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Preliminary communication

Metallocene basicity

III. Protonation of compounds containing two ferrocenyl moieties

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In continuation of our research[1,2] on metallocene basicity, we have investigated the behaviour of several compounds containing two ferrocenyl moieties to protonation in $BF_3 \cdot H_2O$ media. As shown in Table 1, biferrocenyl, diferrocenylmethane, and 1,2-diferrocenylethane, all undergo protonation at both iron atoms. The broadness of the ring resonance signals in the spectra shown in Figure 1a, b, and c, are possibly caused by anisotropic environments resulting from twisting of the two protonated ferrocenyl species, however, paramagnetic broadening by d^5 oxidation products at low concentrations cannot be entirely ruled out. The downfield position of the substituted cyclopentadienyl ring

TABLE 1

PROTON NMR DATA FOR PROTONATED BIFERROCENYL AND DIFERROCENE COMPOUNDS IN $BF_3 \cdot H_2O$

Compound	*Proton observed*	*Chemical shift (τ)* [a]
Biferrocenyl	$H_{2,5}$	4.17
	$H_{3,4}$	4.58
	C_5H_5	4.70
	Fe–H	12.15 [b]
Diferrocenylmethane	CH_2	–
	Rings	4.62 (br)
		ca. 4.53 (sh)
	Fe–H	11.79 [b]
1,2-Diferrocenylethane	C_2H_4	7.33
	Rings	4.70 (br)
		ca. 4.83 (sh)
	Fe–H	11.79 [b]

[a] Tetramethylammonium (TMA^+) bromide used as internal standard (τ 6.67). [b] Integration area of 2 units.

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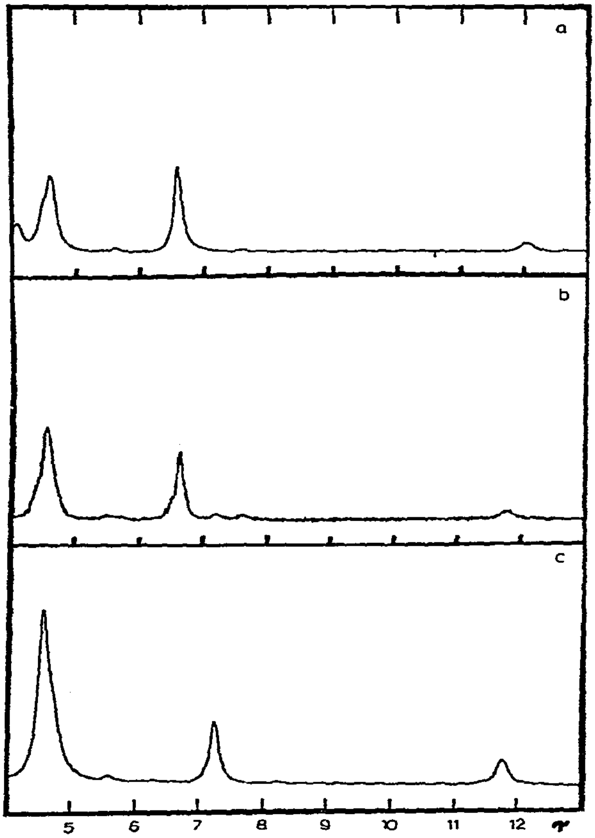

Fig. 1. Proton NMR spectra for biferrocenyl and diferrocene compounds in $BF_3 \cdot H_2O$ media. (a) Biferrocenonium with tetramethyl ammonium ion (TMA^+) as internal standard (τ 6.67) (b) Diferrocenonium-methane with tetramethylammonium ion (TMA^+) as internal standard (τ 6.67). (c) 1,2-Diferrocenonium-ethane.

proton resonances relative to those of the unsubstituted rings, and the gradual diminution of this downfield shift as methylene groupings are inserted between the ferrocenyl moieties suggests that the shift is attributable to electron withdrawal by the protonated ferrocenes*.

