methylprop-1-one (**V**), was isolated as the major product. This dinuclear product may arise because the methyl substituent hinders the heteroannular closure step. 7-Methyl[3]ferrocenophane (**VI**) is prepared by reduction of **IV**.

6,8-Dimethyl[3]ferrocenophane (**X**) was prepared via the alcohol which is recovered in good yield from the reaction of **I** and methylmagnesium iodide as shown in Scheme 3. Both the *cis* and *trans* dimethyl alcohol isomers (**VII** and **VIII**) appear to be produced by this reaction although one was present in trace amounts and was identified only by thin layer chromatography, TLC. TLC also revealed the presence of a third, rapidly eluted, compound which was identified by IR to be the exocyclic alkene **IX** which is formed by dehydration of the alcohols. Reduction of the major alcohol product with lithium

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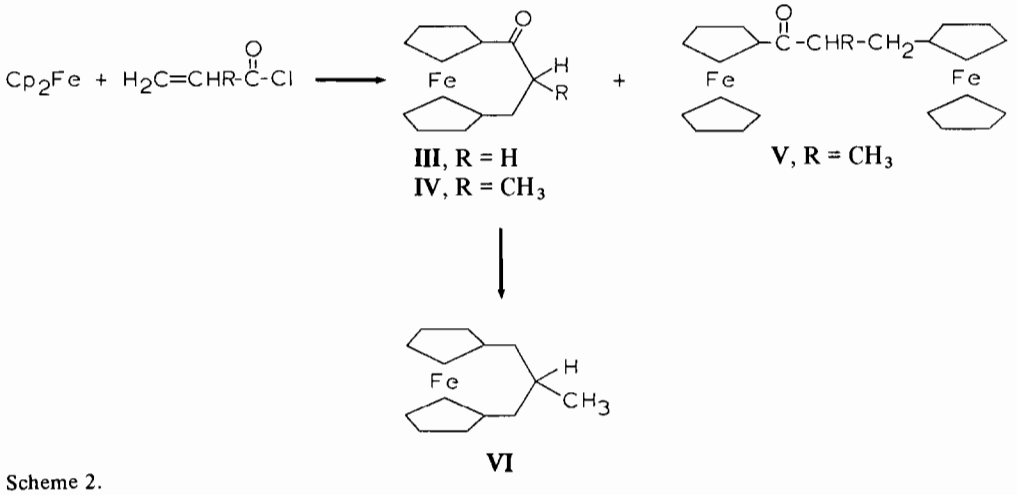
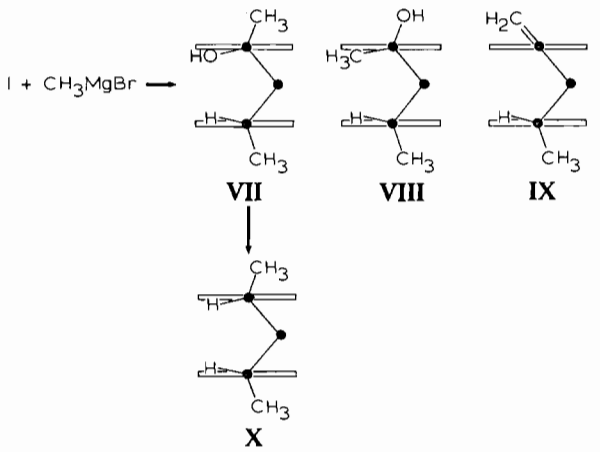


Scheme 2.

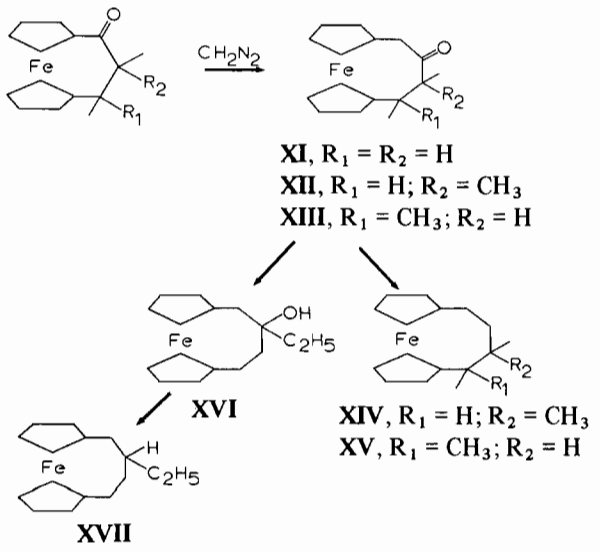


Scheme 3.

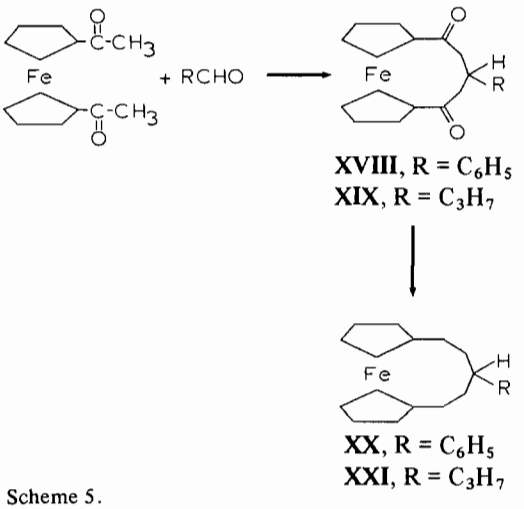
alumium hydride and aluminum chloride (mixed hydrides) gave **X** in high yield. Based on the simplicity of the NMR spectrum of this compound in both deuterochloroform and trifluoroboric acid, we have assigned it the *cis* conformation.

