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The Syntheses of [3]- and [4]Ruthenocenophanes

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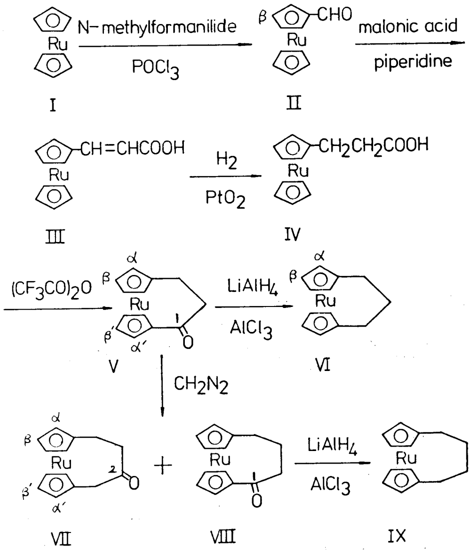
[3]- and [4]ruthenocenophanes as well as other ruthenocene derivatives were synthesized. The preparation of ruthenocenes in this experiment required more forced reaction conditions than those of the corresponding ferrocenes. Two cyclopentadienyl rings of these ruthenocenophanes are found to tilt mutually, and the degree of the ring-tilting of [3]ruthenocenophane is greater than that of the [4] homolog.

A large number of heteroannularly bridged ferrocenes, designated [m]ferrocenophanes, have played important roles in the investigations of the physical and chemical properties of the ferrocene molecule.[2] On the other hand, there have been only a few investigations of [m]ruthenocenophanes or of other ruthenocene derivatives.[3] Recently, the first synthesis of [5]ruthenocenophanes has been reported.[4] This paper will be concerned with the syntheses and characterizations of several new [3]- and [4]ruthenocenophanes. The introduction of a heteroannularly bridged carbon chain into a ruthenocene molecule will cause a distortion of the cyclopentadienyl rings from their normal parallel geometry. The degree of the tilting of two cyclopentadienyl rings and of the conformational flexibility of linking chains is expected to depend on the length of the carbon chain and on the steric circumstances. These steric effects will be discussed on the basis of proton magnetic resonance, infrared and electronic spectra.

Results and Discussion

Synthesis of [3]Ruthenocenophan-1-one (V) and [3]Ruthenocenophane (VI). The introduction of a three-carbon interannular bridge into a ruthenocene molecule was achieved by the cyclization of 3-ruthenocenylpropionic acid (IV) to V. Compound IV was prepared from formylruthenocene (II). Bublitz *et al.* have previously reported that, in the presence of $POCl_3$, the reaction of ruthenocene (I) with *N*-methylformanilide in chlorobenzene led to the formation of II in only a 8% yield.[5] However, we have found that II is formed in a reproducibly good yield (46%) by the reaction of I with *N*-methylformanilide without any solvent in the presence of $POCl_3$. The condensation of II with malonic acid afforded 3-ruthenocenylacrylic acid (III). The hydrogenation of III in ethanol over PtO_2 gave IV quantitatively. An intramolecular Friedel-Crafts-type reaction of IV with trifluoroacetic anhydride required a longer reaction time (two weeks) in refluxing cyclohexane than that needed in the case of the ferrocene derivative.[6] This difference in the reaction conditions of cyclization may be because ruthenocenes are generally less reactive and because the distance between two cyclopentadienyl rings of a ruthenocene is longer than that of a ferrocene.[7,8] Compound VI was prepared by the reduction of V with lithium aluminum hydride-aluminum trichloride in the usual manner.

Synthesis of [4]Ruthenocenophan-2-one (VII) and [4]Ruthenocenophane (IX). In a mixture of methanol and ether, the reaction of V and diazomethane led to the formation of VII, accompanied by a small amount of [4]ruthenocenophan-1-one (VIII), while the reduction of VII with lithium aluminum hydride-aluminum trichloride gave a good yield of IX (Scheme 1).



Scheme 1. Syntheses of ruthenocenophanes.

