Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

METALLOCENE BASICITY

I. RING TILT AND RESTRICTED ROTATION IN PROTONATED ALKYLFERROCENES

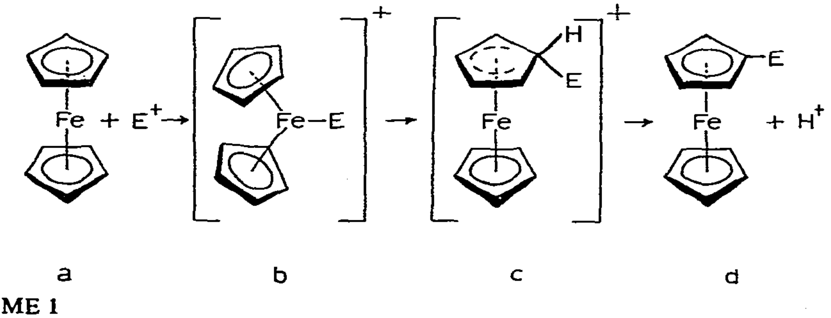
THOMAS E. BITTERWOLF and A. CAMPBELL LING*
Department of Chemistry, West Virginia University, Morgantown, W. Va. 26506 (U.S.A.)

(Received July 20th, 1971)

SUMMARY

Protonation at the metal is shown to occur in boron trifluoride monohydrate solutions of various alkylferrocene compounds. The structure of the resulting ferrocenonium ion is shown to involve tilted rings such that free rotation of substituted rings is no longer possible. Compounds studied include: 1-methyl-, 1,1'-dimethyl-, 1-ethyl-, 1,1'-diethyl-, 1-methyl-1'-ethyl-, and 1-methyl-2,5-dideuterioferrocene.

The discovery of the protonation of ferrocene in strong acids by Richards and coworkers[1] occurred in 1959, only a few years after the first examples of Lewis base behavior had been reported by Birmingham and Wilkinson[2]. Since that time, the nature and extent of the involvement of the iron atom in ferrocene chemistry has received considerable attention because of the obvious possibility that electrophilic attack at the metal could provide an intermediate on the way to ring substitution, as shown in Scheme 1[3].



SCHEME 1

Since the structure and properties of this postulated intermediate are central to the study of this mechanism, it was decided that an extension of Richards' original

---

* Author to whom correspondence should be addressed.

work might be informative. This investigation has produced the first definitive evidence for ferrocenes of the hypothesis by Ballhausen and Dahl[4] that the rings in protonated metallocenes are tilted (or "twisted" in their terminology). These conclusions are based on the close analogy between these complexes and the ferrocenophanes in which, as presented in the elegant work by Watts *et al.*[5], ring tilting produces readily observable NMR effects.

EXPERIMENTAL

A Varian Associates Model T-60 NMR Spectrometer was used throughout. $BF_3 \cdot H_2O$ was freshly prepared as needed, although it was noted that ageing of the acid produced no discernable effect on the recorded spectra. The NMR standard used was pivalic acid. All compounds were either purchased, or prepared by standard techniques. 1-methyl-2,5-dideuterio-ferrocene was prepared by the method of Rausch[6],