[4]Ferrocenophan-7-one and its 8-methyl and 9-methyl derivatives (**XI, XII**, and **XIII**) were prepared as shown in Scheme 4 by diazomethane ring expansion of the appropriate [3]ferrocenophanone. These compounds were readily reduced to the corresponding [4]ferrocenophanes by mixed hydride. 7-Ethyl-[4]ferrocenophane (**XVII**) was prepared by reaction of **XI** with ethyl magnesium bromide followed by reduction of the product alcohol.

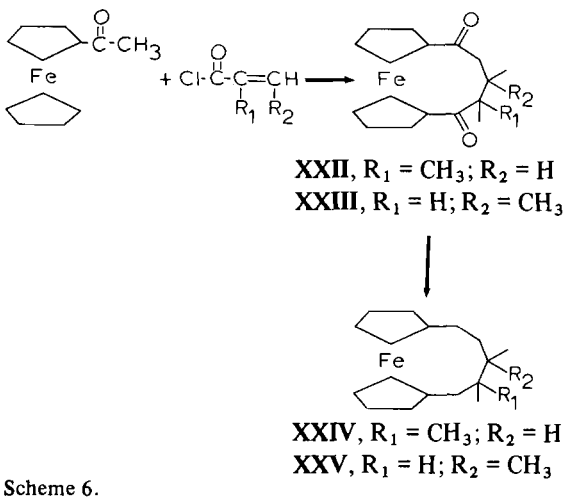
Synthetic routes for [5]ferrocenophanes are presented in Schemes 5–7. [5]Ferrocenophanes which are substituted at the 8 position have been



Scheme 4.



Scheme 5.



Scheme 6.

prepared by condensation of 1,1′diacetylferrocene and an appropriate aldehyde [6, 7]. This procedure is simple and proved effective for the preparation of 8-phenyl- and 8-propyl[5]ferrocenophan-6,10-dione (**XVIII** and **XIX**). An attempted preparation of 8-ethyl[5]ferrocenophan-6,10-dione by this procedure gave 1,1′-bis(2-pentenoyl)ferrocene as the major product which could not be removed from the trace of ferrocenophane which was also formed.

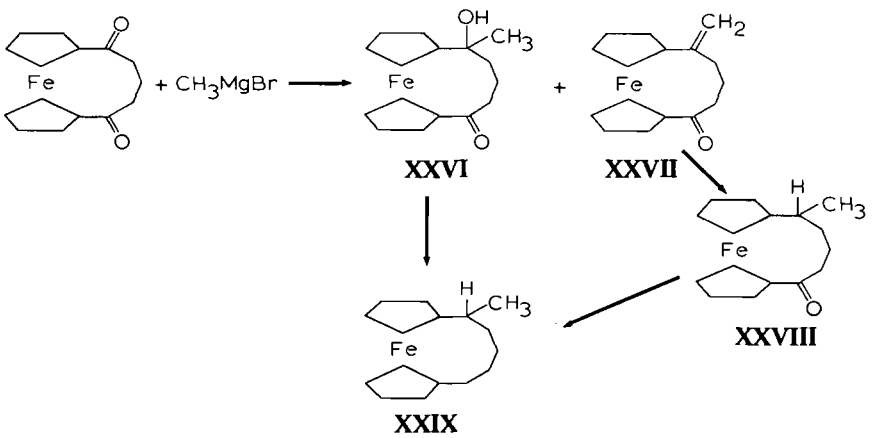
7-Methyl- and 8-methyl[5]ferrocenophane (**XII** and **XXIII**) were prepared by modification of the procedure described by Barr and Watts [7] for the preparation of [5]ferrocenophanes. In this variation, 1-acetyl-1′-acroylferrocenes are prepared by Friedel–Crafts acylation of acetylferrocene, isolated, and then cyclized in base. In the case of the synthesis of **XXIII**, the intermediate was not isolated, rather cyclization occurred under the Friedel–Crafts conditions to yield the bridged compound directly.

6-Methyl[5]ferrocenophane (**XXIX**) was prepared by methylation of [5]ferrocenophan-6,10-dione with methyl magnesium iodide. The Grignard reaction yielded a mixture of products containing the desired alcohol–ketone **XXVI** and at least one alkene–ketone (**XXVII**). The alcohol was reduced to **XXIX** with mixed hydride. The alkene was reduced by catalytic hydrogenation to 10-methyl[5]ferrocenophan-6-one (**XXVIII**) which was then converted to **XXIX** by mixed hydride.

Elemental analyses of the compounds reported here were generally unsatisfactory due to the tendency of the compounds to retain solvents. To confirm the identities of the compounds, mass spectra were recorded on all ferrocenophanes (See 'Experimental'). The mass spectra of ferrocenophanes are quite simple, usually consisting only of the parent mass. In some cases methyl radical loss is also observed. Cyclopentadienyl iron or methylcyclopentadienyl iron fragments are also occasionally observed.

Results and Discussion

The protonation of monobridged ferrocenophanes has been studied in trifluoroboric acid using the ^1H NMR spectra as a probe of the conformations of the protonated species [3]. The conformations of the protonated [3]-, [4]-, and [5]ferrocenophanes are illustrated in Fig. 1. In all cases, the ring proton patterns consist of two, four-proton resonances. Deuteration of the ring positions adjacent to the bridges permitted assignment of the ring proton resonances. For [3]ferrocenophane, it was found that the protons adjacent to the bridge were associated with the upfield resonances, establishing that these protons were equally positioned in the ring-tilted species and closer to the region of closest interannular approach than were the protons displaced from the bridges.



Scheme 7.

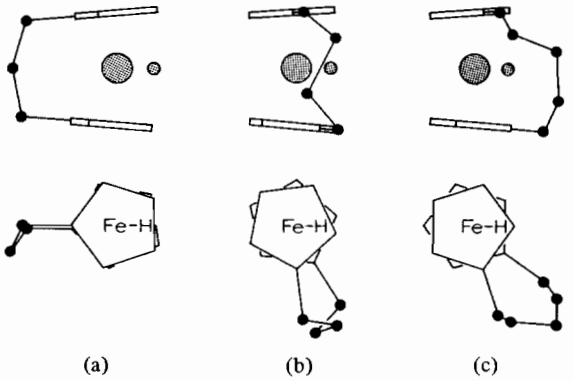


Fig. 1. Average conformations of protonated [n]ferrocenophanes: (a) n = 3, (b) n = 4, (c) n = 5 (see ref. 3).

