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STABLE [3]- AND [4]FERROCENOPHANE CARBONIUM IONS[1]

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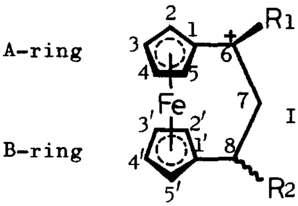
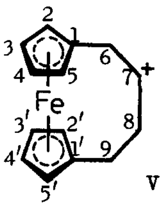
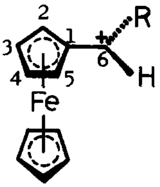
The stabilization mechanism of the π-complex carbonium ions containing metals and aromatic rings is an important subject in the chemistry of the π-complexes.[2-13] In order to obtain information for explanation of the stabilization, we examined PMR spectra of some hydroxyferrocenophanes in trifluoroacetic acid (TFA).



I:R_1=R_2=H
II:R_1=Me,R_2=H
III:R_1=H,R_2=Me
IV:R_1=R_2=Me



V



VI:R=Me
VII:R=Ph

[3]Ferrocenophan-6-ols and [4]ferrocenophan-7-ol* used in the present study were prepared by reduction with $LiAlH_4$, or by the Grignard reaction with CH_3MgI, of the corresponding ketones synthesized by the known methods.[14,15] The signals of PMR spectra were assigned by means of the double resonance technique as described in the previous paper[13] (Table 1).

The PMR spectra of the 6- and 7-hydroxyferrocenophanes in TFA showed the formation of the corresponding stable ferrocenophan-6- and 7-carbonium ions I - V. The splitting patterns of the Cp ring protons were the same as those of the carbo-

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* The melting points of the corresponding hydroxyl derivatives to the cation I-V were as follow: I: 159.5-162°, II: 114.5-115.5°, III: 98-98.5°, IV: 121.5-122° and V: 127-128°.

Table 1 Data of PMR spectra of ferrocenylcarbonium ions in TFA[a,b]

	A-ring protons	B-ring protons	Bridge protons		Methyl protons	
	H_5 H_2 H_4 H_3	$H_{5'}$ $H_{2'}$ $H_{4'}$ $H_{3'}$	H_6	H_7-H_9	C_6-CH_3	C_8-CH_3
I	4.44 5.79[d] 5.79[d] 6.53 ($J_{2,3}$= $J_{3,4}$= $J_{4,5}$= 3.1) ($J_{2,5}$= $J_{3,5}$= 1.3)	6.03 5.05[d] 4.97 5.05[d] ($J_{4;5'}$= 2.6) ($J_{2;5'}$=$J_{3;5'}$= 1.3)	8.10(q) ($J_{3,6}$=0.8, $J_{6,7}$=4.4, $J_{6,7'}$=11.3)	H_7,H_8: 2.85-3.25(m) $H_{7'}$,$H_{8'}$: 3.35-3.75(m)	—	—
II	4.62 5.81[d] 5.81[d] 6.54 ($J_{2,3}$= $J_{3,4}$= 3.2) ($J_{3,5}$= 1.3)	5.81[d] 5.06 4.96 4.69 ($J_{2;3'}$=$J_{3;4'}$=$J_{4;5'}$=2.8) ($J_{2;4'}$=$J_{2;5'}$=$J_{3;5'}$=1.3)	—	H_7,H_8: 2.74-3.27(m) $H_{7'}$,$H_{8'}$: 3.65-4.10(m)	2.86(s)	—
III	4.38 5.79[d] 5.79[d] 6.53 ($J_{2,3}$= $J_{3,4}$= $J_{4,5}$= 3.1) ($J_{2,5}$= $J_{3,5}$= 1.3)	6.17 5.01[d] 5.01[d] 5.01[d] ($J_{4;5'}$= 2.8) ($J_{2;5'}$= $J_{3;5'}$= 1.3)	8.14(q) ($J_{3,6}$=0.8, $J_{6,7}$=11.9, $J_{6,7'}$=4.3)	H_7: 2.90(q) $H_{7'}$,$H_{8'}$: 3.37-3.91(m)	—	1.76(d)
IV	4.54 5.82 5.77 6.57 ($J_{2,3}$= $J_{3,4}$= $J_{4,5}$= 3.2) ($J_{2,5}$= $J_{3,5}$= 1.3)	6.12 4.98 5.10 4.62 ($J_{2;3'}$=$J_{3;4'}$=$J_{4;5'}$=2.8) ($J_{2;4'}$=$J_{2;5'}$=$J_{3;5'}$=1.3)	—	H_7: 2.73-2.87(m) $H_{7'}$,H_8: 3.58-4.15(m)	2.89(s)	1.75(d)
V	3.89 4.03 5.77 6.01 ($J_{2,3}$= $J_{3,4}$=$J_{4,5}$= 2.8) ($J_{2,4}$= $J_{2,5}$= $J_{3,5}$= 1.3)	4.76 5.05 5.37 5.21 ($J_{2;3'}$=$J_{3;4'}$=$J_{4;5'}$=2.8) ($J_{2;4'}$=$J_{2;5'}$=$J_{3;5'}$=1.3)	H_6,$H_{6'}$,H_8,$H_{8'}$,H_9,$H_{9'}$:2.15-3.65(m)	H_7: ca.4.6(m)	—	—
VI[c]	4.49 5.03 6.21 6.36 ($J_{2,3}$= $J_{3,4}$= $J_{4,5}$= 3.0) ($J_{2,4}$= $J_{2,5}$= $J_{3,5}$= 1.3)	5.03	7.12(q) ($J_{2,6}$= 0.6, $J_{3,6}$= 0.8)		2.25(d)	—
VII[c]	4.77 5.52 6.24 6.45 ($J_{2,3}$= $J_{3,4}$= $J_{4,5}$= 3.0) ($J_{2,4}$= $J_{2,5}$= $J_{3,5}$= 1.3)	4.87	8.09(s) ($J_{2,6}$= 0.6, $J_{3,6}$= 0.8)		—	—