In contrast to previous observations on simple ferrocenes[1,2], the protonated compounds discussed thus far undergo slow oxidation *in situ* even though strict precautions were instituted to prevent oxygen from entering the system. The rate of oxidation was observed to decrease as the separation between the ferrocenyls increased. Fortunately, this oxidation did not become severe within the time limits necessary to record and integrate one scan (ca. 10 min), but additional broadening and downfield shifts were noted after about 20 minutes.

In conjunction with Watts[3], an attempt was made to expand this investigation to two [1,1] ferrocenophane derivatives. Watts and Turbitt[4], had previously observed that

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* This conclusion is supported by further examples of protonated ferrocenes containing electron withdrawing substituents, data which will be presented at a later time.

1,1,12,12-tetramethyl[1,1]ferrocenophane was stable to structural decomposition in trifluoroacetic acid solution, but that it did undergo slow oxidation. All attempts by us to protonate the parent [1,1]ferrocenophane, or its 1,12-dimethyl derivative, by excess $BF_3 \cdot H_2O$ to obtain a sample suitable for NMR analysis, resulted in immediate oxidation of the compound, and a considerable amount of gas evolution. The starting compounds could be recovered quantitatively without structural decomposition by reduction with $SnCl_2$, and chromatographic examination of the reduced material confirmed that no new products had been formed.

To further investigate this reaction between ferrocenophane and acid, a microtensiometric examination was performed, which revealed that one mole of a gas (noncondensible at 77 K and assumed to be hydrogen) was evolved for every mole of ferrocenophane. The reaction, in contrast to the slow oxidation of 1,1,12,12-tetramethyl-[1,1]ferrocenophane observed by Watts and Turbitt, was complete within seconds after acid addition.

An explanation of the ready oxidation of the [1,1]ferrocenophanes follows from the evidence presented thus far on the singly bridged ferrocenes, Fc-$(CH_2)_n$-Fc where $n = 0, 1, 2$. Since it has already been shown that the singly bridged ferrocenes are protonated at both ferrocenyl(Fc) moieties, it is reasonable to assume that both irons of the [1,1]ferrocenophanes are protonated in identical acid media as well. Such a diprotonated species would be expected to have a structure similar to that shown in Fig.2, which is based on the known structure of the 1,12-dimethyl derivative[5], as well as the conformational evidence presented in an earlier paper[2]. It should be noted that a simple twisting of the molecule would place the hydrogens within bonding distance of each other, from which conformation H_2 could be eliminated, leaving both metals oxidized. The difference in reaction rates observed by Watts and Turbitt in trifluoroacetic acid, and those reported here, can be accounted for in terms of the substantially

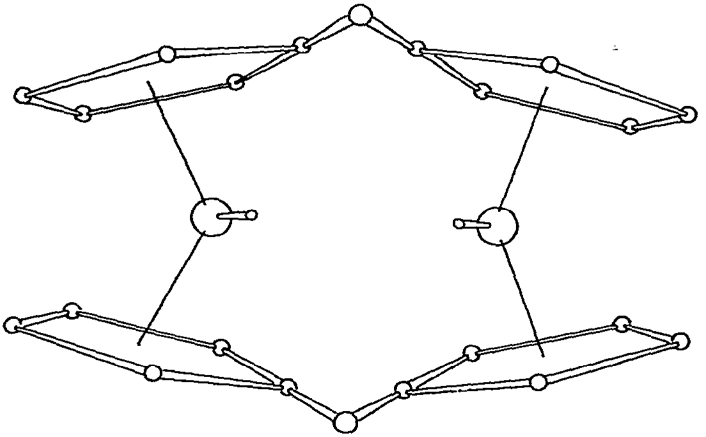

Fig.2. Proposed model for the di-protonated [1,1]ferrocenophane.

lower concentration of double-protonated species in the weaker acid.

The hydrogen evolution reaction could also account for the gradual oxidation of the singly bridged biferrocenyl compounds mentioned above. However, in the case of the singly bridged compounds, oxidation is slowed by the reluctance of the two ferrocene groupings to assume a *syn*-orientation necessary to place the two hydrogens within bonding distance of each other.

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