

Journal of Organometallic Chemistry, 215 (1981) 77–86
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

METALLOCENE BASICITY

V *. PROTONATION OF FERROCENOPHANES IN STRONG AND WEAK ACIDS

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(Received November 14th, 1980)

Summary

Protonation of [3]-, [4]- and [5]ferrocenophanes has been examined in trifluoroboric acid, HBF_3OH , and the results are consistent with the previous models of a long-lived metal protonated species. Selective ring and bridge deuteration has permitted the assignment of proton resonances from which probable conformations of the species have been derived. NMR spectra of [3]- and [4]ferrocenophane in trifluoroacetic acid have been recorded and interpreted in terms of rapid exchange between solvent and ferrocene.

In the previous papers in this series [1–4] we have presented evidence for the metal protonation of ferrocenes in trifluoroboric acid and have utilized NMR spectra of these ferrocenonium ions to determine their probable conformations. The present work continues this study into the protonation and conformational behavior of the ferrocenophanes. This paper will discuss protonation of the simple homoannular- and heteroannular-bridged ferrocenes in trifluoroboric acid and trifluoroacetic acid, and the following papers will examine the protonation of bridge- and ring-substituted ferrocenophanes and multi-bridged ferrocenes.

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Results and discussion

We have reported that simple mono- and 1,1'-dialkylferrocenes are protonated in trifluoroboric acid to give a species which has a high field proton resonance characteristic of a metal-bound hydrogen [1]. In agreement with the earlier observations of Curphey, et al. [5], the ring proton signals of unsubstituted rings were found to be sharp singlets, while the signals of the ring protons on substituted rings were split into two well separated, broad resonances. Deuteration of the 2- and 5- ring positions of methylferrocene permitted assignment of the low field resonances to the hydrogens in these positions and the upper field resonances to the hydrogens in the 3- and 4- ring positions. Although no measurable chemical shift separations are observed for the protons of the substituted rings in unprotonated methyl- and ethylferrocene, separations are observed for the ring protons of the ferrocenophanes [6]. In the case of the ferrocenophanes, the magnitude of the separations has been related to a tilting of the rings away from their usual parallel orientation. In relating this to the protonated alkylferrocenes, it was reasoned that ring-tilting occurs as a consequence of metal protonation and, secondarily, that free rotation about the metal-to-ring axis is sterically disallowed for substituted rings. Unsubstituted rings are free to rotate about the metal-to-ring axis, averaging the magnetic environments of the five ring protons, but the substituted rings are believed to tick-tock about the axis leading to an averaged magnetic environment for the protons at the 2- and 5- positions which is slightly different than that for the protons at positions 3 and 4. As the protons at the 3- and 4- positions were more shielded, we postulated the existence of a shielding field in the region of closest ring approach.

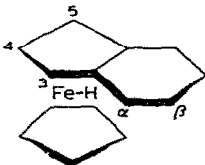
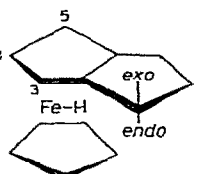
Unlike the parent ferrocenes, for which well resolved spectra of the ring protons can be generally obtained, the ring proton resonances in the spectra of the protonated ferrocenes are generally broad and ill-resolved. Ring-to-iron-hydrogen coupling on the order of 4 Hz or more can usually be resolved but coupling between ring protons or ring-to-iron-hydrogen coupling smaller than this are generally buried. These broad features presumably result from ring oscillations which move the ring protons through different magnetic environments.

[m](1,2)Ferrocenophanes

The NMR spectra of 7,7-dimethyl[3](1,2)ferrocenophane and [4](1,2)ferrocenophane in trifluoroboric acid were recorded and the resulting chemical shift values and their assignments are presented in Table 1. These spectra are similar to those observed for protonated monoalkylferrocenes in that the ring resonance pattern consists of a sharp, five proton singlet and two broader resonances of two and one proton, respectively. The sharp singlet is characteristic for a freely spinning unsubstituted ring, while the remaining resonances indicate that the rotation of the substituted ring is hindered. Assignment of the substituted ring protons based on the integration requires that the upfield resonance be assigned to the unique proton at position 4. In the most likely conformation for this species, shown in Figure 1, the proton at position 4 occupies the region of closest ring approach, adding further support to the existence of a shielding field in this region. The chemical shift differences between the ring protons of the

