

ORGANOMETALLIC COMPOUNDS—IX*^{1, 2}

THE STRUCTURE OF α -FERROCENYL CARBONIUM IONS

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Abstract—The PMR spectra of α -ferrocenylcarbonium ions (I–V) have been examined at 100 MHz to assign the four protons of their substituted cyclopentadienyl rings by means of the double resonance technique. The long-range spin-spin coupling through the carbonium cation center has been observed. A model for the structure of the carbonium ion has been presented.

α -FERROCENYL CARBONIUM ions, which are formed through solvolysis reactions of α -hydroxyferrocene derivatives, are unusually stable.¹ Their structure and the cause of their stability have been discussed on the basis of their physical properties^{2, 7} and reactivity.^{8–9} The PMR spectra of the ions were interpreted by Cais *et al.*² with the model VI,^{1b} in which the Fe atom was assumed to shift towards the carbonyl C atom on the basis of the concept of metal direct participation. Traylor and Ware⁸ presented the model VII, and suggested that their stability was due to the resonance between the cyclopentadienyl ring and the carbonyl cation center, and that the Fe atom would not directly participate in the reactions. Recently, Hill and Wiesner⁶ reported that their results provided no basis for choice between the model VI and VII for the ions, and Feinberg and Rosenblum⁷ suggested that the ions would take a structure which was accompanied with molecular deformations and charge distribution very different from what could be expected in the models already presented.

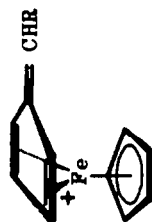
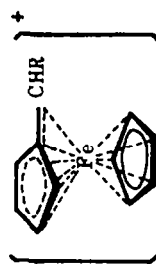
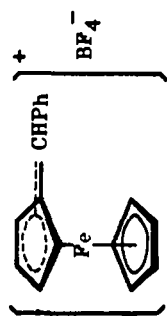
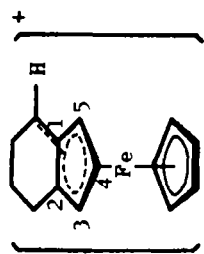
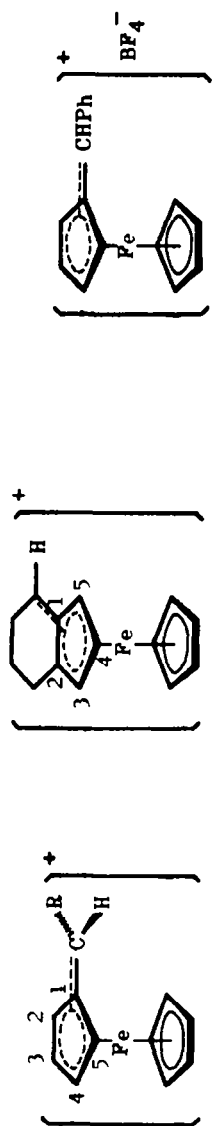
We studied the PMR spectra of the α -ferrocenylmethylcarbonium ion (I), α -ferrocenylethylcarbonium ion (II), α -ferrocenylphenylmethylcarbonium ion (III), 1,2-tetramethylene- α -ferrocenylcarbonium ion (IV), and α -ferrocenylphenylmethylcarbonium ion fluoroborate (V), respectively, in order to determine the exact structure of the ions. As a result, the signals of the substituted cyclopentadienyl ring protons have been assigned to each proton, and a model for the structure of the ions is presented.

RESULTS AND DISCUSSION

The spectra of the ions I–V are shown in Figs 1a–e, respectively. The signals of substituted ring protons of the ion IV appeared at δ 4.55 ppm (one proton) and about δ 6.09 ppm (two protons) as an ABX type, which were assigned from their intensity to the protons H₅, and H₃ and H₄, respectively. The spectra of the carbonium ions formed from the *endo*- and *exo*-isomers of IV agreed with each other. In the symmetric

*1 Part VIII. K. Yamakawa and M. Hisatome, *Tetrahedron* **26**, 4483 (1970).