[a] The spectra were measured with JEOL JNM-4H-100 spectrometer at 100 MHz. The chemical shifts were determined using TMS as internal reference(δ, in ppm). The scale of the coupling constants $J_{i,j}$ is Herz.

[b] Only the coupling constants found with first order approximations are showed in this table.

[c] The data were already reported by the previous paper.[13]

[d] The chemical shifts were not definitely determined because of overlapping with other signals.

nium ions VI and VII,[13] except for the overlapping signals. The distinction in the chemical shifts among the interannular bridge protons indicates that each species in TFA takes a definite conformation but has no rapid inversion.[16,17]

In the spectra of the [3]ferrocenophan-6-carbonium ions I-IV, the coupling constants between the ortho protons in the A-ring were ca. 3.2 Hz, a value similar to those of the ions VI and VII, while the constans in the B-ring were 2.8 Hz. Furthermore, in the carbonium ions I and III, both having a methine proton at 6 position, the long-range coupling between the H_3 and H_6 protons was observed in the same coupling constant as those of the cations VI and VII (0.8 Hz). In spite of their bridged form, these results provide evidence for the existence of the electronic interaction between the cationic center and the A-ring due to near co-planality.[13] Consequently, it has been suggested that the carbonium ions are stabilized by the "hyperconjugation"[3] mechanism.

However, a direct "metal participation"[2,4] in addition to the hyperconjugation for the stabilization of the carbonium ions can not be denied by the above results. The β-ferrocenylcarbonium ion V in which the cationic center is apart from the Cp ring was considerably stable (no decomposition during ca. 1.5 hr at room temperature), although its stability was somewhat lower than the other cations I-IV. In the PMR spectrum of the C_7-carbonium ion V, the ring protons appeared at the higher fields than the other cations, and the coupling constants between the ortho protons of both A- and B-ring were 2.8 Hz. Therefore, there should be no direct interaction between the π-electrons of the rings and the positive charge of the carbinyl carbon. The stabilization of the carbonium ion V would be due to a direct "metal participation",[2,4] since there is no stabilizing factor in the cation except for the Fe atom. The considerably high field shift of the H_7 proton would arise from approach of the proton to the Fe atom.

The proton at 5' position of the cation V appeared at the highest field among the B-ring protons, and the behaviour in the shifts of the B-ring protons was the same as that of the A-ring protons, while in the cations I-IV the 5' protons resonated at the lowest field among the B-ring protons. The anomalous shifts of the ring protons in the cations I-IV would arise from their ring-tilted conformation.[16]

Then, it is concluded that the unusual behaviour in the PMR spectra of ferrocenylcarbonium ions is not only based on simple electronic effects but reflects their molecular deformations which result from the interaction both between the positive charge of the cationic center and the π-electrons of the Cp ring and between the charge and the Fe atom.

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17 The methylene protons of [3]ferrocenophan-6-ones appeared as sharp singlets. Barr and Watts[16] reported that the PMR spectra are good evidence for conformational flexibility of the ferrocenophanes.