TABLE I

NMR PARAMETERS FOR [np (1,2) FERROCENOPHANES (CHEMICAL SHIFTS IN τ)

Compound	Protons observed	CDCl ₃	HBF ₃ OH
[4](1,2) Ferrocenophane 	C ₅ H ₅	6.10	4.48
	H(3), H(5)	6.10	4.57
	H(4)	6.10	5.27
	(CH ₂) _α	7.60	7.00
	(CH ₂) _β	8.20	7.70
	Fe-H	—	12.17
7,7-Dimethyl [3] (1,2) — Ferrocenophane 	C ₅ H ₅	5.97	4.78
	H(3), H(5)	6.0–6.1	4.90
	H(4)	6.0–6.1	5.30
	(CH ₂) _{exo}	7.82	7.34
	(CH ₂) _{endo}	7.45	7.34
	(CH ₃) _{exo}	8.94	8.63
	(CH ₃) _{endo}	8.60	8.46
	Fe-H	—	12.13

substituted rings in these compounds are very large, 0.40 τ and 0.70 τ for the [3]- and [4]ferrocenophanes, respectively, compared with values of 0.16–0.33 τ observed for the alkylferrocenes. A variety of molecular features including degree of ring tilting, rate of ring oscillation and shielding contributions by substituents may contribute to these differences, so no simple analysis is possible.

Samuel has prepared the analogous [4](1,2)titanocenophane dichloride and [4](1,2),[4](1',2')titanocenophane dichloride and has reported their NMR spectra [7]. In contrast to the protonated ferrocenophanes, the one proton resonance falls downfield of the two proton resonance in the spectrum of the titanocenophanes. As the two classes of compounds should be structurally similar, any shielding contribution from the opposite ring to the proton at position 4 should be the same or at least similar in magnitude. The reversal in order of the ring proton chemical shifts for the titanocenophanes may require that the shielding mechanism operative in the ferrocenes is not related to the nearness of the rings, but rather is due to some property of the electron-rich iron.

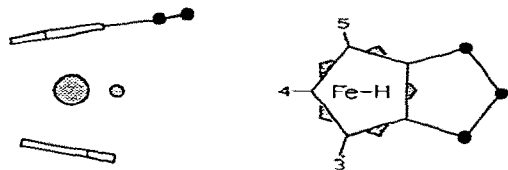


Fig. 1. Average conformations of protonated [3](1,2)ferrocenophane. [4](1,2)Ferrocenophane conformations are expected to be similar.

Alternatively, the reversal may be due to a strong dielectronic shielding of the protons at the 3- and 5- positions by the chlorines in the titanocenophanes.

Changes in the chemical shifts of the rings of the ferrocenophanes are in keeping with earlier observations on the alkylferrocenes. Metal protonation is accompanied by an inductive electron withdrawal from the side chains which is reflected in a downfield shift of the side chain resonances. In the case of [4](1,2)ferrocenophane, the protons on the carbons adjacent to the ring are shifted downfield by 0.60τ , while those on the central carbons are shifted by only 0.50τ .

The case of the 7,7-dimethyl[3](1,2)ferrocenophane is more complex, but the general trends remain the same. Watts, et al. [8] have reported that the bridge protons nearest the iron (*endo*) are deshielded relative to those opposite to the iron (*exo*) in the unprotonated compound. The chemical shift differences between the *endo* and *exo* protons are relatively large, being 0.37τ for the methylene protons and 0.33τ for the methyl protons. In the protonated species, a difference of 0.17τ is observed for the methyl protons and the chemical shifts for the *endo* and *exo* methylene protons are identical. This reduction of the *endo* and *exo* proton chemical shift differences is another indication of the magnetic environmental changes which occur upon protonation.