*2 Presented in part at the 3rd Symposium on the Chemistry of Nonbenzenoid Aromatic Compounds, Symposium Papers pp. 52–54, Osaka, November 26–27 (1969).



carbonium ion I, the substituted ring protons appeared as two triplets (in spacing of 2.2 Hz) centered at δ 4.72 and 6.32 ppm (AA'XX' type). By analogy with the ion IV in the chemical shifts, the triplet at the lower field is assigned to the H₃ and H₄ protons, and then the signal at the higher field to the H₂ and H₅ protons.

On the other hand, four protons of the substituted ring in the ions II and III showed different chemical shifts. When the four protons of the monosubstituted cyclopentadienyl (Cp) ring are magnetically non-equivalent, the signal of each should be

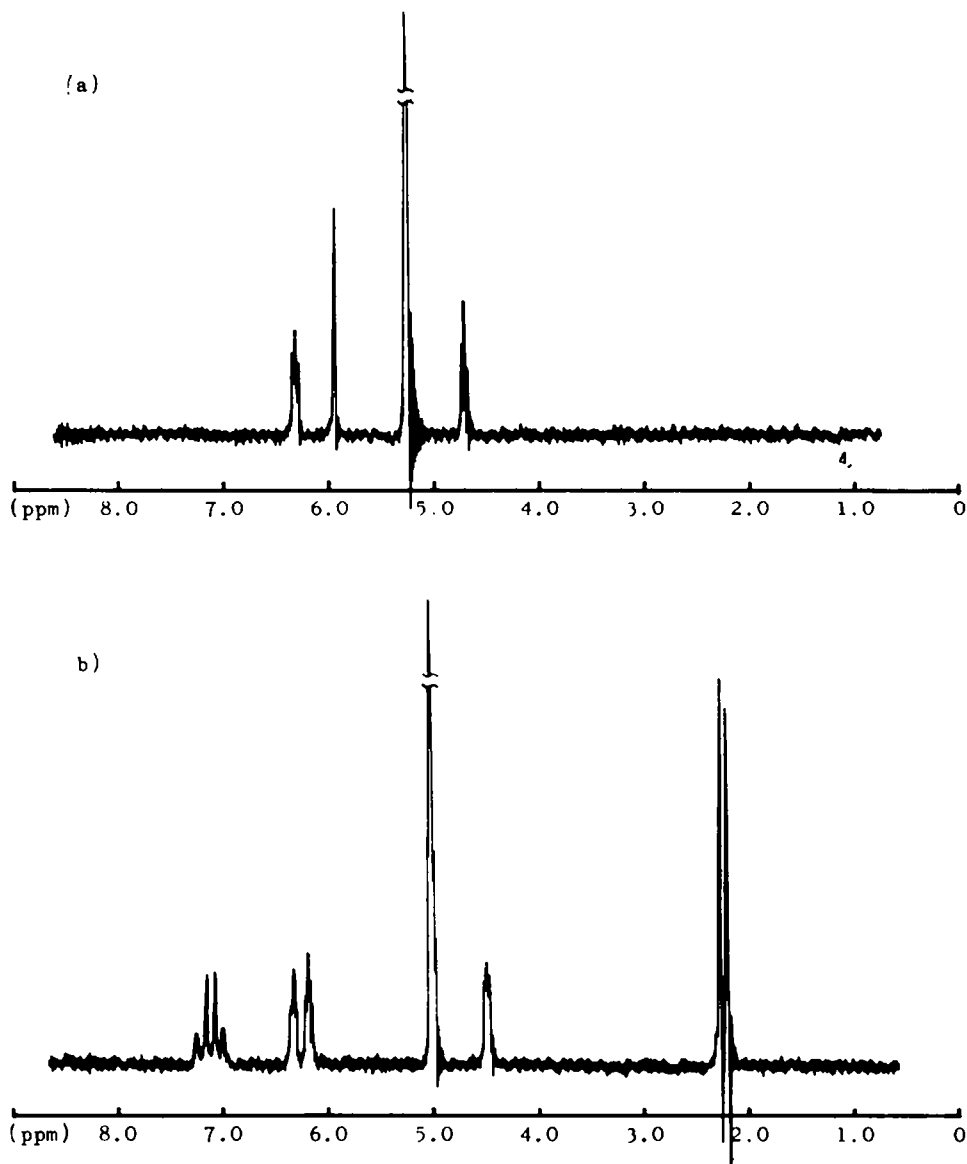


FIG. 1a, 1b

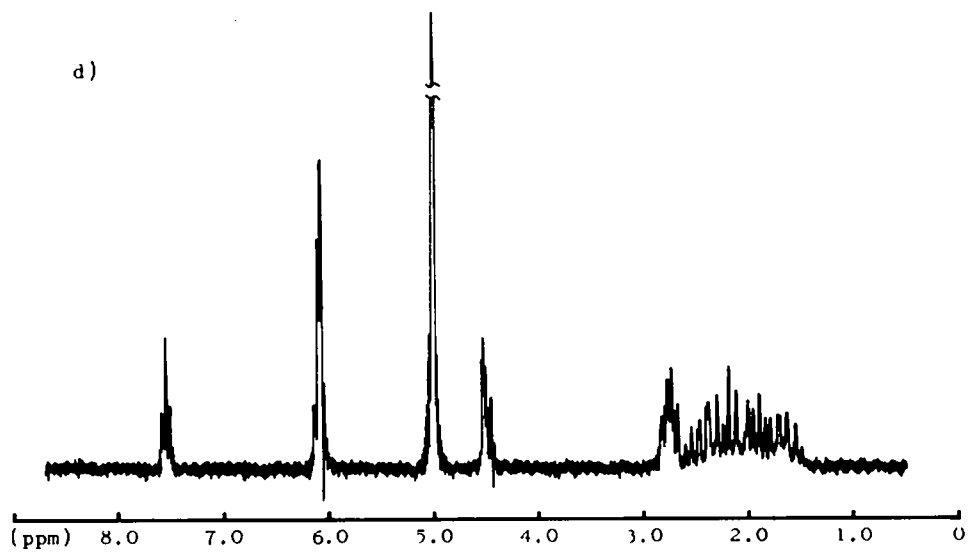
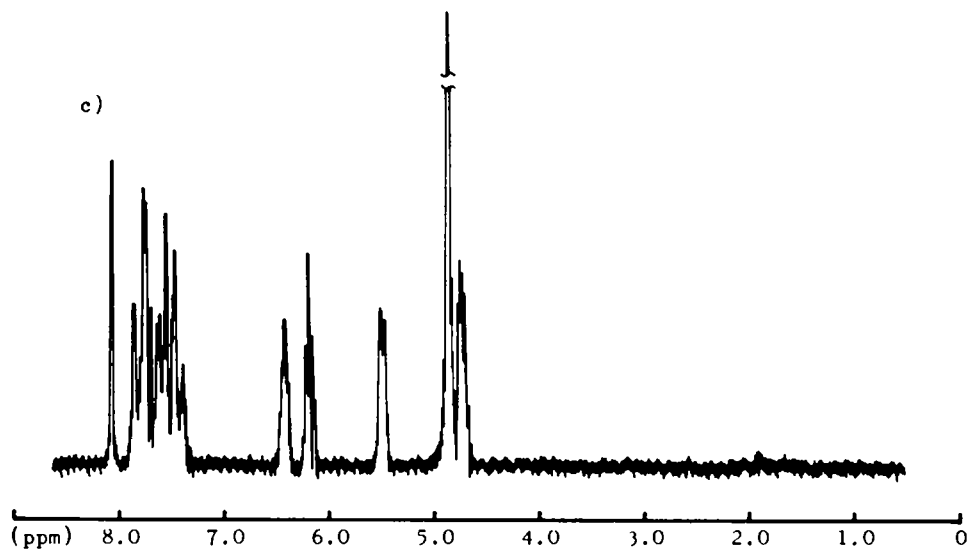


