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Carbon-13 NMR Chemical Shifts of Some Ruthenocenophanes and Ferrocenophanes

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Synopsis. The ^{13}C NMR spectra of ruthenocenophanes, ferrocenophanes and their precursors were measured. The examination of molecular models for metallocenophanes and the spectral data offer some hints about the conformation of the molecules.

We wish to report the carbon chemical shift data of the title compounds and their precursors. The structures of these metallocenophanes are discussed, using the spectral data together with molecular models which were constructed by using the data from X-ray crystallography.[1]

The assignments of the carbon signals were based on standard methods, *i.e.*, the relative intensities, the off-resonance CW decoupling, and a comparison of the signal shift between closely related compounds. In addition, the bridged methylene carbons of [3]- and [4]ruthenocenophanes, and their ferrocenophane homologs were assigned by comparison of their spectra with those of the deuterated compounds which were obtained by the reduction of the corresponding oxo-compounds with $\mathrm{LiAlD_4}$ and $\mathrm{AlCl_3}$ combination. The chemical shifts are collected in Table 1.

Both proton and carbon signals of ruthenocene (**1**)[2] shifted to lower fields than those of ferrocene (**2**).[2,3] Since a linear correlation between the ^{13}C chemical shift and charge density has been established for a series of monocyclic aromatic systems,[4] such a shift difference suggests that the ruthenium atom pulls the π-electrons from cyclopentadienyl rings more than the iron atom does. This is supported by the fact that electrophilic substitutions *e.g.*, Friedel-Crafts reactions, occur to a lesser extent with **1** than with **2**.[5]

The carbon signals of ruthenocenophanes also appeared at a lower field than those of ferrocenophanes, except for the carbonyl carbon signals. The chemical shifts for carbonyl groups of [4]ruthenocenophan-2-one (**5**) and [4]ferrocenophan-2-one (**6**) show almost equal values. The carbonyl carbon signal of [3]ruthenocenophan-1-one (**3**) shifted to a higher field than that of [3]ferrocenophan-1-one (**4**). The upfield shift of the carbonyl carbon signal is observed by an introduction of the electron-withdrawing substituents at the neighboring position. The simplest interpretation of this trend would attribute the increase in shielding to decreased polarization of the π-bond, because the electron-withdrawing effect of the substituent decreases the contribution of the polarized form.[6] Such a difference in the chemical shifts for the carbonyl carbons may be correlated to the resonance contribution of the carbonyl group; $\mathrm{Cp{-}\underset{|}{C}{=}O \leftrightarrow Cp{-}\underset{|}{\overset{+}{C}}{-}\overset{-}{O}}$. In infrared spectra,[7] however, the absorption band of **3** is at 1656 cm^{-1} and that of **4** at 1681 cm^{-1}. The carbonyl stretching band generally shifts to the shorter wavelength by an introduction of the electron-withdrawing group at the neighboring position.[8] We assume that the chemical shift difference of the carbonyl carbons between **3** and **4** is primarily due to the electron delocalization by the conjugation of this carbonyl group with the cyclopentadienyl ring. Since the cyclopentadienyl rings of **4** are tilted to about 9°,[9] the longer distance between the two rings of **3**[7] results in an appreciable strain on the bridge of the carbon chain connecting these two rings, which are supposed to be tilted to a greater extent. The molecular model for [3]oxophanes indicates that the dihedral angle between the plane of the carbonyl group and the adjacent cyclopentadienyl ring becomes small when the cyclopentadienyl rings are tilted to a greater extent (see Fig. 2; θ_2 is smaller than θ_1). The π-orbital of the carbonyl group can effectively conjugate with the π-system of the cyclopentadienyl ring. As a consequence, the carbonyl carbon signal of **3** shifts to higher field and the carbonyl stretching band shifts to longer wavelengths than those of **4**. Lentzner and Watts reported that in the acylation of [3]-, [4]-, and [5]ferrocenophan-1-ones, the product ratio, (acylated product at the ring opposite side to the carbonyl group)/(acylated product at the ring adjacent to the carbonyl group), was found to be much higher for [5]oxophane than for other homologs. The finding that the ratio for [3]oxophane is approximately twice that for [4]-oxophane was perplexing. They commented that the distortion of the ferrocene nucleus occasioned by a 4-carbon bridge may be greater than that occasioned by a 3-carbon bridge.[5] The molecular model used in the present investigation indicates that the dihedral

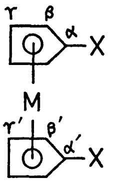

Fig. 1.

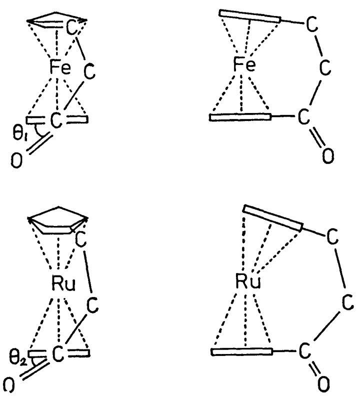

Fig. 2. Conformation models for [3]-ruthenocenophan-1-one and [3]ferrocenophan-1-one.