For both [4]ferrocenophane and [5]ferrocenophane the protons adjacent to the bridges were found to occupy two different magnetic environments. This requirement dictates a geometry in which the bridges are to one side of the ring-tilted moiety so that protons on one side of the bridge are in the region of closest interannular approach (upfield) while the others are in the open face (downfield). In the spectra of both [4]- and [5]ferrocenophane, the chemical shifts of protons in the open face accidentally overlap, as do those in the region of closest interannular approach. From models, it appears that this accidental overlap is at least partially due to oscillations of the rings and bridges which averages the environments of the protons in the two regions.

Introduction of a pair of methyl groups onto the central carbon of the [3]ferrocenophane bridge has almost no effect on the ring proton resonance pattern. The evidence, which has been presented in detail elsewhere [3], indicates that the geometry and bridge oscillatory freedom of the 7,7-dimethyl[3]ferrocenophane are almost identical to that of the [3]ferrocenophane.

In the present research the protonation of bridge substituted ferrocenophanes in trifluoroboric acid proceeded normally. The compounds were stable in the acid without oxidation for periods exceeding 0.5 h. After the spectra were recorded, the recovered compounds were examined for evidence of rearrangement or decomposition by TLC, GC/MS and NMR. In no case was there evidence of rearrangement or decomposition. Chemical shifts and tentative proton assignments are presented in Tables I, II and III.

Introduction of a single methyl group onto the bridge of [3]ferrocenophane sharply alters the appearance of the ring proton resonance pattern. In these compounds, three or four resonances are observed with integrations of 2:4:2 or 2:2:2:2, which requires that the simple symmetry of the unsubstituted species has been broken. Although it is possible that these ring patterns are only the consequence of diamagnetic shielding by the assymmetric bridges, it appears more likely that they reflect an actual conformational change in the protonated species.

The ring proton resonance pattern of protonated **II** consists of three resonances with a relative integration of 2:4:2. The preparation and subsequent protonation of 2′,5′-dideutero-6-methyl[3]ferrocenophane demonstrated that the protons adjacent to the bridge associated with both the upfield and middle

TABLE I. NMR Parameters for Protonated [3]Ferrocenophanes

Compound	Ring protons[a]		Bridge protons[b]		Fe–H
[3]Ferrocenophane	H_2, H_5	4.88	$(CH_2)_3$	2.42	−1.13
	H_3, H_4	5.19 (d, J = 4.0 Hz)			
7,7-Dimethyl[3]ferrocenophane	H_2, H_5	4.88	(CH_2)	2.37	−0.93
	H_3, H_4	5.04	$(CH_3)_2C$	1.34	
6-Methyl[3]ferrocenophane	H_2	4.93	(CH_2)	2.59, 2.47	−1.10
	H_3, H_5	5.13	CH_3	1.64 (d, J = 6 Hz)	
	H_4	5.32			
7-Methyl[3]ferrocenophane	H_2	4.85	$(CH_2)_{exo}$	2.00 (d, J = 12 Hz)	−1.00
	H_3, H_5	5.08, 5.17	$(CH_2)_{endo}$	2.99 (d, J = 12 Hz)	
	H_4	5.40	$CH(CH_3)$	2.5 (broad)	
6,8-Dimethyl[3]ferrocenophane	H_2	4.76	(CH_2)	2.48 (broad)	−1.18
	H_3, H_5	4.90, 5.39	CH_3	1.70 (d, J = 6 Hz)	
	H_4	5.49			

[a]H_3 and H_5 are assigned to midrange protons. In those cases where the midrange resonances are split into two resonances no attempt has been made to assign H_3 or H_5. [b]Tertiary carbon protons are rarely located with certainty and are generally assumed to be part of the methylene resonance.

TABLE II. NMR Parameters for Protonated [4]Ferrocenophanes

Compound	Ring protons[a]	Bridge protons	Fe–H
[4]Ferrocenophane	H_2, H_3 5.15 H_4, H_5 5.40	7,8-(CH_2) 2.16 6,9-(CH_2) 2.97	−2.00
6-Methyl[4]ferrocenophane	4.96 (2H) 5.18 (3H), 5.34 (2H) 5.48 (1H)	7,8-(CH_2) 2.06 6,9-(CH_2) 2.84 CH_3 1.51 (broad)	−2.15
7-Methyl[4]ferrocenophane	5.03 (2H) 5.21 (2H), 5.28 (3H) 5.45 (1H)	7,8-(CH_2) 2.10 6,9-(CH_2) 2.94 CH_3 1.38	−2.00
7-Ethyl[4]ferrocenophane	5.07 (2H) 5.32 (5H) 5.56 (1H)	7,8-(CH_2) 1.85 6,9-(CH_2) 3.06 $C\underline{H}_2CH_3$ 1.85 $CH_2C\underline{H}_3$ 1.34	−1.86

[a]Cyclopentadienyl ring resonances have been grouped into low, middle and high sets, but no specific ring protons have been assigned to these resonances.

