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Synthesis of [3](1,1′)[3](3,3′)- and [4](1,1′)[4](3,3′)Ruthenocenophanes

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[3](1,1′)[3](3,3′)- and [4](1,1′)[4](3,3′)Ruthenocenophanes were synthesized *via* cyclization of the propionic acid derivatives of [3](1,1′)- and [4](1,1′)ruthenocenophanes with polyphosphoric acid or trifluoroacetic anhydride, respectively. The ^{1}H NMR, IR, and electronic spectra of these dibridged ruthenocenes were measured and compared with those of monobridged ruthenocenes.

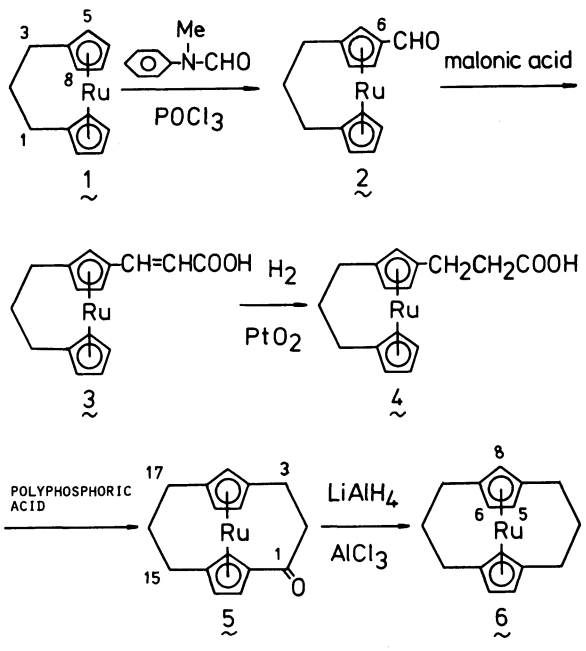
There have been a large number of studies[1–19] on heteroannularly multibridged ferrocenes including tri-, tetra-, and pentamethylene chains, because their unusual chemical and physical properties can be compared with those of cyclophanes.[20] However, no synthetic work on multibridged ruthenocenes has been found in the literature. Studies on the bridged ruthenocenes include our previous description of the synthesis and properties of [3](1,1′)- and [4](1,1′)ruthenocenophanes.[21] The synthesis of [5](1,1′)ruthenocenophanes[22] with substituents in their chains has been reported by Nesmeyanov *et al.* The precise structures of [3](1,1′)- and [4](1,1′)ruthenocenophanes have been uncovered by X-ray crystal analysis.[23] Since the distance between two cyclopentadienyl (Cp) rings in ruthenocene[24] is longer than that in ferrocene,[25] the steric strain in ruthenocenophanes can be expected to be larger than that in the corresponding ferrocenophanes. In this paper, we wish to describe the synthesis and spectral properties of [3](1,1′)[3](3,3′)- and [4](1,1′)[4](3,3′)ruthenocenophanes[26] and compare these results with those of the corresponding monobridged ruthenocenes.

Results and Discussion

[3][3]- and [4][4]Ferrocenophanes can be prepared *via* a stepwise cyclization and/or bridge enlargement in more advantageous yields than a one-step process.[2,7] Accordingly, we synthesized [3](1,1′)[3](3,3′)- and [4](1,1′)[4](3,3′)ruthenocenophanes (**6** and **15**) from the corresponding monobridged compounds.