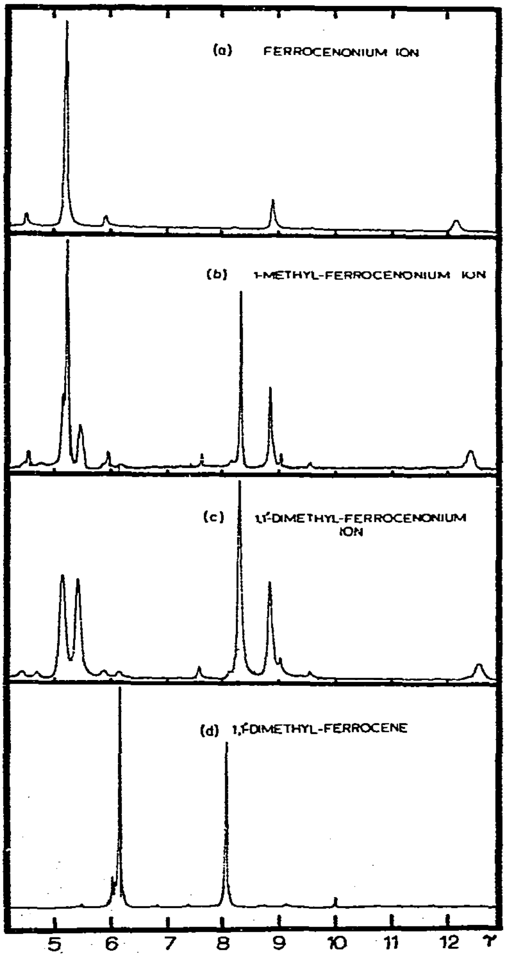


Fig. 1. NMR spectra of ferrocene derivatives and protonated ferrocene derivatives.

TABLE 1

NMR DATA FOR VARIOUS SUBSTITUTED FERROCENES IN $BF_3 \cdot H_2O$ SOLUTION

Parent compound	*Proton observed in ferrocenonium complex*	*Chemical shift*[a] (τ)	Δ(*parent*)[b] (τ)	Δ(*doublet*)[d] (*Hz*)
Ferrocene	C_5H_5	5.06	−0.90	—
	Fe–H	12.03		
1-Methylferrocene	CH_3	8.23	+0.16	
	C_5H_4	5.15[c]	−1.02	19
	C_5H_5	5.22	−0.83	
	Fe–H	12.33		
1-Ethylferrocene	CH_3	8.98	+0.13	
	CH_2	8.15	+0.48	
	C_5H_4	5.05[c]	−0.99	14
	C_5H_5	4.98	−1.02	
	Fe–H	12.22		
1,1′-Dimethylferrocene	CH_3	8.22	+0.15	
	C_5H_4	5.23[c]	−0.94	17
	Fe–H	12.52		
1,1′-Diethylferrocene	CH_3	9.00	+0.15	
	CH_2	7.83	+0.15	
	C_5H_4	5.10[c]	−1.02	13
	Fe–H	12.33		
1-Methyl-1′-ethylferrocene	CH_3 (methyl)	8.03	−0.09	
	C_5H_4	5.15[c]	−1.05	16
	CH_3 (ethyl)	8.85	−0.07	
	CH_2	7.70	−0.07	
	Fe–H	12.27		

[a] Relative to pivalic acid (2,2-dimethylpropanoic acid) at τ 8.77 corresponding to 74 Hz below TMS.

[b] Change is calculated from the parent compound in CCl_4 solution.

[c] Values for the mid-point of the symmetric doublet.

[d] Difference in chemical shift for the A_2B_2 doublet ring proton resonance.

and found to be 70% deuterated by NMR integration. While no specific efforts were made to remove air from the NMR tubes, it should be noted that the $BF_3 \cdot H_2O$ degasses slightly when placed in the tubes thus effectively removing most of the air. The reaction of air with protonated ferrocene is discussed elsewhere[17].

RESULTS

The NMR spectra for ferrocene, 1-methylferrocene and 1,1′-dimethylferrocene in $BF_3 \cdot H_2O$ are shown in Fig. 1. Chemical shifts and other pertinent data are presented in Table 1.