TABLE 1. CARBON-CHEMICAL SHIFTS OF RUTHENOCENOPHANES, FERROCENOPHANES, AND THEIR PRECURSORS[a]

X	M	Compd No.						1	2	3	4
H	Ru	**1**			70.0						
	Fe	**2**			67.7[b]						
			α	α′	β,β′,γ,γ′						
$\alpha\text{-}\overset{1}{\mathrm{C}}\mathrm{O}\overset{2}{\mathrm{C}}\mathrm{H_2}\overset{3}{\mathrm{C}}\mathrm{H_2}\text{-}\alpha'$	Ru	**3**	138.8	92.2	71.1, 72.9, 73.6, 75.4			208.5	46.2	32.0	
	Fe	**4**	128.3	88.0	69.2, 70.3, 71.1, 72.5			211.9	44.1	31.6	
			87.6	74.0	68.8, 69.8, 70.2, 72.0			210.1	43.8	31.1[c]	
$\alpha\text{-}\overset{1}{\mathrm{C}}\mathrm{H_2}\overset{2}{\mathrm{C}}\mathrm{O}\overset{3}{\mathrm{C}}\mathrm{H_2}\overset{4}{\mathrm{C}}\mathrm{H_2}\text{-}\alpha'$	Ru	**5**	93.4	81.6	70.0, 70.4, 72.3, 72.4			45.3	206.7	42.1	27.3
	Fe	**6**	86.5	76.6	68.3, 68.9			(41.5)[d]	206.5	(41.3)	25.7
$\alpha\text{-}\overset{1}{\mathrm{C}}\mathrm{H_2}\overset{2}{\mathrm{C}}\mathrm{H_2}\overset{3}{\mathrm{C}}\mathrm{H_2}\text{-}\alpha'$	Ru	**7**	85.7	85.7	71.4, 71.6			38.2	24.6	38.2	
	Fe	**8**	85.4	85.4	68.1, 69.3			35.0	24.5	35.0	
			85.2	85.2	67.9, 69.1			35.1	24.2	35.1[c]	
$\alpha\text{-}\overset{1}{\mathrm{C}}\mathrm{H_2}\overset{2}{\mathrm{C}}\mathrm{H_2}\overset{3}{\mathrm{C}}\mathrm{H_2}\overset{3}{\mathrm{C}}\mathrm{H_2}\text{-}\alpha'$	Ru	**9**	91.6	91.6	69.7, 71.7			30.6	29.1	29.1	30.6
	Fe	**10**	88.0	88.0	65.7, 65.9			29.3	27.0	27.0	29.3
					β	γ	α′,β′,γ′				
α-CHO	Ru	**11**	84.8		71.0	74.4	72.2	189.6			
	Fe	**12**	79.6		68.2	72.9	69.6	192.9			
			79.2		68.0	72.6	69.2	192.2[b]			
$\alpha\text{-}\overset{1}{\mathrm{C}}\mathrm{H}{=}\overset{2}{\mathrm{C}}\mathrm{H}\overset{3}{\mathrm{C}}\mathrm{OOH}$	Ru	**13**	82.8		70.2	71.9	71.2	143.1	115.4	167.3	
(in DMSO-d_6)	Fe	**14**	78.5		68.3	70.4	69.2	144.7	115.6	167.3	
$\alpha\text{-}\overset{1}{\mathrm{C}}\mathrm{H_2}\overset{2}{\mathrm{C}}\mathrm{H_2}\overset{3}{\mathrm{C}}\mathrm{OOH}$	Ru	**15**	91.7		69.0	70.2	70.1	23.7	35.7	173.6	
(in DMSO-d_6)	Fe	**16**	87.1		66.7	67.5	68.1	24.3	34.9	174.5	

a) In $CDCl_3$ unless otherwise indicated. b) Ref. 3. c) A. N. Nesmeyanov, G. B. Shul'pin, and M. I. Rybinskaya, *Dokl. Akad. Nauk. SSSR*, **218**, 1107 (1974). d) Values in parentheses may be interchanged.

angle between the plane of the carbonyl group and the adjacent cyclopentadienyl ring becomes small when the number of carbon of the bridge diminishes from 4 to 3. In consequence, the carbonyl-cyclopentadienyl conjugation would be stronger for the latter ketone. The product ratio which they obtained seems quite reasonable.

The ^{13}C NMR spectra of precursors of phane compounds: formylruthenocene (**11**), ruthenocenylacrylic acid (**13**), ruthenocenylpropionic acid (**15**) and their ferrocene homologs, **12**, **14**, and **16**, were also measured. Similarly to the case of the parent and phane compounds, the carbon signals of cyclopentadienyl rings of ruthenocenes are located at lower fields than those of ferrocenes.

Experimental

NMR Spectra. The ^{13}C FT-NMR spectra were obtained at 25.15 MHz with a JEOL JNM-MH-100 instrument equipped with a JNM-MFT-100 Fourier transform accessory; the instrument was controlled with a JEC-6 spectrum computer. Samples were observed in 5 mm spinning tubes at 15±5% solutions in $CDCl_3$ or DMSO-d_6 at 28 °C. The solvent provided the internal lock signal. The measurement conditions were as follows: pulse width, 27.5 μs (*ca.* 45°); repetition time, 4 s; spectral width, 6.25 kHz; data points, 8192; acquistion time, 0.65 s. Noise modulated proton decoupling was carried out at a nominal power of 20 W and the off-resonance was carried out at a nominal power of 7 W. All chemical shifts are expressed in δ (ppm; downfield from internal Me_4Si). Each observed chemical shift is estimated to be accurate to $\delta \pm 0.1$.

Materials. The compounds employed in this work have been previously prepared: ferrocenophanes and ferrocenes,[10] ruthenocenophanes, and ruthenocenes.[7]

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