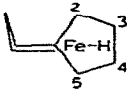
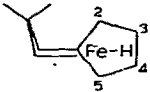
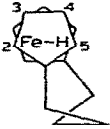
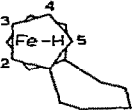
[m] Ferrocenophanes

The NMR spectra of the simple heteroannularly bridged ferrocenes, [3]ferrocenophane, 7,7-dimethyl[3]ferrocenophane, [4]ferrocenophane and [5]ferrocenophane have been recorded with trifluoroboric acid as the solvent. Chemical shift values and proton assignments for the protonated species are presented in Table 2. Ring proton assignments for the unsubstituted ferrocenophanes are supported by preparation and subsequent protonation of 2,5-dideutero derivatives of the ferrocenophanes. Bridge proton assignments were established by the preparation of specifically deuterated derivatives from ketones of known structure. All ferrocenophanes underwent protonation at the metal as evidenced by the high field, one proton resonance in the range of 11.0 to 12.0 τ . Bridge proton resonances of [3]ferrocenophane and its dimethyl derivative are sharp as in the parent compound and the resonances of the bridge protons in [4]- and [5]ferrocenophane closely resemble those of the unprotonated compounds in both line shape and width.

The ring proton resonances of [3]ferrocenophane and its dimethyl derivative are very similar with two, well separated proton resonances. The lower field resonance is resolved into two distinct maxima in the case of the [3]ferrocenophane, but is broad and unresolved in the case of the dimethyl compound. Deuteration of the 2- and 5- positions of [3]ferrocenophane allowed the unambiguous assignment of the higher field resonance to these protons. In keeping with the previous shielding arguments, the protons adjacent to the bridge must occupy or be adjacent to the region of closest ring approach. As the parent compound is known to be slightly tilted in the direction of the bridge the most likely conformation for the protonated species is one in which the bridge retains the position of closest interring approach. This conformation is illustrated in Fig. 2a.

The splitting of the downfield ring proton resonance in [3]ferrocenophane

TABLE 2
NMR PARAMETERS FOR [*n*]FERROCENOPHANES (CHEMICAL SHIFTS IN τ)

Compound	Protons observed	CDCl ₃	HBF ₃ OH
[3] Ferrocenophane 	H(2), H(5) H(3), H(4) (CH ₂) ₃ Fe-H	6.11 6.11 8.04 —	5.12 4.82 (d, <i>J</i> = 4 Hz) 7.58 11.13 (q, <i>J</i> = 4 Hz)
7,7-Dimethyl- [3] Ferrocenophane 	H(2), H(5) H(3), H(4) (CH ₂) ₂ (CH ₃) ₂ Fe-H	5.97 6.06 8.05 8.36 —	5.12 4.96 7.63 8.66 10.93
[4] Ferrocenophane 	H(2), H(3) H(4), H(5) (CH ₂) _α (CH ₂) _β Fe-H	6.09 6.09 7.60 8.13 —	4.85 4.60 7.03 7.84 12.00
[5] Ferrocenophane 	H(2), H(3) H(4), H(5) (CH ₂) _α (CH ₂) _{β,γ} Fe-H	6.03, 6.12 6.03, 6.12 7.71 8.05 —	4.97 4.52 7.42 8.25 11.72

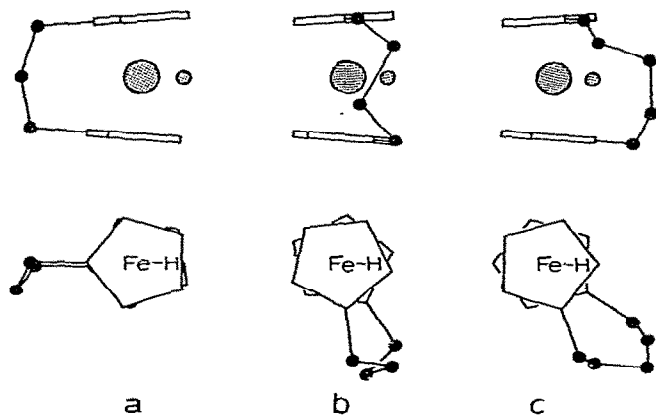


Fig. 2. Average conformations of the protonated bridged ferrocenophanes: (a) [3]ferrocenophane, (b) [4]ferrocenophane, (c) [5]ferrocenophane. These conformations are based on Dreiding stereomodels assuming a 10–15° ring tilting.