DISCUSSION

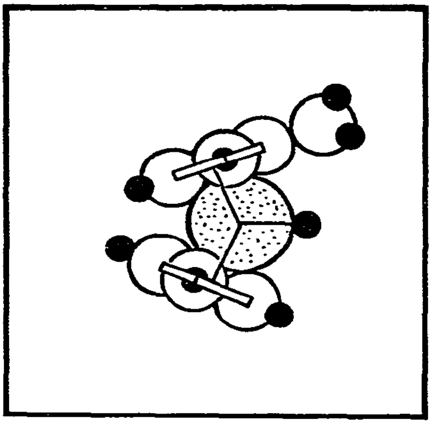
In their discussion of bonding of dicyclopentadienylmetal hydrides and protonated complexes, Ballhausen and Dahl[4] demonstrated that considerable tilting of the rings (up to a dihedral angle of 145°) could occur with little reduction in the metal to ring bond strength. This tilting, and concurrent rehybridization of the metal "non-bonding" *d* orbitals, has been used to explain the structures and formulations of all known metallocene hydrides and proton or Lewis acid adducts, and has been expanded to include protonated metal carbonyl systems as well. Kotz and Pedrotty[7] have recently reviewed the literature in this broad field.

While ring tilting has been confirmed by X-ray crystallography for several metallocenes,[8] evidence for its occurrence in non-bridged ferrocenes is sparse, but ESR analysis of radical species produced by γ radiolysis of crystalline ferrocene at low temperatures has produced evidence for ring tilted species[9]. A recent X-ray investigation by deBoer *et al.*[10] of 1,1'-dimethylferrocenium triiodide has shown that the methyl groups are eclipsed with an indicated dihedral angle between the rings of ca. 6°. This angle is in contrast to the parallel rings found by Gray and Schlueter[11] for the ferrocenium trichloroacetate salt which tends to support deBoer's assumption that the tilt is a result of electronic repulsions between the adjacent methyls. IR studies by Pavlik and coworkers[12] on ferrocenonium tetrachloroaluminate have offered some pertinent evidence for ring tilting resulting from protonation.

In contrast to the non-bridged compounds, the bridged ferrocenophane compounds [3] ferrocenophan-1-one[13] and 1,1,2,2-tetramethyl-[2] ferrocenophane[14] have been shown by X-ray crystallography to have dihedral angles of 9° and 27°, respectively. These and other ferrocenophane compounds have been extensively studied by Watts and coworkers[5], who have demonstrated that ring tilting leads to a characteristic NMR A_2B_2 pattern from the ring protons, in which the separation ($\Delta\tau$) of the A_2B_2 pattern is directly dependent upon the angle of tilt. The pattern arises from the differential shielding experienced by the α and β protons due to the distortion of the molecule by the bridge.

In agreement with Richards[1], we find that ferrocene in $BF_3 \cdot H_2O$ (Fig. 1a) exhibits a sharp doublet at τ 5.06 and a broad peak at τ 12.03. The sharply defined ring resonance implies that the two rings are free to rotate as they are in the unprotonated compound. Similarly, it was found that the proton resonance from the unsubstituted ring in protonated 1-methyl- and 1-ethyl-ferrocene appears as a sharp doublet, and thus is presumed to be free to rotate also. On the other hand, ring resonance from the substituted ring leads to a doublet with relatively broad constituent peaks. (Fig. 1b). Further, the ring resonance from 1,1'-diethylferrocene is a broad symmetrical doublet. Since methyl and ethyl substituents have been reported to have little influence on the chemical shift of ring protons in substituted ferrocenes[15], it seems clear that the observed difference in chemical shifts must arise from some other source. This point is clearly illustrated for 1,1'-dimethylferrocene and its ferrocenonium analog by comparison of Fig. 1c with 1d.

An explanation of the observed differences can be made if it is assumed that protonation at the metal leads to tilting of the rings with concomitant restricted rotation. It is energetically unfavorable, therefore, for a substituent to reside in the region of closest approach, the "pinch position" (Fig. 2). The substituted rings, however, are assumed to be free to oscillate about the ring-metal axis in a manner that Watts[16] describes as a "tick–tock" mechanism. Time averaging of the protons over the positions in the static models illustrated in Fig. 3 predicts that the α proton spend $\frac{1}{3}$ of their time in position a, $\frac{1}{3}$ in position b and $\frac{1}{3}$ in position c. The β protons on the contrary, spend $\frac{1}{3}$ of their time in position b but $\frac{2}{3}$ in position c. As the a, b and c posi-