FIG. 1c, 1d

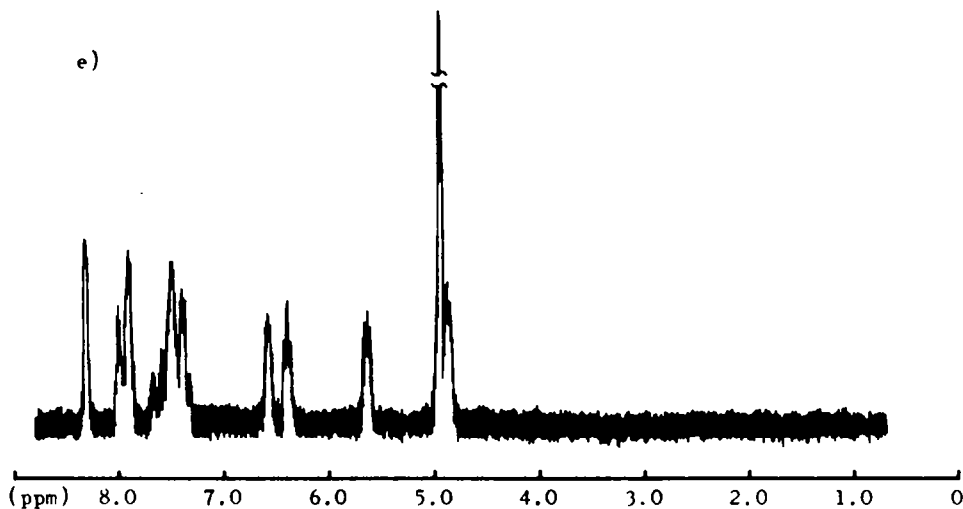
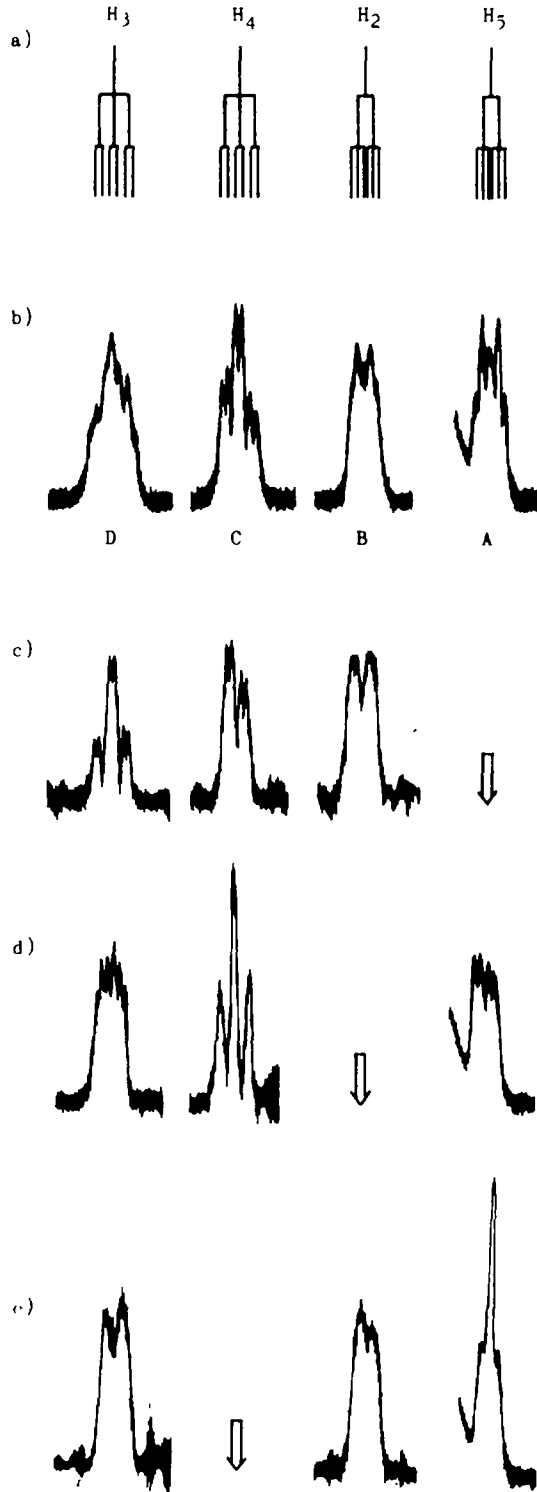