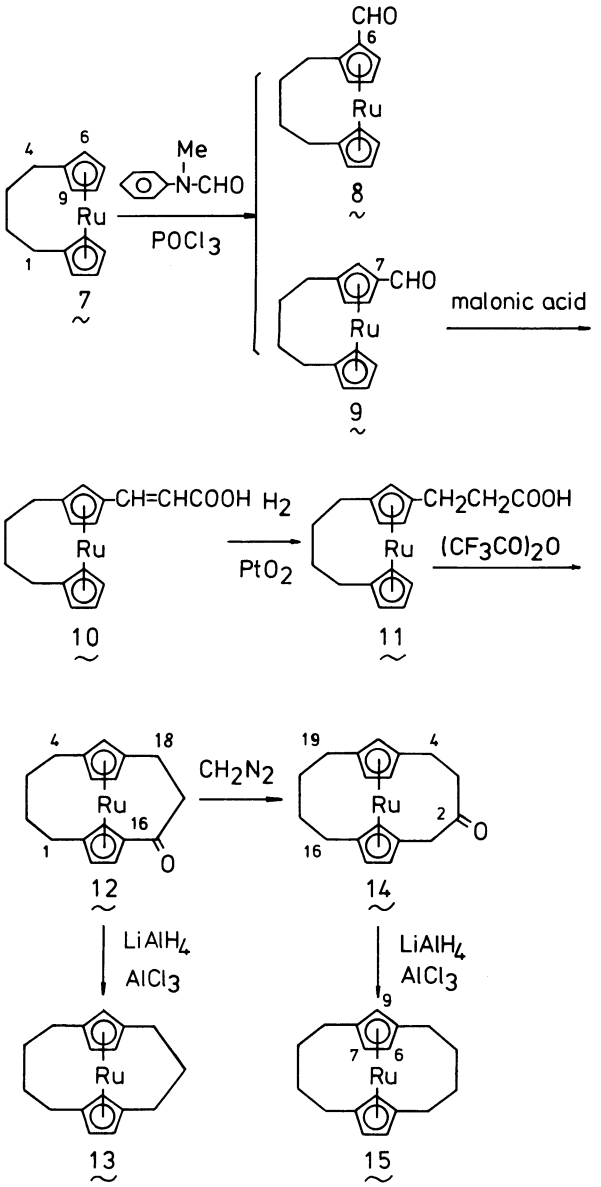
Synthesis of [3][3]Ruthenocenophanes. 6-Formyl[3](1,1′)ruthenocenophane (**2**) was synthesized in 52% yield by formylation of [3](1,1′)ruthenocenophane (**1**) with *N*-methylformanilide and $POCl_3$ without any solvent.[21] A small amount of the isomer, 5-formyl[3](1,1′)ruthenocenophane, which was not isolated in pure state, was also produced. Condensation of **2** with malonic acid in the presence of piperidine gave 6-(2-carboxyvinyl)[3](1,1′)ruthenocenophane (**3**) in good yield, and the subsequent hydrogenation of **3** over PtO_2 afforded 6-(2-carboxyethyl)[3](1,1′)ruthenocenophane (**4**). Cyclization of **4** with polyphosphoric acid gave [3](1,1′)[3](3,3′)ruthenocenophan-1-one (**5**) in 54% yield, while the reaction of **4** with trifluoroacetic anhydride did not produce **5**. [3](1,1′)[3](3,3′)Ruthenocenophane (**6**) was obtained by reduction of **5** with lithium aluminum hydride–aluminum trichloride in the usual manner (Scheme 1).

Synthesis of [4][3]- and [4][4]Ruthenocenophanes. Formylation of [4](1,1′)ruthenocenophane (**7**) with *N*-methylformanilide and $POCl_3$ without any solvent afforded 6-formyl- and 7-formyl[4](1,1′)ruthenocenophanes (**8** and **9**) in 12 and 79% yields, respectively. 7-(2-Carboxyethyl)[4](1,1′)ruthenocenophane (**11**) was prepared from **9** in good yield, in a manner similar to the one utilized in the preparation of **4**. Cyclization of **11** with trifluoroacetic anhydride in refluxing cyclohexane for 2 weeks[21] gave [4](1,1′)[3](3,3′)ruthenocenophan-16-one (**12**) in 80% yield. Bridge enlargement of **12** with diazomethane led to formation of [4](1,1′)-[4](3,3′)ruthenocenophan-2-one (**14**) in 83% yield, accompanied by a small amount of the isomer, [4](1,1′)-[4](3,3′)ruthenocenophan-1-one, which was not isolated in pure state. Reduction of **12** and **14** with lithium aluminum hydride–aluminum trichloride in the usual manner gave good yields of [4](1,1′)[3](3,3′)- and [4](1,1′)[4](3,3′)ruthenocenophanes (**13** and **15**), respectively (Scheme 2).



Scheme 1. Synthesis of [3][3]ruthenocenophanes.