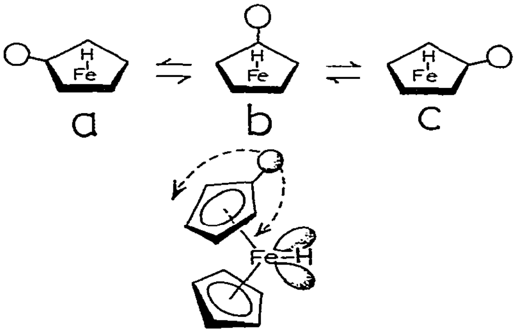


Fig. 2. Diagrammatic representation of protonated 1-methylferrocene, showing ring tilt and consequent restricted rotation at the pinch position. (●, hydrogen; ○, carbon; ⊛, iron).

Fig. 3. "Tick–tock" mechanism of restricted rotation in ring substituted ferrocenonium cations.

tions would be expected to differ in their relative shielding (*cf.* the ferrocenophane analogy) it follows that the α and β positions would have different chemical shifts, as observed.

Deuteration of the α position in methylferrocene* allowed assignment of the lower absorption to the α protons. It is significant that these α proton absorptions generally lie below, but very close to the position of the unsubstituted rings, while the β protons are higher by 0.22 to 0.32 ppm. Similarity between the α protons and the unsubstituted rings is expected, since time averaging of the unsubstituted ring protons indicates that they each spend $\frac{2}{5}$ of their time in the "pinch position", which is only slightly more than expected for the α protons. The β protons, on the other hand, spend a predominant fraction of their time very close to the plane of the iron hybrid orbitals which could account for their increased shielding, although their immediate proximity to the π electrons of the second ring may be an equally significant contributing factor. It is hoped that studies of the protonated ferrocenophanes will help to clarify this last point.

In addition to the A_2B_2 pattern, other features of these spectra warrant comment at this time. If it can be assumed, to a first approximation, that the difference in chemical shift between α and β protons represents a measure of the degree of ring tilt, as noted previously for the ferrocenophane series, then the order of decreasing tilt: $Me > Me_2 > MeEt > Et > Et_2$ can be established. This pattern is similar to that observed for the order of decreasing τ for the Fe–H protons: $Me_2 > Me > Et_2 > MeEt > Et > H$. Although it is tempting to seek to relate trends to relative metal basicity**, it is still not clear to what extent steric interactions of the alkyl groups might be affect-

---

* Under the experimental conditions, the deuterated methylferrocene compound was found to undergo hydrogen exchange and complete loss of deuterium within 20 minutes.

** This pattern follows the order of decreasing basicity, $Et_2 > Et > H$, observed by Sorokin[18] for p*K*a measurements.

ing the degree of tilting, or what importance dielectric shielding by the alkyls might play in determining the position of the Fe–H resonance[15].

A further consequence of protonation is that the alkyl substituent resonance tends to shift slightly upfield, while the ring protons (as observed for other protonated transition metal complexes[7]) shift significantly downfield. The reasons for the alkyl shift are not yet fully understood, but may be a combination of inductive electronic effects and Fe–H dielectric shielding[15]. We regard the major factor contributing to the downfield shift of the ring protons to be electron withdrawal from the metal to ligand bands as a result of the formation of the metal–proton bond. The forward σ and π bonding appears to play only a small part in the observed shift[19]. A full discussion of the role and consequences of the metal to ligand bonding in ferrocene and related compounds will be presented at a later time.

There are several conclusions and speculations which appear to be justified at this time. First, the spectra which we have presented appear to dispel absolutely the suggestion by Traylor and Ware[20] that the observed NMR for unsubstituted ferrocenonium arises from a rapid exchange of the proton between the cyclopentadienyl rings. Such behavior would result in far more complicated spectra for the substituted rings than are, in fact, observed.