TABLE III. NMR Parameters for Protonated [5]Ferrocenophanes

Compound	Ring protons[a]	Bridge protons	Fe–H
[5]Ferrocenophane	H_2, H_3 5.03 H_4, H_5 5.48	7,8,9-(CH_2) 1.75 6,10-(CH_2) 2.58	−1.72
6-Methyl[5]ferrocenophane	4.77 (1H) 4.85 (1H), 5.40–5.59 (2H) 5.84 (2H)	7,8,9-(CH_2) 1.87 6,10-(CH_2) 2.75 CH_3 1.52	−1.52
7-Methyl[5]ferrocenophane	5.51 (2H) 5.15 (2H), 5.56 (2H) 5.77 (2H)	7,8,9-(CH_2) 1.80 6,10-(CH_2) 2.59 CH_3 1.33	−1.58
8-Methyl[5]ferrocenophane	5.88 (2H) 5.43 (4H) 5.84 (2H)	7,8,9-(CH_2) 1.83 6,10-(CH_2) 2.68 CH_3 1.25	−1.63
8-Propyl[5]ferrocenophane	5.02 (2H) 5.53 (2H), 5.67 (2H) 6.00 (2H)	7,8,9-(CH_2) 1.90 6,10-(CH_2) 2.87 $C_2\underline{H}_4CH_3$ 1.90 $C_2H_4C\underline{H}_3$ 1.33	- 1.49
8-Phenyl[5]ferrocenophane	4.64 (2H) 5.30 (4H) 5.65 (2H)	7,9-(CH_2) 1.85 6,10-(CH_2) 2.37 $C\underline{H}(C_5H_5)$ 2.77 $CH(C_5\underline{H}_5)$ 7.50	−1.50

[a]Cyclopentadienyl ring resonances have been grouped into low, middle and high sets. No specific ring protons have been assigned to these resonances.

resonances in the 2:4:2 pattern. This observation is analogous to that for [4]- and [5]ferrocenophane in which protons which are in two roughly equivalent positions in the nonprotonated species occupy magnetically different environments in the protonated species. A conformation of **II** which incorporates these features is illustrated in Fig. 2. In this conformation, it is assumed that the bridge oscillation is restricted by the presence of the single methyl group. The bridge assumes a position which is slightly off-center of the ring-tilted moiety, placing one of the ring protons adjacent to the bridge in a

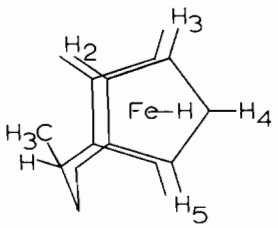


Fig. 2. Probable conformation of protonated 6-methyl[3]-ferrocenophane.

different environment than the other. A similar conformation can be used to explain the ring proton patterns of protonated **VI** and **X**.

Bridge substituents on [4]- and [5]ferrocenophanes result in an increase in complexity of the ring resonance patterns as was observed for the [3]ferrocenophanes. In general, it appears that the bridge substitution produces a species in which the environmental similarities which led to the accidental overlap of the ring protons in the simple ferrocenophanes are disrupted. As it is again unlikely that the bridge substituent will have a direct shielding effect on the ring proton chemical shifts (except perhaps the phenyl ring in **XX**) we suggest that these effects are probably the result of restrictions of the bridge oscillatory freedom.

Coupling between ring protons in the open face and the iron–hydrogen have been observed for several protonated ferrocenophanes [2, 3]. For example, the downfield ring proton resonance in the spectrum of [3]ferrocenophane is split into a doublet, presumably due to coupling with the iron–hydrogen. In many of the bridge substituted ferrocenophanes examined here, the downfield ring proton resonance is broadened, but in no case has it been possible to resolve any splitting. In the case of **X** the iron–hydrogen resonance is resolved into a triplet indicating coupling with two protons in the open face. The iron–hydrogen resonance of protonated **VI** may also be a poorly resolved triplet. In both cases, the observation of an iron–hydrogen triplet supports the conformations illustrated in Fig. 2 in which only two ring protons are positioned for coupling with the iron–hydrogen rather than the four protons which are observed in unsubstituted [3]ferrocenophane.

We have for some time been seeking patterns in the chemical shifts of the iron–hydrogen resonances of protonated ferrocenes. We have found that these chemical shifts are sensitive to the number and position of ring alkyl substituents, generally shifting upfield with greater alkyl substitution. These shifts are also sensitive to diamagnetic shielding by the ring substituents and, we think, to the degree of tilting of the ferrocenyl moiety upon protonation. Comparison of iron–hydrogen chemical shifts to the $E_{1/2}$ values for several parent ferrocenes showed no correlation at all [8].

In the case of the substituted ferrocenophanes, the iron–hydrogen chemical shifts are found to be dependent only upon the length of the interannular bridge. This relationship is illustrated in Table IV. The order of increasing chemical shift is found to be [3] < [5] < [4], for which no simple explanation is apparent. The similarities between the chemical shifts for each set of ferrocenophanes indicates that although the oscillatory motion may be restricted, there is probably little change in the bulk geometry of the protonated species when bridge substituents are added.

TABLE IV. Summary of Iron–Hydride Chemical Shifts

Substituent and position	Bridge length		
	[3]	[4]	[5]
H	−1.13	−2.00	−1.72
6-CH_3	−1.10	−2.15	−1.52
7-CH_3	−1.00	−2.00	−1.58
8-CH_3			−1.63
7,7-$(CH_3)_2$	−0.93		
6,8-$(CH_3)_2$	−1.18		
7-C_2H_5		−1.86	
8-C_3H_7			−1.49
8-C_6H_5			−1.50
Average	−1.07	−2.00	−1.57

Experimental

NMR spectra were recorded on a Varian Associates A60-A NMR spectrometer at room temperature. NMR samples for protonation studies were prepared by previously published procedures to rigorously exclude oxygen from the sample [3]. No compound oxidation was observed during periods of 0.5 h. All samples were recovered from trifluoroboric acid and examined by TLC to determine if decomposition or rearrangement had occurred in the acid. In several cases, recovered samples were also examined by NMR and GC/MS, but in no case was decomposition or rearrangement observed. All chemical shifts are recorded in ppm. Tetramethylammonium tetrafluoroborate (3.33 ppm relative to TMS) was used as an NMR standard in all protonation studies.