^1H NMR Spectra. The chemical shifts of Cp ring protons in [*m*](1,1′)- and [*m*](1,1′)[*n*](3,3′)ruthenocenophanes (*m*, *n*=3, 4), together with those of the corresponding ferrocenophanes, are listed in Table 1. The signals observed in the ^1H NMR spectra of these ruthenocenophanes are assigned on the basis of the analogy to those of the corresponding ferrocenophanes and tri- and tetrabridged ferrocenes. The Cp ring protons of dibridged ruthenocenes **6** and **15** shift to lower fields than those of the corresponding ferrocenophanes **6′** and **15′**. These results are in accordance with those of ruthenocene and ferrocene.[27]



Scheme 2. Synthesis of [4][3]- and [4][4]Ruthenocenophanes.

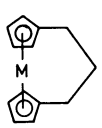
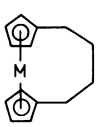
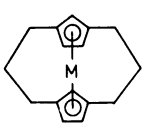
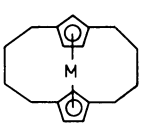
The inductive effects of the methyl and ethyl groups have been reported to influence the chemical shifts of Cp ring protons only to a small extent in the ^1H NMR spectra of alkylferrocenes.[28] The differences in the chemical shifts of dimethyl and diethyl 1,1′-ruthenocenes are 0.05[29] and 0.04 ppm, respectively (Table 2). Accordingly, the nonequivalence of the Cp ring protons in ruthenocenophanes and ferrocenophanes cannot be due to the inductive effects of methylene bridges.

The difference in chemical shifts of Cp ring protons of monobridged ruthenocenes **1** and **7** are 0.23 and 0.14 ppm, respectively. We have previously discussed these chemical shifts and splittings of Cp ring protons in **1** and **7**, and have proposed that the nonequivalent shielding of Cp rings from their original parallel geometry.[21] Such a shift difference seems to be closely related to the dihedral angles of two Cp rings in **1** and **7**; these dihedral angles are found to be *ca.* 15° and 2°, respectively.[23]

On the other hand, the difference in the chemical shifts of the Cp ring protons of [3](1,1′)ferrocenophane (**1′**) and of [4](1,1′)ferrocenophane (**7′**) is 0.04 ppm; the corresponding difference for [3](1,1′)[3](3,3′)ferrocenophane (**6′**) is 0.05 and for [4](1,1′)[4](3,3′)ferrocenophane (**15′**) is 0.08 ppm. Hisatome *et al.* have not given clear-cut explanations of these results.[15] Simple molecular models for **1′** and **7′** suggest that the dihedral angles for the two Cp rings in **1′** and **7′** are *ca.* 0°. It has been reported that the dihedral angle of two Cp rings in **6′** is 9°.[30] Again, a simple molecular model for **15′** suggests that the dihedral angle in **15′** is *ca.* 0°.

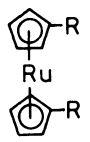
Such a correlation between shift difference in Cp ring protons and the dihedral angle of two Cp rings in the monobridged systems is not found in the dibridged systems. In ruthenocenophane system, the difference in the chemical shifts of Cp ring protons of **6** is 0.12 and that of **15** is 0.21 ppm. The distance between two Cp rings in ruthenocene[24] is longer than

Table 1. Chemical shifts of Cp ring protons in ruthenocenophanes and ferrocenophanes (δ)[a]

Compound								
M	M=Ru, **1**; M=Fe, **1′**		M=Ru, **7**; M=Fe, **7′**		M=Ru, **6**; M=Fe, **6′**		M=Ru, **15**; M=Fe, **15′**	
	H(5, 8)	H(6, 7)	H(6, 9)	H(7, 8)	H(5, 6)	H(8)	H(6, 7)	H(9)
Ru	4.42	4.65	4.58	4.44	4.43	4.31	4.47	4.68
Fe[b]	3.98	4.02	4.14 4.13	4.10	3.89	3.84	3.96	4.04

a) In $CDCl_3$. b) Ref. 15.

TABLE 2. CHEMICAL SHIFTS OF Cp RING PROTONS IN DIALKYL 1,1′-RUTHENOCENES (δ)



	H(2, 5)	H(3, 4)	R	
R=Me[a]	4.34	4.29	-Me	1.89
R=Et[b]	4.44	4.40	-Me	1.07(t, J=7.4 Hz)
			$-CH_2-$	2.91(q, J=7.4 Hz)

a) Ref. 29 in CCl_4. b) This work in $CDCl_3$.