and perhaps also the broadening of this resonance in the dimethyl derivative are probably the result of spin-spin coupling between these ring protons and the iron-hydrogen. The iron-hydrogen resonance in the spectrum of [3]ferrocenophane is broadened and appears to be a rough quintet for which the separations are 4.0 Hz, identical to that of the downfield ring-proton doublet. Although a spin decoupling experiment was not possible with the existing instrument, iron-hydrogen coupling of about 2 Hz has been observed in the spectrum of protonated ferrocene and values up to 18 Hz have been recorded in our studies [9]. The magnitude of the coupling constant in the protonated ferrocenophanes appears to be dependent upon the dihedral angle between the iron-hydrogen and the ring-hydrogen, with the coupling constant decreasing with an increase in the angle. A coupling constant of 4 Hz is typical of ring protons having about a 36° dihedral angle with the iron-hydrogen. Coupling between the iron-hydrogen and the ring protons at positions 2 and 5 cannot be excluded, but are not resolved.

The spectra of [4]- and [5]ferrocenophane in trifluoroboric acid are similar with the ring proton resonances split into two signals. The upfield resonance of the protonated [4]ferrocenophane is broadened relative to the downfield resonance, while the opposite is true for the protonated [5]ferrocenophane. No iron-hydrogen multiplicity is resolved in either case. Deuteration of the 2- and 5- ring positions of both ferrocenophanes reduces the intensity of the low and high field resonances equally.

The spectral evidence requires that the protons which occupy similar ring positions relative to the bridge must be exposed to different magnetic environments in the protonated species. This requirement immediately rules out any conformation in which the bridge is symmetrically positioned in either the region of closest ring approach or the open face. It is, however, consistent with a conformation in which the bridge is to the side of the ring-tilted ferrocene. The conformations illustrated in Figures 2b and 2c are average conformations recognizing that a degree of oscillation of the bridges and rings is allowed within the limits imposed by the length of the bridge. An oscillation about the open face of the species, such as that illustrated in Figure 3, is either precluded or is slow on the NMR time scale.

The simple ring resonance patterns in the spectra of [4]- and [5]ferrocenophane require that the ring protons are divided into two distinct magnetic environments by the asymmetric placement of the bridge. In keeping with previous arguments, we assign the protons in the region of closest approach, arbitrarily the set 2, 2', 3 and 3', to the upfield signal, and the remaining pro-

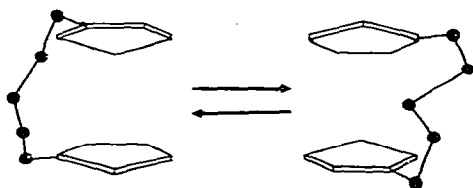


Fig. 3. Side to side bridge flip of a long bridge. This oscillation is either blocked or slow on the NMR time scale.

tons which are in the open face to the downfield signal. The simplicity of the ring proton resonances are deceptive and result from the accidental overlap of the resonances of the proton pairs in the two environments. As will be reported later [9], introduction of alkyl bridge substituents gives rise to more complex ring proton patterns, apparently because the substituents reduce the oscillatory freedom of the bridges and in turn limit the tick-tocking of the rings.

The shapes and line widths of the bridge proton resonances of the ferrocenophanes are unaffected by protonation of the iron, but there are changes in the chemical shifts which reflect both the effects of electron withdrawal and the diamagnetic anisotropy of the protonated species. For example, the sharp methylene resonances of protonated [3]ferrocenophane and its dimethyl derivative are shifted downfield by 0.46 and 0.42 τ , respectively, which is in accord with the expected electron withdrawal accompanying protonation. In contrast, the methyl resonance in the spectrum of the dimethyl derivative is shifted upfield by 0.30 τ , indicating that the methyl groups must be immersed in a shielding field at some point along their path. The position and shape of this field is further defined by the fact that it affects the bridge methyls but apparently not the central methylene protons of the parent [3]ferrocenophane. It is most likely that the source of this shielding is the field in the region of closest ring approach which is accessible to the bridge methyls but not to the methylene protons. It is also possible that the methyl groups might approach the iron atom more closely in the protonated species than they do in the parent, which would also have the effect of shielding the methyl protons.