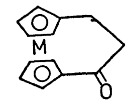
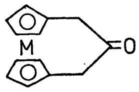
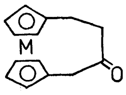
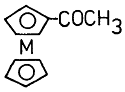
Proton Magnetic Resonance Spectra. The details of the ^1H NMR spectra of ruthenocenes, together with the reported spectra of ferrocenes,[9] are summarized in Table 1. The assignments of the signals of ruthenocene derivatives are based on those of the corresponding ferrocenes and multibridged ferrocenophanes.[10] It has previously been reported that, in the ^1H NMR spectra of ferrocene derivatives, alkyl substituents do not cause a noticeable difference in the chemical shift between α- and β-protons of the cyclopentadienyl rings to which they are attached.[9] The most striking manifestation of the ring tilt in [m]ferrocenophanes with different bridge lengths is the variation in the cyclopentadienyl ring proton patterns.[9] In the case of VI, the protons of cyclopentadienyl rings appear as two unsymmetrical triplets separated by 0.23 ppm, corresponding to an A_2B_2 system where vicinal and cross-ring coupling constants are approximately equal and considerably smaller than the chemical shift difference between unlike protons.[9] Compound IX also shows two triplets separated by 0.11 ppm. On the basis of the ^1H NMR spectrum, Rinehart *et al.*[11] have suggested that the tilting rings of [3]ferrocenophane serve to bring the α-protons of the rings closer to the Fe atom

TABLE 1. ^{1}H NMR CHEMICAL SHIFTS OF

Compound	Cyclopentadienyl proton				
	H_α	H_β	$\lvert H_\beta - H_\alpha \rvert$	$H_{\alpha'}$	$H_{\beta'}$
Formylruthenocene (II)	$4.85^{t\ d)}$ (J=1.8 Hz)	5.08^t (J=1.8 Hz)	0.23	$4.65^{s\ a)}$	
3-Ruthenocenylacrylic acid (III)	4.71^t (J=1.8 Hz)	4.99^t (J=1.8 Hz)	0.28	4.55^s	
3-Ruthenocenylpropionic acid (IV)	$4.4—4.7^{m\ e)}$		—	$4.4—4.7^m$	
[3]Ruthenocenophan-1-one (V)	4.60^t (J=1.4 Hz)	4.86^t (J=1.4 Hz)	0.26	5.10^t (J=1.4 Hz)	4.97^t (J=1.4 Hz)
[3]Ruthenocenophane (VI)	4.37^t (J=1.8 Hz)	4.60^t (J=1.8 Hz)	0.23	—	—
[4]Ruthenocenophan-2-one (VII)	4.46^t (J=1.6 Hz)	4.67^t (J=1.6 Hz)	0.21	4.67^t (J=1.6 Hz)	4.46^t (J=1.6 Hz)
[4]Ruthenocenophane (IX)	4.46^t (J=1.5 Hz)	4.57^t (J=1.5 Hz)	0.11	—	—
1,1,2,2-Tetramethyl-[2]ferrocenophane[f)]	3.98^t	4.52^t	0.54	—	—
[3]Ferrocenophane[f)]	3.87^t	4.01^t	0.14	—	—
[4]Ferrocenophane[f)]	3.93^s		0.00	—	—
[3]Ferrocenophan-1-one[f)]					
[4]Ferrocenophan-2-one[f)]					

a) Singlet. b) Broad singlet. c) Doublet. d) Triplet. e) Multiplet. f) Ref. 9.

TABLE 2. THE CARBONYL STRETCHING FREQUENCIES OF RUTHENOCENE AND FERROCENE DERIVATIVES (cm^{-1})

Compound				
M				
Ru	1656[a)]		1710[a)]	1658[b)]
Fe	1681[c)]	1703[d)]	1706[c)]	1658[b)]

a) In a KBr pellet and a Nujol mull. b) Ref. 7; in a KBr pellet. c) Ref. 6. d) Ref. 12; in CCl_4.

than the β-protons, therefore, the former experience a greater shielding influence. Extending this hypothesis, the larger splitting of the ring proton resonance of VI implies a greater dihedral angle of the two rings compared to the [4] homolog (IX). Barr and Watts have reported that the singlet resonance of [4]ferrocenophane is in accord with an undistorted ferrocene nucleus.[9)] On the other hand, the splitting of the ring proton resonance of IX seems to suggest that the rings are mutually inclined to some extent, in contrast to the case of [4]ferreocenophane. This difference might be due to the distance between the two cyclopentadienyl rings of a ruthenocene being longer by 1.1 Å than that of a ferrocene.[8)] Since the peak separation of VI is greater than that of IX, furthermore, the rings of the former might be tilted more than those of the latter.

