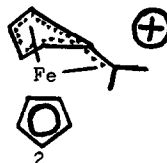# THE STRUCTURE OF α-FERROCENYL

CARBONIUM IONS

R. G. Sutherland[*], J. R. Sutton and W. M. Horspool[†]
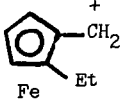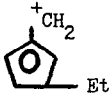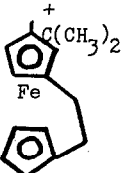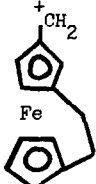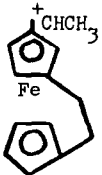
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The stability of α-ferrocenylcarboniums and the stereoselectivity of their reactions has given rise to considerable controversy as to the electronic and structural factors responsible for their unusual stability (1). However, it is clear that only the models presented by Richards (2) and Cais (3) as exemplified by structures 1 and 2 are in accord with the nmr results reported by various workers (4, 1c). We report on experiments which were designed to probe the differences between 1 and 2. Hence 1 requires a molecular distortion to allow better direct overlap between the vacant orbital and the iron atom. This process would convert the substituted ligand into a fulvene type ligand and it would be expected that any molecular feature which would prevent the required movement of the iron atom would result in the "destabilisation" of such a cation. Since 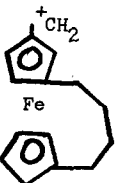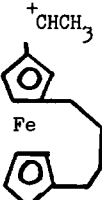Cais's model requires a bending mode of molecular distortion across $C_{2,5}$ with a displacement of the cationic centre towards the iron atom it would be predicted that such a model would not be destabilised as readily as that of Richards'. Accordingly we have synthesised a large number of α-ferrocenylcarbonium ions which are constrained by a [3] and a [4] carbon bridge and compared them with corresponding cations derived from 1,1-diethylferrocene which would have similar steric and electronic effects present. Some of our results are shown, in the table. Three parameters have been used to support structure 1. These are Δν, the chemical shift difference between ring protons $H_{2,5}$ and $H_{3,4}$; the variation

Ion	$\Delta\nu$, H_z	$\overset{+}{\delta}$C–H	δRing U	$\overset{+}{\delta}$C–R
3.	94	5.83, 5.67	4.97	–
4.	94	5.68	complex 4.75–5.08	–
5.	65	–	complex 4.49–4.58	$\overset{+}{}$ C–CH$_3$ 2.12, 2.22
6.	88	5.67, 5.50	complex 6.05–4.42	–
7.	96	5.76	complex 5.72–4.80	–
8.	89	6.70(q) 6.53(q)	5.47–4.46	$\overset{+}{}$ C–CH$_3$ 2.13 (d) 2.02 (d)

Ion	$\Delta\nu$,Hz	$\overset{+}{\delta}$C-H	δRing U	$\overset{+}{\delta}$C-R
9. $\overset{+}{C}HCH_3$ [structure: ferrocenophane with Fe]	95	6.91(q)	5.39→4.56	2.18(d)

of the chemical shift of H_6 directly attached to the cationic centre and the chemical shift of the protons of the unsubstituted ring. Experimentally it was found that the cations derived from the [3]- and [4]- ferrocenophanes were just as stable as those derived from simpler substrates. The $\Delta\nu$ values found differ little from those observed for the corresponding primary, secondary and tertiary cations which are 96, 89 and 81 Hz respectively. The chemical shifts of the carbinyl protons are quite similar to that of their unbridged counterparts which further weakens any hypothesis involving gross movement of the metal atom. It has previously been observed that the position of the unsubstituted cyclopentadienyl ring resonance varied with the substitution pattern of the cationic centre; the signal from a secondary ion being at lower field than that of a tertiary ion. It is more difficult to compare this feature since the "unsubstituted" ring resonances from bridged systems are widely spread. If we compare the mean chemical shifts of the bridged ions' unsubstituted ring we find that they are of very similar chemical shifts to their nonbridged counterparts. This indicates that the total shielding effect on the ring is not markedly affected by the imposition of a poly-methylene bridge. A surprising aspect of this study was the finding that there was a wide spread of the resonances for the unsubstituted ring in contrast to the singlet found in eg. [3] ferrocenophane indeed the ring multiplet found at lowest field in 6 belongs to the unsubstituted ring and the spread of resonance is greater in that ring than in the ring carrying the cationic centre. A similar effect is also seen in ion 4. The above results appear to support Cais model since the bridge should interfere with a lateral iron movement but not with bending of the cyclopentadienyl ring. A recent theoretical treatment due to Gleiter (5) also favors Cais's earlier proposal.

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References:

1. a. J. H. Richards and E. A. Hill, J. Amer. Chem. Soc., <u>81</u>, 3484 (1959)

    b. T. G. Traylor and J. C. Ware, J. Amer. Chem. Soc. <u>89</u>, 2304 (1967)

    c. J. Feinberg and M. Rosenblum, J. Amer. Chem. Soc. <u>91</u>, 4342 (1969)

2. E. A. Hill and J. H. Richards, J. Amer. Chem. Soc. <u>83</u>, 3840 (1961)

3. M. Cais, Organometallic Chem. Rev., 1966, <u>1</u>, 435

4. a. M. Cais, J. J. Dannenberg, A. Eisenstadt, M. I. Levenberg and J. H. Richards,
            Tetrahedron Letters, 1966, 1695

    b. W. M. Horspool and R. G. Sutherland, Chem. Commun., 1967, 786

    c. T. O. Turbitt and W. E. Watts, J. Organometal Chem., <u>49</u>, C30 (1973); Chem Commun.,
            1973, 182

    d. D. W. Slocum and C. R. Ernst, J. Org. Chem., <u>38</u>, 1621 (1973)

5. R. Gleiter and R. Seeger, Helv. Chim. Acta, <u>54</u>, 1217 (1971)