Assignment of bridge proton resonances in the spectra of [4]- and [5]ferrocenophane was made through the use of specifically deuterated compounds prepared from bridged ketones of known structure. It was found that in both the protonated and unprotonated cases, the methylenes adjacent to the rings have a resonance downfield of the nonadjacent methylenes. Protonation causes the resonance of the adjacent methylenes to shift downfield by 0.57 and 0.29 τ for the [4]- and [5]ferrocenophanes, respectively. The nonadjacent methylenes of [4]ferrocenophane are shifted downfield by 0.29 τ while the nonadjacent methylenes of [5]ferrocenophane are shifted upfield by 0.20 τ . This difference in behavior of these two sets of nonadjacent methylenes is certainly not related to any reversal of the inductive withdrawal imposed by the presence of one more bridge methylene, but is more likely a sign that the central bridge methylenes in the longer bridge are encountering a region of shielding not seen by the shorter bridge. As the only major geometric difference between these two com-

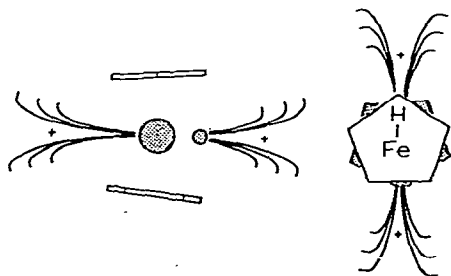


Fig. 4. Proposed contours of diamagnetic anisotropy of protonated ferrocenes.

pounds is that the longer bridge is expected to be able to extend further into the open face of the molecule, we suggest that this shielding field lies along the iron-hydrogen axis and is the symmetric complement of the field in the region of closest ring approach. The general contours of this region are given in Fig. 4.

Trifluoroacetic acid solvent system

NMR spectra of ferrocene in a variety of acid media including HBF_3OH [1-5], HFSO_3 [9,10], HBF_4 [11], a mixture of trifluoroacetic acid and HBF_3OH [5], and pure trifluoroacetic acid [5] have been recorded. In all solvents except trifluoroacetic only the metal-protonated species was observed. In trifluoroacetic acid, no iron-hydrogen resonance was observed, but the chemical shift of the ferrocene was intermediate between that of protonated ferrocene and unprotonated ferrocene, leading Curphey, et al. [5] to conclude that rapid proton exchange between the solvent and the ferrocene was occurring.

In 1972, Illuminati and his coworkers [12] reported that the integration of the unsubstituted ring resonance of bromoferrocene increased from five to six protons when the compound is in a benzene solution with trifluoroacetic acid. The conclusion which was drawn from this was that a long-lived sigma complex was the major species in this weaker acid medium. Although Illuminati, et al. [13] later noted that this experiment could not be reproduced, the obvious importance of the observation prompted us to attempt to reproduce Illuminati's experiment.

In our hands, the NMR spectrum of bromoferrocene in benzene with trifluoroacetic acid broadens with time due to oxidation, but no change in the relative areas of the substituted and unsubstituted ring resonances was detected. Analysis of the reaction products by GC/MS showed that both ferrocene and bromoferrocene were present. The ferrocene is presumably formed from bromoferrocene by the protodehalogenation reaction first reported by Nesmeyanov, et al. [14], and found by us to occur almost instantaneously when bromoferrocene is dissolved in trifluoroboric acid.

To further test the possibility of forming ring-protonated intermediates in moderately strong acids, ferrocene and several ferrocenophanes were examined in trifluoroacetic acid. It was found that [5]ferrocenophane and 8-phenyl-[5]ferrocenophane were insufficiently soluble in the acid to permit a spectrum to be recorded, but ferrocene, [3]ferrocenophane and [4]ferrocenophane were successfully studied.

Sample preparation for studies in trifluoroacetic acid was generally more stringent than that employed with trifluoroboric acid, since both oxygen and light had to be avoided. The sensitivity of ferrocenes to irreversible photooxidation by trihaloacetic acids and their anhydrides was reported by us as part of our investigation of the reactions of protonated ferrocenes with oxygen and sulfur dioxide [2], and has also been noted by Castagnola, et al. [15].