The bridging methylene protons of VI and IX appear as one broad singlet and two multiplets respectively. In the case of V and VII, again, bridging methylene protons appear as two triplets and as two triplets and one singlet respectively. On the other hand, the methylene protons of [3]ferrocenophan-1-one and [4]ferrocenophan-2-one appear as sharp singlets, and Barr and Watts have suggested that facile conformational interconversion within the bridge is clearly indicated by the appearance of the bridging methylene protons as sharp singlets in the ^{1}H NMR spectra of [3]- and [4]ferrocenophane classes.[9)] These results, therefore, seem to indicate that [3]- and [4]ruthenocenophanes (V, VII) have a smaller conformational flexibility than the corresponding ferrocenophanes.

Infrared Spectra. The values of the carbonyl-stretching absorptions of ruthenocenes, together with the reported values of the corresponding ferrocenes,[6,7,12)] are given in Table 2. The absorption bands of the ruthenocene series are located at positions similar to those of the corresponding ferrocenes except for [3]ruthenocenophan-1-one (V). The difference in the carbonyl-stretching frequencies of V and acetylruthenocene is only 2 cm^{-1}, while that of [3]ferrocenophan-1-one and acetylferrocene is 23 cm^{-1}. In view of the following three factors: (i) the distance between two cyclopentadienyl rings of a ruthenocene is longer than that of a ferrocene,[8)] (ii) the ^{1}H NMR chemical shift difference between the α- and β-protons of the cyclopentadienyl rings in ruthenocenophanes is larger than that in the corresponding ferrocenophanes, and (iii) the IR absorption bands of acetylruthenocene, acetylferrocene and V, in which π-orbitals of carbonyl groups can effectively conjugate with π-systems of cyclopentadienyl rings, are located at lower frequencies than those of [4]ruthenocenophan-2-one (VII), [4]ferrocenophan-2-one, and [3]ferrocenophan-1-one,[6,13)] though these spectra should have been measured in dilute solutions, it is assumed that the cyclopentadienyl rings of ruthenocenophanes are more inclined than those of the corresponding ferrocenophanes.

Electronic Spectra. The details of the electronic spectra of ruthenocene derivatives are listed in Table 3. Figure 1 shows the electronic spectra of VI and IX, along with that of ruthenocene (I) in ethanol. The

RUTHENOCENE AND FERROCENE DERIVATIVES (δ).

Bridged Methylene Proton				Substituent	
H_1	H_2	H_3	H_4		
—	—	—	—	9.71^{s} (-CHO)	
—	—	—	—	5.95, $7.21^{d\ c)}$	(J=15.6 Hz, *trans* olefinic protons)
—	—	—	—	$2.55^{bs\ b)}$	(methylene protons)
—	2.74^{t} (J=3.6 Hz)	2.82^{t} (J=3.6 Hz)	—	—	
1.76^{bs}	1.76^{bs}	—	—	—	
3.24^{s}	—	2.66^{t} (J=8.4 Hz)	2.76^{t} (J=9.6 Hz)	—	
2.1—2.6^{m}	1.3—1.8^{m}	—	—	—	
—	—	—	—	—	
1.95^{s}	1.95^{s}	—	—	—	
1.4—1.5^{m}	1.0—1.2^{m}	—	—	—	
—	2.99^{s}	2.99^{s}	—	—	
3.30^{s}	—	2.77^{s}	2.77^{s}	—	

TABLE 3. ELECTRONIC SPECTRA OF RUTHENOCENE DERIVATIVES[a)]

Compound	λ_{max} (nm) (ε)		
Ruthenocene (I)		274 (286)	324 (268)
Formylruthenocene (II)		251 (13100)	344 (1460)
3-Ruthenocenylacrylic acid (III)	226 (5000)$^{sh\ b)}$	268 (8020)	346 (1380)
3-Ruthenocenylpropionic acid (IV)			300 (731)
[3]Ruthenocenophan-1-one (V)		251 (4900)	292 (1020)^{sh}, 332 (697)^{sh}
[3]Ruthenocenophane (VI)		265 (384)^{sh}	325 (603)
[4]Ruthenocenophan-2-one (VII)		269 (1120)^{sh}	
[4]Ruthenocenophane (IX)			317 (302)

a) In absolute EtOH. b) Shoulder.