FIG 1. PMR spectra of α -ferrocenylcarbonium ions; (a) α -ferrocenylmethylcarbonium ion (I); (b) α -ferrocenylethylcarbonium ion (II); (c) α -ferrocenylphenylmethylcarbonium ion (III); (d) 1,2-tetramethylene- α -ferrocenylcarbonium ion (IV); (e) fluoroborate of α -ferrocenylphenylmethylcarbonium ion (V).

expected to be split as shown in Fig 2a in the first order analysis. In the actually observed spectrum of III, the A and B signals corresponded to the patterns of the H_5 and H_2 protons, and the C and D signals to H_4 and H_3 , respectively, although B and D were observed as broad signals (Fig 2b). When the signal A was irradiated, the other three signals changed into double doublets ($J = 3.0$ and 1.3 Hz) for B and C, and to a triplet ($J = 3.0$ Hz) for D which showed additional small splitting ($J = 0.8$ Hz), as shown in Fig 2c. The J values of 3.0 and 1.3 Hz should be taken as the spin-spin coupling constants between the ortho protons and between the meta protons, respectively. Therefore, each pair of the signals A and C, C and D, or D and B should correspond to the pair of the protons adjacent to each other, i.e., the protons H_5 and H_4 , H_4 and H_3 , or H_3 and H_2 , respectively. The results from irradiation of the other three signals were as shown in Figs 2d-f, and then the same assignment as described above was deduced from the patterns of the decoupled signals.

In the normal spectrum of the ion III, the signals B and D were broadened, whereas the signals A and C were sharp. Upon irradiation of the methine signal (8.09 ppm, s), B and D changed into sharp lines as expected from Fig 2a, while A and C remained unchanged (Fig 2g). It was reported that, in the derivatives of inden ($X = CH_2$ in VIII) and benzofuran ($X = O$ in VIII), the coupling constants between the 3 and 7 protons were 0.7–1.0 Hz.¹⁰ In the substituted benzofuran ($X = O$, $R_1 = CO_2CH_3$ in VIII) the observed values were ${}^4J_{3,4} = \pm 0.12$ Hz, and ${}^5J_{3,7} = \pm 0.60$ Hz.¹¹ Thus, in the system containing an aromatic ring, it is considered that the long-range coupling constant shows a larger value when the two interacting nuclei are oriented in a coplanar zig-zag form. Therefore, in the present species, the protons which can be coupled with the methine proton H_6 by 0.8–0.6 Hz are the protons H_3 and H_2 among the four ring protons (see IX and X). As a result, the signals A, B, C, and D were



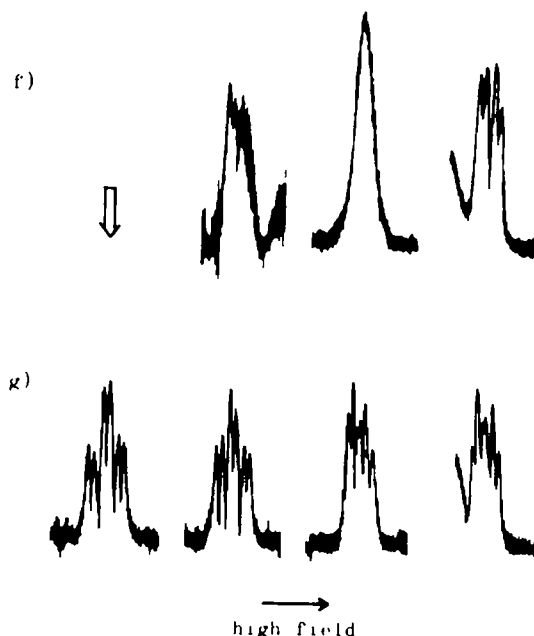


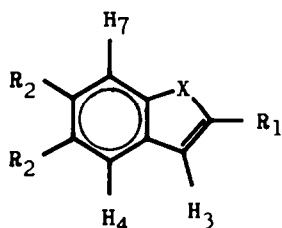
FIG 2. Spectra of substituted cyclopentadienyl ring protons in α -ferrocenylphenylmethyl-carbonium ion; (a) spin-spin splitting of expected spectrum; (b) observed normal spectrum; (c)–(g) spectra when A, B, C, D and methine signals were irradiated, respectively. The large arrow indicates the point of irradiation, in each case.

assigned to the protons H_5 , H_2 , H_4 , and H_3 , respectively. Moreover, the presence of significant coupling interaction between the methine proton and the proton H_2 or H_3 suggests that the carbinyl carbon forms an sp^2 orbital, and that the sp^2 plane and the Cp ring are in the relation of co-planarity in NMR time scale.