NMR spectra of the neutral compounds were recorded in deuterochloroform with TMS as a standard. IR spectra were recorded on a Perkin-Elmer 467 Grating Spectrophotometer using either the neat oils or a deuterochloroform solution of the solids. Mass spectra were recorded on a Hewlett Packard Model 5990A GC/MS operating at a temperature of 150 °C, and a block temperature of 160 °C with a

flow rate of 30 ml/min. Mass spectral data are reported as observed mass followed by relative intensity in parenthesis.

Compound Preparation

8-Methyl[3]ferrocenophan-6-one (I)

3-Ferrocenylbutanoic acid was prepared by the Reformatski procedure of DeRe and Sianesi [9]. 3-Ferrocenylbutanoic acid, 1.5 g (5.51 mmol), was dissolved in 40 ml of methylene chloride. A solution of 3 ml of trifluoroacetic acid anhydride in 20 ml of methylene chloride was added to the ferrocenylbutanoic acid solution and the resulting mixture refluxed for 6 h then poured onto 500 ml of water. The organic layer was separated, washed with water, 10% sodium bicarbonate solution and again with water, and then dried over magnesium sulfate. TLC of the organic layer showed only one component. After solvent removal the resulting oil was recrystallized from ethyl ether to yield an orange solid, melting point (m.p.) 105–110 °C. NMR: 4.90(1H, m), 4.71(2H, m), 4.49(1H, m), 4.36(2H, m), 4.04-(2H, broad m), 3.23(2H, m), 2.62(1H, m), 1.24(3H, d, $J = 6.5$ Hz). IR: (in cm^{-1}) 3100(w), 2920(m), 1660(s) (carbonyl), 1450(s), 1390(w), 1370(m), 1300(w), 1290(m), 1260(m), 1230(m), 1160(w), 1090(s), 1070(s), 1030(s), 932(w), 890(w), 862(m), 813(s).

6-Methyl[3]ferrocenophane (II)

I, 250 mg (1.02 mmol), was reduced with 0.20 g of lithium aluminum hydride and 1.00 g of aluminum chloride in 50 ml of ethyl ether. The reaction mixture was refluxed for 3 h then cautiously worked up by addition of ethylacetate, methanol and water. The organic layer was separated, washed with water, 10% sodium bicarbonate solution and again with water, then dried over magnesium sulfate. After removal of the solvent, the yellow oil was chromatographed on a 20 cm × 1 cm silica gel column using petroleum ether as the elutant. One band was removed which was shown by TLC and GC/MS to contain only one component. The resulting compound was recrystallized from petroleum ether, m.p. 58–60 °C. NMR: 4.02(8H, s), 1.97(5H, m), 1.20(3H, d, $J = 6.5$ Hz). IR: 3120(w), 2950(m), 1460(sh), 1450(m), 1400(m), 1330(m), 1220(m), 1050(s), 1030(s), 942(m), 916(m), 853(s), 808(s). GC/MS: Retention time, 1.0 min: 225.0(18.6), 238.2(11.7), 240.2(11.7), 240.2 (M^+, 100.0), 241.1(17.7). *Anal.* Calc. for $C_{14}H_{16}Fe$: C, 70.0; H, 6.67. Found: C, 67.9; H, 6.60%.

7-Methyl[3]ferrocenophan-6-one (IV)

Using the one-step annelation procedure of Turbitt and Watts [5], the low temperature acylation of ferrocene with methacryloyl chloride was carried out. In our hands, chromatography of the reaction mixture yielded two products, the desired bridged ketone and a tan solid, m.p. 159–169 °C. NMR: 4.70(2H, m), 4.48(2H, m), 4.10(5H, s), 1.2(integration indeterminate, m). IR: 3100(w), 2900(w), 1670(s) (carbonyl), 1440(m), 1380(m), 1260(m), 1240(m), 1110(m), 1055(s), 1030(m), 1000(m), 980(m), 900(m), 862(m), 828(s). Reduction of the tan solid with mixed hydrides yielded an orange solid, m.p. 103–108 °C. NMR: 4.05(s), 4.01(s), 2.26(m), 0.72(d, $J = 7.0$ Hz). IR: 3110(w), 2940(m), 1470(w), 1400(w), 1380(w), 1110(s), 1040(m), 1030(m), 1005(m), 920(m), 910(sh), 850(w), 813(s). GC/MS: Retention time, 8.1 min: 186.1(10.4), 199.1(64.3), 200.2(16.2), 212.2(12.3), 213.1(24.0), 240.2(63.6), 241.1(16.9), 361.0(44.8), 424.1(16.9) 426.1 (M^+, 100.0), 427.1(29.2). These data are consistent with the tan solid being 1,3-diferrocenyl-2-methylprop-1-one (**V**) which is reduced to 1,3-diferrocenyl-2-methylpropane.

7-Methyl[3]ferrocenophane (VI)

Reduction of **IV** using mixed hydrides yielded a yellow solid, m.p. 74.5–75.0 °C. NMR: 4.00(8H, s), 2.5–2.2(4H, m), 1.6–1.3(2H, m), 1.50(3H, d, $J = 6.0$ Hz). IR: 3110(w), 2910(s), 1460(m), 1400(w), 1380(w), 1290(w), 1220(w), 1110(w), 1040(s), 1025(s), 930(m), 915(w), 855(m), 810(m). GC/MS: Retention time. 1.1 min: 238.2(9.6), 240.1 (M^+, 100.0), 241.2(17.0). *Anal.* Calc. for $C_{14}H_{16}Fe$: C, 70.0; H, 6.67. Found: C, 69.3; H, 6.78%. Hutchcroft [11] has prepared this compound by an alternate route and the NMR spectra which he reports for this compound and those reported here are in agreement.