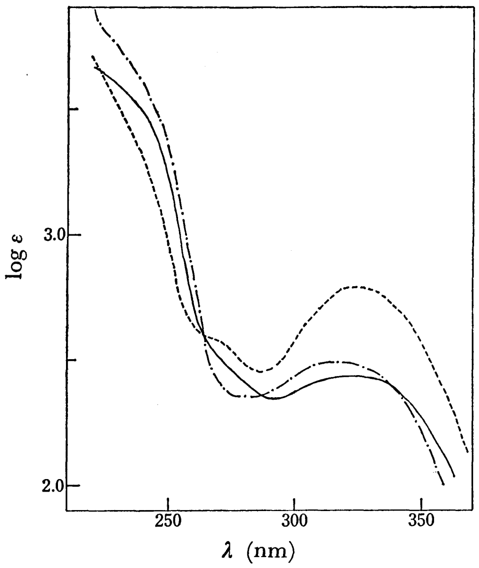


Fig. 1. The electronic spectra, taken in abs. ethanol: (——) ruthenocene (I), (----) [3]ruthenocenophane (VI) and (—·—·—) [4]ruthenocenophane (IX).

electronic spectra of d^6 metallocene including I have been thoroughly studied.[14)] According to the earlier band assignments, the absorption peak in the 320—330 nm region for each compound corresponds to the spin-allowed d-d transitions (two $^1A_{1g}\rightarrow{}^1E_{1g}$ and one $^1A_{1g}\rightarrow{}^1E_{2g}$), and the intense band at *ca.* 240 nm is associated with the charge transfer transitions of metal to ligand and ligand to metal. Although the spin-allowed d-d bands of I, VI and IX are located at similar positions, the band intensity of VI is much higher than that of I or IX. On the contrary, the intensity of the charge transfer bands of VI is lower than that of I or IX. The intensity of the spin-allowed d-d bands of IX is slightly higher than that of I, though their over-all spectra resemble each other. The cyclopentadienyl rings are distorted from their normal sandwich geometry when they are connected by short chains. The ^1H NMR study suggested that the cyclopentadienyl rings of VI are more inclined than those of IX. Thus, the ring-tilting will bring about an increase in the intensity of the spin-allowed d-d bands and a depression in the intensity of the charge transfer bands. The inclination of the cyclopentadienyl rings upon the introduction of bridging chains seems to alter the degree of the overlap between the metal d-orbitals and the p-orbitals of cyclopentadienyl rings. Furthermore, the ligand-field strength is changed with a distortion of rings from their normal parallel geometry. These effects might change the spectra of the present ruthenofcene derivatives.

Experimental

Materials. All the melting points are uncorrected. Ruthenocene (I) was prepared according to the method described by Hofer and Schlögl.3)

Measurements. The ^{1}H NMR spectra were obtained with a JEOL JNM-PMX-60 spectrometer (60 MHz) at room temperature. All the chemical shifts are expressed in δ (ppm; downfield from internal Me_4Si). The IR spectra were measured in KBr pellets with a Hitachi Model 285 infrared spectrometer. The electronic spectra were recorded with a Shimadzu Double 40-R spectrophotometer at room temperature.

Formylruthenocene (II). Into a flask containing 8.0 g (0.035 mol) of ruthenocene (I), we vigorously stirred three portions of 12.46 g (0.092 mol) of *N*-methylformanilide and 8.82 g (0.057 mol) of phosphoryl chloride every 2 h at 90 °C under a nitrogen atmosphere. After the addition of 86.4 g of sodium acetate trihydrate in 400 ml of water, the solution was refluxed for 1 h, and then stirred overnight at room temperature. The solution was extracted three times with ether which had been washed successively with a hydrochloric acid solution (1 M), water, saturated sodium hydrogencarbonate, and finally brine, and then dried over anhydrous sodium sulfate. The ether extract, concentrated to 100 ml, was shaken with a solution of 36 g of sodium hydrogensulfite in 400 ml of water. The hydrogensulfite addition compound was washed with ether and then dried. The hydrogensulfite addition compound was taken up in 200 ml of a sodium hydroxide solution (2 M), and the liberated aldehyde was extracted into ether. The combined ether extract was washed with brine and then dried over anhydrous sodium sulfate. After the removal of the solvent, the sublimation of the crude product gave 4.2 g (46%) of formylruthenocene (II); mp 103—104 °C(hexane-dichloromethane), (lit,3) 86—87 °C). IR(KBr) 1649 cm^{-1} (C=O). Found: C, 50.92; H, 3.85%. Calcd for $C_{11}H_{10}RuO$: C, 50.97; H, 3.89%.