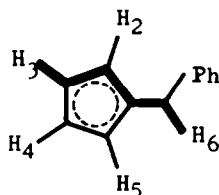
The spectrum of the fluoroborate of ferrocenylphenylmethylcarbonium ion (V) in acetone- d_6 showed almost the same pattern as that of the cation III in TFA except for the signal of the phenyl group, although the chemical shifts were somewhat different. Then, it can be considered that α -hydroxyphenylmethylferrocene in TFA exists in a completely cationic form. The species V in acetone- d_6 decomposed so easily that its spectrum could not be studied in detail.

In the case of II, the cyclopentadienyl ring protons appeared at δ 4.49, 6.21, and 6.36 ppm (a portion of proton for each signal), and at δ 5.03 ppm (six protons). The former three signals had the same patterns as those of H_5 , H_4 , and H_3 in the ion III (Fig. 2b), respectively. Irradiation of the signal at δ 5.03 ppm converted the other three signals to the same patterns as observed by irradiation of the proton H_2 in the ion III (Fig 2d). Therefore, the signal of one proton in the substituted ring is completely overlapped by the signal of unsubstituted ring protons. The signals of the substituted ring protons were assigned as listed in Table I in the same way as in the case of III.

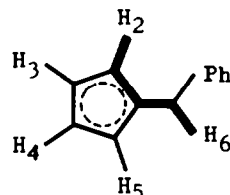
From the PMR spectra of α -ferrocenylcarbonium ions, Cais *et al.*² suggested that the deshielding of the protons H_3 and H_4 on the substituted ring with respect to the protons H_2 and H_5 could be explained on the basis of structure VI, and that the



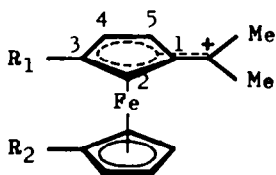
VIII



IX



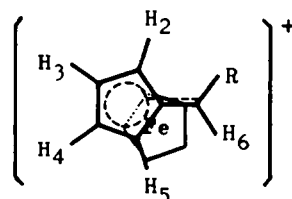
X



XI: $R_1=R_2=H$

XII: $R_1=R_2=Me$

XIII: $R_1=R_2=(CH_2)_3$



XIV

effect of the induced field was caused by the magnetic anisotropy of the Fe atom. On the other hand, Feinberg and Rosenblum⁷ studied the PMR spectra of the cation XII and the bridged cation XIII, and found that there was no significant difference in chemical shift of the disubstituted-ring protons and the Me protons at the tertiary cationic center between the cation XII and XIII. As a result they concluded that it was unlikely that the metal atom was displaced towards the carbonium ion center, as in the model VI.

In comparison of our results on the α -ferrocenylcarbonium ion III with the data of 6-phenylfulvene (H_2 , δ 6.709 ppm; H_3 , δ 6.627 ppm; H_4 , δ 6.457 ppm; H_5 , δ 6.311 ppm) in acetone,¹² the protons H_2 and H_5 in the ion III appeared at an unusually higher field than those in 6-phenylfulvene, while the resonant region of the protons H_3 and H_4 was almost the same in both. Furthermore, the difference in chemical shifts between the protons H_2 and H_5 is about 0.4 ppm in the latter, but 0.75 ppm in the former. A reasonable explanation for the character of the α -ferrocenylcarbonium ion would be an influence of the anisotropic effect of the Fe atom or the non-equivalence in the charge density at each carbon of the Cp ring, that is, non-equivalence of the bonds between each of the C atoms and the Fe atom.