TABLE 3. CHEMICAL SHIFTS OF METHYLENE PROTONS OF BRIDGES IN RUTHENOCENOPHANES AND FERROCENOPHANES (δ)[a]

Compound	Methylene protons of bridges
1	1.76 (bs)[c,e]
7	1.3—1.8 (m)[d,e] 2.1—2.6 (m)
6	1.72 (bs) 2.22 (bs)
15	1.4—1.6 (m) 2.1—2.3 (m)
1′	1.95 (s)[b,f]
7′	1.4—1.5 (m)[f] 2.0—2.2 (m)
6′	0.9—1.3 (m)[g]
15′	1.60—1.90 (m)[h] 2.20—2.55 (m)

a) In $CDCl_3$. b) Singlet. c) Broad singlet. d) Multiplet. e) Ref. 21. f) This work. g) Ref. 33. h) Ref. 7.

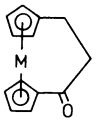
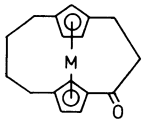
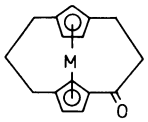
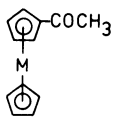
that in ferrocene[25] by 0.36 Å. Accordingly, the dihedral angle in **6** may be more than 9°, which may be larger than that in **15**. On the basis of molecular model examinations, the considerable strain in **6** and **15** might result in the deviations of two Cp rings from their original sp^2 planes. This might affect the chemical shifts and splittings of the Cp ring protons in **6** and **15**. Such an assumption would be confirmed by X-ray crystal analysis.

The chemical shifts of methylene protons of bridges in [*m*](1,1′)- and [*m*](1,1′)[*n*](3,3′)ruthenocenophanes (*m*, *n*=3, 4), together with those of the corresponding ferrocenophanes, are summarized in Table 3. The methylene protons of **7** and **15** with one and two tetramethylene bridges show two multiplets. However, methylene protons of **1** with one trimethylene bridge show one broad singlet, while those of **6** with two trimethylene bridges show two broad singlets. This seems to suggest that **6** has a more rigid structure than **1**, in contrast to the systems of **7** and **15**. On the other hand, **6′** shows one multiplet, in contrast to **6**. Although **15′** shows two multiplets, similar to **15**, the widths of the multiplets in **15′** are larger than those in **15**. These results suggest that the ruthenocenophanes **6** and **15** have more rigid structures than those of the corresponding ferrocenophanes **6′** and **15′**, and that **6** has the most rigid structure among these phane compounds.

IR Spectra. The frequencies of carbonyl-stretching absorptions in [*m*](1,1′)- and [*m*](1,1′)[*n*](3,3′)-ruthenocenophanones (*m*, *n*=3, 4), together with those of the corresponding ferrocenophanones, are listed in Table 4. In our previous paper,[21] the carbonyl-stretching vibrations have suggested that the π-orbitals of the carbonyl group effectively conjugate with the π-systems of the adjacent Cp ring in [3](1,1′)-ruthenocenophan-1-one (1656 cm^{-1}), as in acetylruthenocene (1658 cm^{-1}). The dihedral angle between the plane of the carbonyl group and the plane of the adjacent Cp ring has been considered to become smaller when two Cp rings are tilted to a greater extent. We have confirmed this assumption from the ^{13}C NMR measurements of several ruthenocenophanones and ferrocene homologs.[31] The carbonyl group in the ruthenocenophanone **5** with two trimethylene bridges is located at higher frequency (1686 cm^{-1}) than that in [3](1,1′)ruthenocenophan-1-one with one trimethylene bridge. A similar trend is observed in ferrocene homologs; [3](1,1′)ferrocenophan-1-one (1658 cm^{-1}) and [3](1,1′)[3](3,3′)ferrocenophan-1-one (1665 cm^{-1}). Owing to an additional trimethylene bridge, therefore, the dihedral angles between the carbonyl group and the adjacent Cp ring in **5** and the corresponding ferrocenophanone might be larger than those in [3](1,1′)ruthenocenophan-1-one and the corresponding ferrocenophanone.