6,8-Dimethyl-8-hydroxy[3]ferrocenophane (VII)

Methyl magnesium iodide was prepared under nitrogen in a Schlenk reaction vessel by addition of 1.00 g (7.00 mmol) of methyl iodide in 20 ml anhydrous ether to 0.15 g of magneisum. The resulting Grignard reagent was transferred to a fritted addition funnel and added slowly to 1.00 g (3.93 mmol) of **I** dissolved in 20 ml of ethyl ether. Reaction was immediate with the formation of a yellow precipitate. After 2 h, water was added and the organic layer separated, washed with water and dried over magnesium sulfate. After solvent removal the yellow oil was taken up with 95:5 petroleum ether: ethyl ether and chromatographed on a 50 cm × 2 cm silica gel column. Three bands were collected. The first band contained a small amount of a yellow compound believed to be an alkene (**IX**) formed by dehydration of the product alcohols. The second band was evaporated to yield 800 mg (80.1%) of a yellow solid, m.p. 123–124 °C. NMR: 4.37(1H, m), 4.2–3.9(7H, m), 2.59(1H, m), 2.10(2H, m), 1.68(1H, s), 1.49(3H, s), 1.20(3H, d, $J = 6.5$ Hz). IR: 3600(w), 3155(w), 2960(m), 1795(m), 1465(s), 1380(s),

1250(s), 1218(w), 1170(w), 1090(m), 1029(w), 862(m), 680(s). GC/MS: Retention time, 2.2 min: 55.8(43.5), 91.1(12.0), 120.9(65.3), 121.9(9.7), 134.0(26.6), 145.0(12.0), 146.9(16.1), 159.9(25.0), 177.9(20.2), 185.9(18.5), 199.0(11.3), 211.9(44.4), 212.9(12.1), 226.1(13.7), 227.0(26.6), 252.0(100.0), 253.0(20.2). 269.9 (M^+, 89.5), 270.9(16.9). The third yellow band yielded a small amount of yellow solid. NMR: 4.45(1H, m), 4.3–3.9(7H, m), 2.7–1.8(7H, m), 1.58(3H, s), 1.20(3H, d, J = 6.1 Hz). IR: 3600(w), 3155(w), 2960(s), 2930(s), 2860(sh), 1795(w), 1720(m), 1460(s), 1380(s), 1285(m), 1250(m), 1165(w), 1125(sh), 1095(m), 1029(m), 862(m), 650(s). Addition of acid to either the second or third product gave a dehydration product which appeared by TLC to be identical to the first compound described above.

6,8-Dimethyl[3]ferrocenophane (X)

Reduction of 0.50 g (1.9 mmol) of **VII** from the alcohol preparation above with lithium aluminum hydride and aluminum chloride as described previously yielded a yellow oil which was chromatographed on a 20 X 1 cm silica gel column using petroleum ether as an elutant. Removal of the solvent gave a yellow solid, m.p. 93–95 °C. NMR: 4.04(6H, s), 3.98(2H, m), 2.3–1.7(4H, m), 1.18(6H, d, J = 7.0 Hz). Ir: 3110(w), 2950(m), 1460(m), 1400(w), 1390(m), 1220(m), 1050(s), 1030(s), 942(m), 916(m), 853(s), 808(s). GC/MS: Retention time, 1.1 min: 239.2(15.2), 252.2(10.3), 254.2(M^+, 100.0), 255.1(21.1).

2,5-Dideutero-8-methyl-8-hydroxy[3]ferrocenophane

2,5-Dideutero[3]ferrocenophan-8-one, 0.50 g (2.1 mmol), prepared by the procedure described by Vigo [10], was dissolved in 30 ml of ethyl ether under nitrogen. To this solution 1.3 ml of 1.6 M methyl lithium in hexane was added slowly. A yellow solid formed immediately. After 1 h, the reaction mixture was separated, washed with water and dried over magnesium sulfate. The residue was chromatographed on a 30 cm X 2 cm silica gel column using 95:5 petroleum ether:ethyl ether yielding a small amount of unreacted ketone, followed by a yellow band which was evaporated to yield a yellow solid, m.p. 102–105 °C. NMR; 4.36(1.3H, m), 4.02(5.3H, m), 2.15(4H, m), 1.67(1H, s), 1.52(3H, s), 70% deuterated. IR: 3580(m), 3440(m), 3120(w), 3080(w), 2969(sh), 2940(sh), 2900(s), 2840(m), 1800(m, broad), 1450(m), 1375(s), 1300(m), 1246(m), 1220(w), 1187(w), 1155(w), 1090(m), 1030(m), 862(m), 810(m).

2,5-Dideutero-8-methyl[3]ferrocenophane

Reduction of the dideutero alcohol above with mixed hydride in ethyl ether yielded the product in quantitative yield. Properties of this compound are identical to those listed for 6-methyl[3]ferrocenophane.

8-Methyl[4]ferrocenophan-7-one (XII)

IV, 1.0 g (3.9 mmol), were dissolved in 40 ml of methanol. 1.3 g (5.9 mmol) of Diazald were dissolved in 20 ml of methanol and the two solutions were combined in a 250 ml flask. The flask was placed in an ice bath and the solution stirred. Potassium hydroxide, 0.3 g, was dissolved in a minimum amount of water and then diluted to 5 ml with methanol. This potassium hydroxide solution was added slowly to the chilled ferrocene–Diazald solution. After all of the potassium hydroxide solution had been added, the reaction mixture was stored at 2.0 °C overnight. The reaction mixture was acidified with acetic acid, concentrated to low volume, taken up with ethyl ether and washed with water and 10% sodium bicarbonate solution. After washing the ether solution was dried over magnesium sulfate. The residue after solvent removal was taken up in 10:1 petroleum ether:ethyl ether and chromatographed on a 20 cm X 1 cm silica gel column. A yellow band was eluted from the column and concentrated to yield a small quantity of yellow solid which had an initial melting point of 75–79 °C. Sublimation of this yellow solid gave orange crystals, m.p. 89–90 °C. NMR: 4.2–4.0(8H, broad s), 3.3–2.5(4H, m), 1.14(3H, d, J = 7.0 Hz). Note, one proton signal is lost in the noise. IR: 3100(w), 2920(m), 1710(s) (carbonyl), 1460(m), 1400(m), 1280(m), 1200(w), 1030(m), 928(m), 912(m), 860(w), 815(m).