It is also clear from the absence of absorptions attributable to a σ ring complex that this complex has a lifetime which is very short compared to that of the protonated species and thus a concentration below the detectable limit for NMR. The immediate proximity of the metal bound proton to the ring in ferrocenonium would also obviously facilitate exchange. It appears highly probable that hydrogen exchange (and other reactions involving electrophilic proton attack) occur via rearrangement of the ferrocenonium species. This mechanism is outlined in Scheme 1, where E^+ is H^+, and, as described by Setkina and Kursanov[21], is consistent with the known kinetic data.

It is also interesting to speculate on the effect that the observed ring tilting might have on the relative site reactivity of ferrocene. It is clear from the earlier discussion that if the rings are free to oscillate, then the α position will be adjacent to a metal bound electrophile for a statistically longer period than the β position. However, if the electrophile is sufficiently large the possibility arises that the ring substituent might be constrained to the positions shown in Fig. 3a and 3c thus placing both the α and β positions in convenient proximity for attack. The experimental evidence available at this time[22] is insufficient to enable us to draw any conclusions on this intramolecular steric effect and we present it here only as an indication to those attempting to interpret site reactivities in electrophilic reactions of ferrocene.

ACKNOWLEDGMENTS

We thank the Research Corporation for partial support of this project.

REFERENCES

1 T. J. Curphey, J. O. Santer, M. Rosenblum and J. H. Richards, *J. Amer. Chem. Soc.*, 82 (1960) 5249.
2 G. Wilkinson and J. M. Birmingham, *J. Amer. Chem. Soc.*, 77 (1955) 3689.
3 M. Rosenblum, *Chemistry of the Iron Group of Metallocenes, Part I*, Wiley–Interscience, New York, 1965.
4 J. P. Dahl and C. J. Ballhausen, *Acta Chem. Scand.*, 15 (1961) 1333.

5 T. H. Barr and W. E. Watts, *Tetrahedron*, 24 (1968) 6111.

6 M. D. Rausch and A. Siegel, *J. Organometal. Chem.*, 17 (1969) 117.

7 J. C. Kotz and D. C. Pedrotty, *Organometal. Chem. Rev. A*, 4 (1969) 479.

8 P. S. Wheatley, in J. D. Dunitz and J. A. Ibers (Eds.), *Perspectives in Structural Chemistry, Vol.* 1, Wiley, New York, 1967.

9 L. Saito, *J. Chem. Phys.*, 50 (1969) 3539.

10 J. W. Bais, J. J. de Boer and D. Bright, *Inorg. Chim. Acta*, 5 (1971) 605.

11 H. B. Gray and A. Schlueter, personal communication.

12 (a) I. Pavlik and J. Klikorka, *Proc. 9th Intern. Conf. Coordin. Chem.*, Page 21; (b) I. Pavlik and J. Klikorka, *Coll. Czech. Chem. Comm.*, 30 (1965) 664.

13 M. B. Laing and K. N. Trueblood, *Acta Cryst.*, 19 (1965) 373.

14 N. D. Jones, R. E. Marsh and J. H. Richards, *Acta Cryst.*, 19 (1965) 330.

15 K. L. Reinhard, Jr., D. E. Bublitz and D. Gustafson, *J. Amer. Chem. Soc.*, 85 (1963) 970.

16 W. E. Watts, personal communication.

17 T. E. Bitterwolf and A. C. Ling, *J. Organometal. Chem.*, 40 (1972) C29.

18 J. A. Sorokin and G. A. Domratchev, *Trudy po Chimii i Chim. Technologii*, (1961) 665.

19 J. C. Kotz and D. G. Pedrotty, *J. Organometal. Chem.*, 22 (1970) 425.

20 (a) T. G. Traylor and J. C. Ware, *J. Amer. Chem. Soc.*, 89 (1967) 2304.
(b) T. G. Traylor and J. C. Ware, *Tetrahedron Letters*, (1965) 1295.

21 V. N. Setkina and D. N. Kursanov, *Russian Chem. Rev.*, 37 (1968) 737.

22 D. W. Slocum and C. R. Ernst, *Organometal. Chem. Rev. A*, 6 (1970) 337.