The chemical shifts and spectral assignments for the ferrocenes in trifluoroacetic acid are presented in Table 3 along with the values for these compounds in deuterochloroform and trifluoroboric acid. Comparison of these values in the different solvents shows that, with one exception, the resonances of the ferrocenes in trifluoroacetic acid fall between those of the unprotonated and fully protonated species. No iron-hydrogen resonance is found in the spectra in tri-

TABLE 3

NMR PARAMETERS FOR [*n*]FERROCENOPHANES IN SELECTED SOLVENTS (CHEMICAL SHIFTS IN τ)

Compound	Proton observed	CDCl ₃	CF ₃ CO ₂ H	HF ₃ BOH
[3]Ferrocenophane	(CH ₂) ₃	8.04	7.90	7.58
	C ₅ H ₄	6.11(8 H)	5.22(4 H) 4.97(4 H)	5.12(4 H) 4.82(4 H)
[4]Ferrocenophane	(CH ₂) _β	8.13	8.78	7.84
	(CH ₂) _α	7.60	7.33	7.03
	C ₅ H ₄	6.09	5.27(5 H) 5.04(4 H)	4.85(4 H) 4.60(4 H)

fluoroacetic acid, nor is there any increase in the integration of the ring proton resonances relative to the bridge resonances which might indicate the formation of a long-lived ring protonated species. The ring resonances of the ferrocenophanes are split into two four-proton singlets whose separations are only slightly smaller than those of the protonated species. The bridge resonances of both compounds retain the shape observed in the other solvents. The only unusual feature is that the chemical shifts of the central methylene protons of [4]ferrocenophane are displaced upfield of their position in the unprotonated species, rather than downfield as would have been expected.

The general features of these spectra reinforce the original conclusion of Curphey, et al. [5] that rapid proton exchange between the ferrocene and the solvent is occurring, but they do not provide unambiguous evidence for the identity of the predominant protonated species in this exchange. The similarity of the ring proton resonances in trifluoroacetic acid and in trifluoroboric acid hint at a structural similarity between the species in the two solvents. Also the strongly upfield shift of the central bridge methylenes in [4]ferrocenophane can be interpreted as resulting from the shielding of the bridge by a field created along the axis of a rapidly equilibrating iron-hydrogen bond. Unfortunately, these conclusions must be regarded as tentative until further studies on the behavior of ferrocenes in acids can be conducted.

Experimental

NMR spectra were recorded on a Varian Associates A-60A NMR Spectrometer at an ambient temperature of 30–40°C. Tetramethylammonium tetrafluoroborate and tetramethylammonium bromide were used as standards as the 6.67 τ ammonium resonance is sharp and unaffected by the acid environment.

Sample preparation

Trifluoroboric acid. 10 mg of standard and 30–35 mg of ferrocene compound were placed in an NMR tube and the tube was evacuated. After 10 minutes, the tube was filled with nitrogen, acid was rapidly added, and the mixed sample was placed into the instrument. All spectra were recorded within ten minutes of mixing.

Trifluoroacetic acid. The fundamental procedures for the sample preparation

described above were followed except that an amber NMR tube was used and the acid was transferred to the NMR tube by trap-to-trap distillation.

Sample decomposition screening

After recording the spectrum of a sample, the contents of the NMR tube were poured into 2 ml of water and shaken with ethyl ether to remove the ferrocene. If oxidation was indicated by blue coloration in the water layer, tin(II) chloride was added to reduce the oxidized material which was then extracted with a second aliquot of ether. The ether extracts were washed with water and dried over sodium sulfate. TLC comparison of the ether extracts with samples of the authentic compounds were made. In no instance was decomposition or rearrangement observed at the level detectable by TLC.

Materials

Original samples of several ferrocenophanes were the generous gifts of Drs. William Watts and T. Derrick Turbitt. Later samples were prepared by established literature methods and conformed to expected physical and spectral properties. 2,5-Dideutero derivatives were prepared via 2,5-dideutero(dimethylaminomethyl)ferrocene prepared by the method of Rausch and Siegel [16]. Deuterated derivatives were found to be 70% deuterated in the 2,5-positions by NMR integration.

Acknowledgements

We wish to thank Drs. William Watts and T. Derrick Turbitt for their gifts of compounds and numerous suggestions and Dr. Charles Rowell for his editorial advice. We thank the Research Corporation and the Naval Academy Research Council for their support of this research.

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