7-Methyl[4]ferrocenophane (XIV)

Reduction of **XII** with mixed hydrides yielded a yellow solid after chromatography on silica gel with petroleum ether as an eluant, m.p. 66–67 °C. NMR: 4.08(2H, m), 4.02(6H, m), 2.6–0.8 (complex pattern, integration indeterminate, methyl doublet centered at 1.05, J = 5.5 Hz). GC/MS: Retention time, 1.5 min: 121.1(7.5), 134.1(16.7), 212.1(23.9), 213.1(8.1), 239.2(5.1), 252.2(21.9), 254.2(M^+, 100.0), 255.1(22.6).

9-Methyl[4]ferrocenophan-7-one (XIII)

Methylene insertion was carried out on **I** as described for the preparation of **XII** above. Ethyl ether extracts of the reaction mixture were evaporated to give a yellow–orange solid which was taken up in 95:5 petroleum ether:ethyl ether and chromatographed on a 20 cm X 1 cm silica gel column. A light yellow band was recovered which yielded a yellow solid after solvent removal, m.p. 91–93 °C. NMR: 4.10(8H, s), 3.4–1.4(5H, m), 1.14(3H, d, J = 6.5 Hz). IR: 3110(w), 2950(m), 1700(s) (carbonyl), 1450(w), 1400(m), 1310(m), 1280(s), 1220(w),

1170(w), 1100(m), 1040(s), 1030(s), 945(w), 927(m), 898(m), 855(m), 813(s).

6-Methyl[4]ferrocenophane (XV)

Reduction of **XIII** with mixed hydrides yielded a yellow oil after chromatography on silica gel with petroleum ether as an elutant. NMR: 4.0(8H, s), 2.7–0.9(10H, complex multiplet with methyl doublet centered at 1.05, J = 7.0 Hz). GC/MS: Retention time, 1.4 min: 121.0(11.2), 226.1(19.3), 237.1(10.7), 239.1(36.4), 252.1(37.0), 253.2(10.5), 254.2(M^+, 100.0), 255.2(20.4).

7-Ethyl-7-hydroxy[4]ferrocenophane (XVI)

Ethyl magnesium bromide, 2.0 mmol, was prepared from ethyl bromide and excess magnesium with ethyl ether as a solvent. This reactant was added dropwise to a solution of 0.5 g (2.0 mmol) of [4]-ferrocenophan-7-one in ethyl ether. Immediate formation of a yellow precipitate occurred. The reaction mixture was stirred for 2 h. After addition of water to the reaction mixture, the ether layer was separated, washed with water and dried over magnesium sulfate. The residue from solvent removal was taken up in benzene and chromatographed on silica gel. A trace of unreacted ketone was eluted before the main band of alcohol. No alkene was observed. A yellow solid was recovered in high yield, m.p. 72–76 °C. NMR: 4.3–4.0 (8H, m), 2.6 (1H, s), 2.5–0.8 (indeterminate integration, complex multiplet).

7-Ethyl[4]ferrocenophane (XVII)

Reduction of **XVI** with mixed hydrides followed by column chromatography on silica gel using petroleum ether as an elutant yielded a yellow solid, m.p. 72–76 °C. NMR: 4.04(8H, m), 3.1–0.9(12H, m). IR: 3100(w), 2920(s), 1460(m), 1380(w), 1330(w), 1230(w), 1100(w), 1040(m), 1030(m), 940(m), 927(m), 910(m), 854(m), 813(s). GC/MS: Retention time, 2.0 min: 56.0(11.9), 134.1(10.1), 212.0(15.5), 266.0(16.2), 268.0(M^+, 100.0), 269.0(19.9).

8-Propyl[5]ferrocenophane (XXI)

Condensation of butanal with 1,1′-diacetylferrocene in ethanolic solution according to the procedure of Furdik, Toma and Suchy [6] gave 8-propyl-[5]ferrocenophan-6,10-dione (**XIX**) as a yellow solid, m.p. 244–245 °C (literature: 239–240 °C). Reduction of this compound with mixed hydrides yielded a yellow solid, m.p. 77–79 °C. IR: 3110(w), 2950(s), 1470(m), 1400(m), 1390(m), 1220(m), 1100(m), 1040(m), 1030(m), 910(m), 860(m), 817(s). GC/MS: Retention time, 5.3 min: 213.1(10.3), 294.2(27.3), 296.3(M^+, 100.0), 297.2(29.6).

7-Methyl[5]ferrocenophan-6,10-dione (XXII)

The bridged diketone was prepared by the procedure described by Barr and Watts [7], for the preparation of [5]ferrocenophan-6,10-dione and 8-phenyl-[5]ferrocenophan-6,10-dione. The Perrier complex of methacryloyl chloride was prepared by stirring 2.08 g (20 mmol) of methacryloyl chloride with an excess of aluminum chloride in 20 ml of methylene chloride. After 2 h, the solution was transferred to a fritted funnel and added dropwise to a stirred solution of 4.6 g (20 mmol) of acetylferrocene in 100 ml of methylene chloride. After 20 h, the reaction mixture was poured onto 500 ml of water and the organic layer was separated and washed with water, 10% sodium bicarbonate and again with water. After drying over magnesium sulfate, the mehylene chloride was removed and the residue was taken up in benzene and chromatographed on a 30 cm × 2 cm silica gel column. Elution with benzene first removed a trace of unreacted acetylferrocene, followed by a dark red band which yielded a red oil upon solvent removal. NMR: 4.84(4H, m), 4.58(4H, m), 2.36(3H, s), 1.26(3H, d, J = 7.0 Hz). This oil was taken up in 60 ml of ethanol and 2.0 g of sodium hydroxide in a minimum amount of water was added. The reaction mixture was stirred at room temperature overnight at which time a solid had formed in the flask. 50 ml of methylene chloride was added to the ethanol suspension and the solid was dissolved before addition of 100 ml of water. The organic layer was separated, washed with water and dried over magnesium sulfate. TLC of the reaction mixture showed that none of the starting material remained. Removal of the methylene chloride left an orange solid, m.p. 178–180 °C. This solid was sublimed to yield 100 mg of a yellow–orange crystalline solid, m.p. 180–182 °C. NMR: 4.94(2H, m), 4.75(2H, m), 4.58(4H, m), 2.6–2.2(4H, m), 1.14(3H, d, J = 7.0 Hz). IR: 3109(w), 3090(w), 2920(w), 1665(s) (carbonyl), 1451(m), 1382(m), 1261(m), 1065(m), 1036(m), 892(w), 882(w), 838(m).