Electronic Spectra. The spectra of trimethylene bridged ruthenocenes **6** and **1** and tetramethylene bridged ruthenocenes **15** and **7** are shown in Figs. 1 and 2, respectively. The intensities of the charge transfer band in the 230—260 nm region and the spin-allowed d-d band in 310—340 nm region of the dibridged ruthenocene **6** increase as compared with those of the monobridged ruthenocene **1** (Fig. 1). In the spectrum of the dibridged ruthenocene **15**, again, the intensity of the charge transfer band increases, while the intensity of spin-allowed d-d band decreases relative to that for the monobridged ruthenocene **7** (Fig. 2). We have previously reported that the ring-tilting would increase the intensity of the spin-allowed d-d band in the electronic spectra of **1** and **7**.[21] Recently, the dihedral angles of two Cp rings in **1** and **7** have been found to be *ca.* 15° and 2°, respectively.[23] These results suggest that the intensity of the spin-allowed d-d band might be affected by the steric strain at the Ru atom, and that **6** might be the most compressed among [*m*](1,1′)- and [*m*](1,1′)[*n*](3,3′)ruthenocenophanes (*m*, *n*=3, 4).

TABLE 4. CARBONYL-STRETCHING FREQUENCIES IN RUTHENOCENOPHANONES AND FERROCENOPHANONES (cm^{-1})[a]

Compound / M				
Ru	1656[b]	1652	1686	1658[e]
Fe	1681[d] 1658[g]	1662[c]	1665[f]	1658[e]

a) In KBr pellets. b) Ref. 21. c) Ref. 32. d) Ref. 33. e) Ref. 7. f) Ref. 2. g) This work.

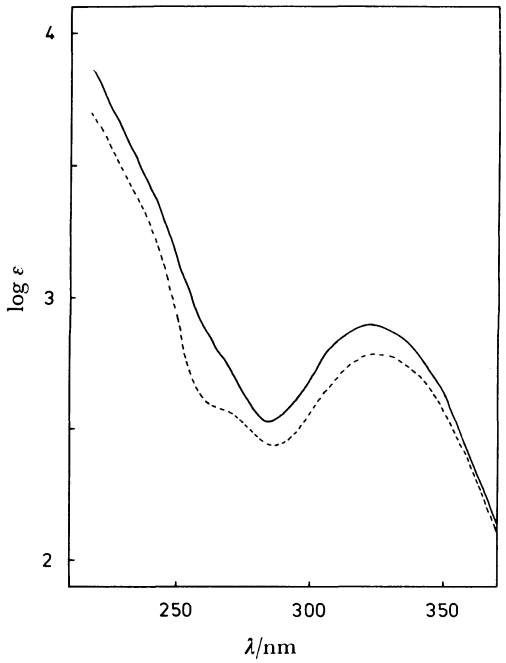


Fig. 1. Electronic spectra in abs EtOH: (——) [3](1,1′)-[3](3,3′)ruthenocenophane (**6**) and (----) [3](1,1′)-ruthenocenophane (**1**).

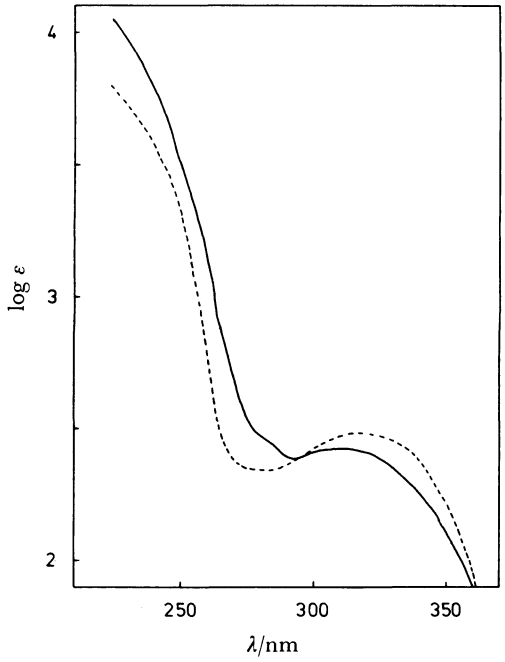


Fig. 2. Electronic spectra in abs EtOH: (–) [4](1,1′)-[4](3,3′)ruthenocenophane (**15**) and (----) [4](1,1′)-ruthenocenophane (**7**).

Experimental

Measurements. All the melting points are uncorrected. The ^1H NMR spectra were obtained in $CDCl_3$ with a JEOL JNM-FX 100 spectrometer (100 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. All IR spectral data are expressed in cm^{-1}. The electronic spectra were recorded in abs EtOH with a Hitachi Model 100—60 double beam spectrophotometer at room temperature. All absorption frequencies are given in λ (nm). The mass spectra were obtained with a JEOL JMS-DX 300 mass spectrometer using a direct insertion probe at 70 eV ionizing energy.