3-Ruthenocenylacrylic Acid (III). The aldehyde (II) (5.5 g), malonic acid (5.5 g), and piperidine (1.3 ml) were dissolved in pyridine (100 ml), and the mixture was heated at 100 °C for 2 h under a nitrogen atmosphere. The cooled solution was diluted with water and extracted with chloroform. The chloroform extract was washed with dilute hydrochloric acid and water, and then extracted with a 2 M sodium hydroxide solution. The acidification of the aqueous layer precipitated 3-ruthenocenylacrylic acid (III) (5.4 g; 85%); mp 228—229 °C (dioxane-water). IR(KBr) 1666 (C=O) and 1612 cm^{-1} (C=C). Found: C, 51.71; H, 4.18%. Calcd for $C_{13}H_{12}RuO_2$: C, 51.83; H, 4.02%.

3-Ruthenocenylpropionic Acid (IV). The hydrogenation of 4.0 g (0.013 mol) of III in 400 ml of ethanol over 50 mg of PtO_2 gave 4.0 g (98%) of 3-ruthenocenylpropionic acid (IV); mp 99—100 °C (petroleum ether). IR(KBr) 1824 cm^{-1} (C=O). Found: C, 51.68; H, 4.61%. Calcd for $C_{13}H_{14}RuO_2$: C, 51.49; H, 4.65%.

[3]Ruthenocenophan-1-one (V). A solution of 3.00 g (0.0099 mol) of IV and 50 g (0.238 mol) of trifluoroacetic anhydride in 800 ml of cyclohexane was refluxed for 2 weeks under a nitrogen atmosphere. The cooled solution was poured into a saturated sodium hydrogencarbonate solution, extracted three times with ether which had been washed to neutrality, and then dried over anhydrous sodium sulfate. The removal of the solvent left 2.26 g (80%) of the crude product; mp 175—176 °C (acetone-water). Found: C, 54.74; H, 4.12%. Calcd for $C_{13}H_{12}RuO$: C, 54.74; H, 4.24%.

[3]Ruthenocenophane (VI). An ether solution (150 ml) of V (1.0 g) was added to a suspension of litihum aluminum hydride (0.2 g) and aluminum trichloride (0.8 g) in ether (50 ml). After refluxing for 4 h, the excess reagent was decomposed with moist ether and then with water. The resulting reaction mixture was extracted three times with ether which had been washed with water, saturated sodium hydrogencarbonate and finally brine, and then dried over anhydrous sodium sulfate. The removal of the solvent left 0.84 g (90%) of the crude product; mp 123—124 °C (hexane). Found: C, 57.30; H, 5.23%. Calcd for $C_{13}H_{14}Ru$: C, 57.56; H, 5.20%.

[4]Ruthenocenophan-2-one (VII) and [4]Ruthenocenophan-1-one (VIII). To a solution of 2.0 g (0.0070 mol) of V in 100 ml of methanol and 150 ml of ether, we added 100 ml of an etheral solution containing 0.050 mol of diazomethane. The solution was kept at 0 °C in the dark for 10 h, and then evaporated *in vacuo*. The residue was column-chromatographed over silica gel. The first band, eluted with benzene, yielded 1.5 g (71%) of [4]ruthenocenophan-2-one (VII); mp 165—166 °C (hexane-dichloromethane). Found: C, 56.12; H, 4.78%. Calcd for $C_{14}H_{14}RuO$: C, 56.19; H, 4.72%.

The second band, eluted with benzene-ethyl acetate (4 : 1), yielded a small amount of [4]ruthenocenophan-1-one (VIII) which was not isolated in the pure state.

[4]Ruthenocenophane (IX). This compound was prepared in a 73% yield under the same conditions as VI; mp 73—74 °C (benzene). Found: C, 58.89; H, 5.88%. Calcd for $C_{14}H_{16}Ru$: C, 58.94; H, 5.65%.

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