7-Methyl[5]ferrocenophane (XXIV)

Reduction of the diketone, **XXII**, with mixed hydrides yielded a yellow–orange solid, m.p. 60–64 °C. NMR: 4.06(8H, m), 2.5–1.7(9H, m), 1.2–0.9(3H, m). IR: 3110(w), 2950(s), 1460(m), 1400(m), 1380(m), 1220(w), 1100(m), 1040(m), 1030(m), 910(m), 816(s). GC/MS: Retention time, 2.4 min: 266.1(33.8), 268.1 (M^+, 100.0), 269.1(20.0).

8-Methyl[5]ferrocenophan-6,10-dione (XXIII)

Using the procedure described above, the Perrier complex of crotonyl chloride was reacted with acetylferrocene. Work-up of this reaction gave a tan solid, m.p. 257–258 °C (literature: 251.5–253.0 °C [6]). NMR: 4.81(4H, m), 4.56(4H, m), 2.5–2.0(5H, m), 1.25(3H, d, J = 6.5 Hz). IR: 3120(w), 3080(w),

2960(w), 1660(s) (carbonyl), 1460(s), 1430(m), 1400(m), 1382(s), 1356(m), 1303(m), 1250(s), 1109(m), 1058(m), 1035(m), 907(m), 864(m), 852(m), 833(m).

8-Methyl[5]ferrocenophane (XXV)

Reduction of **XXIII** yielded a yellow solid, m.p. 66–67 °C. NMR 4.2–3.8(8H, m), 2.30–1.75(9H, m), 0.99(3H, d, J = 7.0 Hz). IR: 3106(w), 2860(s), 1450(s), 1370(m), 1330(m), 1326(m), 1210(m), 1040(s), 1025(s), 965(m), 920(m), 905(w), 875(m), 855(m), 813(m). GC/MS: Retention time, 2.4 min: 266.1(29.8), 268.1(M^+, 100.0), 269.1(19.4).

10-Methyl-10-hydroxy[5]ferrocenophan-6-one (XXVI)

Methyl magnesium iodide, 7.1 mmol, was prepared from 1.0 g (7.1 mmol) of methyl iodide and 0.5 g of magnesium in ethyl ether. After formation of the Grignard reagent was complete, it was added dropwise to a stirred solution of 2.0 g (7.1 mmol) of [5]-ferrocenophan-6,10-dione in 20 ml of ethyl ether. The ferrocene solution acquired a pink color during the addition. After 3 h ethanol and then water were added to quench the reaction. The organic layer was separated, washed with water and dried over magnesium sulfate. Removal of the solvent left a red oil which was taken up in methylene chloride and chromatographed on a 30 cm × 1 cm silica gel column with methylene chloride as the elutant. A yellow band followed by two red bands were recovered from the column.

The first yellow band yielded a small amount of yellow solid which was not further investigated. The first red band yielded 0.70 g of a red solid, m.p. 100–110 °C. NMR: 5.60(0.5 H, t, J = 9.0 Hz), 5.08 (1H, s), 4.75–4.15(8H, m), 2.8–2.1(5.5H, m), 1.85-(1.5H, d, J = 9.0 Hz). This solid is believed to be a mixture of isomeric bridge alkenes which are formed by dehydration of the product alcohol. Catalytic hydrogenation of this red solid in methanol solution using Pd/C as a catalyst yielded an orange solid after recrystallization from ethanol–hexane, m.p. 123–124 °C. NMR: 4.76(1H, s), 4.48(3H, m), 4.05(4H, s), 2.9–1.5(6–7H, m), 1.02(3H, d, J = 7.0 Hz). IR: 3080(w), 2975(sh), 2958(m), 2925(m), 1646(s) (carbonyl), 1452(s), 1395(m), 1382(m), 1370(m), 1330(w), 1280(s), 1260(m), 1200(w), 1154(w), 1100(w), 1030(m), 940(w), 822(s), 800(m). The reduced compound is presumed to be 10-methyl-[5]ferrocenophan-6-one (**XXVIII**).

The third band yielded a red solid in small yield, m.p. 144–148 °C. NMR: 5.0–4.1 (10H, m), 2.8–1.9(5H, m), 1.26(3H, s). IR: 3480(w), 3160(w), 3100(w), 2950(m), 1650(s) (carbonyl), 1460(s), 1382(m), 1272(m), 1250(m), 1090(m), 1035(m), 860(m), 828(m). This compound is presumed to be **XXVI**.

6-Methyl[5]ferrocenophane (XXIX)

Reduction of either **XXVI** or **XXVIII** with mixed hydrides yielded **XXIX** as a red oil. NMR: 4.2–3.8 (8H, m), 2.7–1.4(9H, m), 1.02(3H, d, J = 6.5 Hz). GC/MS: Retention time, 2.1 min: 121.2(13.3), 134.1(13.5), 251.2(13.1), 252.1(30.3), 253.2(19.4), 254.2(51.0), 266.1(28.5), 268.1(M^+, 100.0), 269.1-(19.0).

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