Materials. [3](1,1′)- and [4](1,1′)Ruthenocenophanes (**1** and **7**) were prepared according to the method in the literature.[21] Column chromatographic separations were carried out with Merck Kieselgel 60 (70—230 mesh), Wakogel C-200 (200 mesh), Mallinckrodt silicic acid (100 mesh) or Kanto Kagaku silica gel (100 mesh). All the synthetic reactions were performed under a N_2 atmosphere.

6-Formyl[3](1,1′)ruthenocenophane (2). A mixture of [3](1,1′)ruthenocenophane (**1**) (3.0 g, 11 mmol), *N*-methylformanilide (1.7 g, 13 mmol) and $POCl_3$ (3.7 g, 24 mmol) was vigorously stirred at 70 °C for 4 h. After the addition of sodium acetate trihydrate (16.5 g) in water (100 ml), the solution was stirred at 70 °C for 2 h, and then extracted with ether. The residue was chromatographed over silica gel with benzene–ethyl acetate as eluent. The first band eluted with benzene yielded a small amount of 5-formyl[3](1,1′)-ruthenocenophane, which was not isolated in pure state.

The second band eluted with benzene–ethyl acetate (40:1) yielded **2** (1.7 g, 52%), pale orange prisms, mp 90—91 °C (hexane–ethyl acetate). ^1H NMR: δ=1.76 (4H, bs, bridged $-CH_2-$), 1.84(2H, bs, bridged $-CH_2-$), 4.39 (1H, dd, J=1.3 and 3.1 Hz, Cp), 4.57 (1H, dd, J=1.5 and 2.9 Hz, Cp), 4.75 (3H, m, Cp), 4.95 (1H, t, J=1.2 Hz, Cp), 5.05 (1H, dd, J=1.2 and 2.4 Hz, Cp) and 9.65 (1H, s, −CHO). IR: 1650 (C=O). Electronic spectrum ($\lambda_{max}(\varepsilon)$): 253 (10500) and 345 (2960). MS (*m/z*): 299 (M^+, 71) and 270 ([M−CHO]$^+$, 100). Found: C, 55.93; H, 4.62%. Calcd for $C_{14}H_{14}ORu$: C, 56.18; H, 4.71%.

6-(2-Carboxyvinyl)[3](1,1′)ruthenocenophane (3). A solution of **2** (1.0 g, 3.3 mmol), malonic acid (0.69 g, 6.6 mmol) and piperidine (0.24 g) in dry pyridine (15 ml) was stirred at 100 °C for 3 h. The cooled solution was diluted with water and extracted with chloroform. The extract was washed with dil HCl and water, and then extracted with a 2 M NaOH solution (1 M=1 mol dm^{-3}). The aqueous layer

was acidified with dil HCl, and placed in a refrigerator overnight. The precipitates were found to be **3** (0.95 g, 84%), orange plates, mp 205—206 °C (EtOH). ^{1}H NMR: δ=1.74 (4H, bs, bridged -CH_2-), 1.89 (2H, bs, bridged -CH_2-), 4.34 (1H, m, Cp), 4.56 (3H, m, Cp), 4.74 (2H, m, Cp), 4.89 (1H, m, Cp), 5.90 and 7.53 (2H, an AX system, J=15.5 Hz, *trans* olefinic protons). IR: 1665 (C=O) and 1605 (C=C). $\lambda_{max}(\varepsilon)$: 275 (17600) and 365 (714). MS: 341 (M^+, 100), 296([M−CO_2-H]$^+$, 87) and 270 ([M−CH=$CHCO_2H$]$^+$, 11). Found: C, 56.43; H, 5.16%. Calcd for $C_{16}H_{16}O_2Ru$: C, 56.30; H, 4.72%.