We now consider as follows in order to explain our results. On the formation of the carbonium ion at the carbonyl carbon, a divalent Fe atom in the ferrocenyl group would be so apt to interact with the cation center that the iron shifts towards the carbonyl carbon. If the plane of the sp^2 orbital is co-planar with the cyclopentadienyl ring, as mentioned already, the Fe atom would slide to the opposite direction from the bulky substituent due to the steric hinderance, as shown in the model XIV. As a result, the H_5 proton would come close to the Fe atom to resonate at the highest field among the substituted-ring protons due to the diamagnetic anisotropic effect of the

TABLE I. DATA ON PMR SPECTRA OF α -FERROCENYL CARBONIUM IONS IN TRIFLUOROACETIC ACID (δ , ppm)

Compounds	Substituted Cp ring protons				Unsubstituted ring protons	H ₆	—CH ₃
	H ₅	H ₂	H ₄	H ₃			
I	4.72	4.72	6.32	6.32	5.27	5.95	—
II	4.49	5.03	6.21	6.36	5.03	7.12	2.25
		$(J_{2,3} = J_{3,4} = J_{4,5} = 3.0 \text{ Hz})$				$(J_{2,6} = 0.6 \text{ Hz})$	
		$(J_{2,4} = J_{3,5} = J_{2,5} = 1.3 \text{ Hz})$				$(J_{3,6} = 0.8 \text{ Hz})$	
III	4.77	5.52	6.24	6.45	4.87	8.09	—
		$(J_{2,3} = J_{3,4} = J_{4,5} = 3.0 \text{ Hz})$				$(J_{2,6} = 0.6 \text{ Hz})$	
		$(J_{2,4} = J_{3,5} = J_{2,5} = 1.3 \text{ Hz})$				$(J_{3,6} = 0.8 \text{ Hz})$	
IV	4.55	—	ca 6.09	ca 6.09	5.02	7.57	—
V ^a	4.90	5.67	6.42	6.61	4.98	8.32	—
XI ^b	5.00	5.00	6.33	6.33	4.88	—	2.28
XII ^b	4.73	4.88	6.07	—	4.63–4.82	—	2.20
XIII ^b	4.90	5.05	6.05	—	4.60–4.80	—	2.22 2.32

^a In acetone-d₆

^b Reference 3b. The data were obtained employing tetramethylammonium bromide as internal standard (δ 3.30), and given in ppm from TMS. The peaks for H₅ and H₂ were not assigned to each proton.

Fe atom or to an increase in the charge distribution at the C₅ by transfer donation of some electronic charge from the Fe atom. The shift would be also possible in the bridged carbonium ion XIII if the Fe atom slides towards the C₅, because of its tilted conformation caused by bridging with three methylene groups.

EXPERIMENTAL

Carbonium ions

The α -ferrocenylcarbonium ions were formed by dissolving the corresponding α -ferrocenylcarbinols in commercial 100% trifluoroacetic acid (TFA)¹³ below -10° ($2\text{--}5\%$, w/v). The ions I, II, III, and IV were formed from α -hydroxymethylferrocene¹⁴ (m.p. $80\text{--}82^\circ$), α -hydroxyethylferrocene¹⁵ (m.p. $77\text{--}78^\circ$), α -hydroxyphenylmethylferrocene¹⁶ (m.p. $80\text{--}81^\circ$), and α -hydroxy-1,2-tetramethyleneferrocene¹⁷ (*endo*-isomer; m.p. $76\text{--}78^\circ$ and *exo*-isomer; oil), respectively.

The fluoroborate V was prepared according to the method reported by Cais and Eisenstadt,¹⁸ and identified by the IR spectrum (ν_{BF} : $1030\text{--}1120 \text{ cm}^{-1}$).

PMR spectra

The ions I–IV in TFA did not decompose at room temp for at least 3 hr, while V was easily decomposed at room temp in acetone-d₆. The PMR spectrum of V, therefore, was recorded immediately after sampling, but could not be studied in detail.

All PMR spectra were run by a JEOL-JNM-4H-100 spectrometer at 100 MHz, and measured at room temp with TMS as internal standard. Normal spectra were run by a field/frequency stabilized mode. For double resonance experiments, JEOL JNM-SD-30 spin decoupler instrument was used, and the spectra were recorded at a sweep width of $9 \times 1/10$ ppm and a sweep time of 5 min by a frequency sweep. Chemical shifts were calibrated by a digital frequency counter. Coupling constants were obtained directly from the calibrated charts.

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