6-(2-Carboxyethyl)[3](1,1′)ruthenocenophane (4). A solution of **3** (4.0 g, 12 mmol) in ethanol (500 ml) was hydrogenated over PtO_2 (50 mg) at room temperature for 20 h under H_2 1 atm to give **4** (4.0 g, 99%), yellow needles, mp 131—132 °C (EtOH). ^{1}H NMR: δ=1.73 (6H, bs, bridged -CH_2-), 2.50 (4H, s, -CH_2- of -$CH_2CH_2CO_2H$), 4.32 (1H, m, Cp), 4.36 (2H, m, Cp), 4.44 (1H, m, Cp), 4.54 (2H, m, Cp), and 4.63 (1H, m, Cp). IR: 1686 (C=O). $\lambda_{max}(\varepsilon)$: 270^{sh} (646) and 324 (898). MS: 343 (M^+, 75) and 284 ([M−CH_2CO_2-H]$^+$, 100). Found: C, 56.01; H, 5.24%. Calcd for $C_{16}H_{18}O_2Ru$: C, 55.97; H, 5.28%.

[3](1,1′)[3](3,3′)Ruthenocenophan-1-one (5). A suspension of **4** (0.80 g, 2.3 mmol) and polyphosphoric acid (400 g) was vigorously stirred at 100 °C for 24 h. The cooled solution was poured into ice-cold water, and extracted with chloroform. The residue was chromatographed over silica gel with benzene-ethyl acetate (5:1) to give **5** (0.40 g, 54%), deep yellow needles, mp 150—151 °C (hexane-ethyl acetate). ^{1}H NMR: δ=1.69 (4H, bs, bridged -CH_2-), 1.78 (2H, bs, bridged -CH_2-), 2.4—3.2 (4H, m, H(2) and H(3) of bridged -CH_2-), 4.4—4.5 (2H, m, Cp), 4.5—4.6 (1H, m, Cp), 4.6—4.7 (1H, m, Cp), 4.78 (1H, s, Cp), and 4.82 (1H, s, Cp). $\lambda_{max}(\varepsilon)$: 254 (5830), 340^{sh} (1160), and 372 (1320). MS: 325 (M^+, 100), 297 ([M−CO]$^+$, 70), 283 ([M−CH_2CO]$^+$, 11), and 269 ([M−CH_2CH_2CO]$^+$,9). Found: C, 59.23; H, 5.11%. Calcd for $C_{16}H_{16}ORu$: C, 59.06; H, 4.96%.

[3](1,1′)[3](3,3′)Ruthenocenophane (6). A solution of **5** (0.40 g, 1.2 mmol) in dry ether (50 ml) was added dropwise to a suspension of $LiAlH_4$ (0.60 g, 16 mmol) and $AlCl_3$ (3.2 g, 24 mmol) in dry ether (50 ml). After refluxing for 4 h, the reaction mixtures were extracted with ether. The residue was chromatographed over silica gel with benzene to yield **6** (0.30 g, 78%), pale yellow needles, mp 114—115 °C (ethyl acetate). $\lambda_{max}(\varepsilon)$: 272^{sh} (481) and 322 (778). MS: 311 (M^+, 100), 297([M−CH_2]$^+$, 16), and 283([M-CH_2CH_2]$^+$, 7). Found: C, 62.01; H, 5.40%. Calcd for $C_{16}H_{18}Ru$: C, 61.72; H, 5.83%.

6-Formyl- and 7-formyl[4](1,1′)ruthenocenophanes (8 and 9). [4](1,1′)Ruthenocenophane (**7**) (1.5 g, 5.3 mmol), *N*-methylformanilide (0.78 g, 5.8 mmol), and $POCl_3$ (0.89 g, 5.8 mmol) were stirred at 70 °C for 4 h. After the addition of sodium acetate trihydrate (7.2 g) in water (50 ml), the solution was stirred at 70 °C for 2 h. The residue was separated into two bands by chromatography over silica gel with hexane-ethyl acetate as eluent. The first band eluted with hexane-ethyl acetate (20:1) yielded **8** (0.20 g, 12%), deep yellow prisms, mp 144—145 °C (hexane-ethyl acetate). ^{1}H NMR: δ=1.5—1.7 (4H, m, H(2) and H(3) of bridged -CH_2-), 2.2—2.5 (4H, m, H(1) and H(4) of bridged -CH_2-), 4.45 (1H, m, Cp), 4.58 (2H, t, J=2.2 Hz, Cp), and 4.66 (1H, m, Cp), 4.74(1H, d, J=2.9 Hz, Cp), 4.92 (2H, m, Cp), and 9.97 (1H, s, -CHO). IR: 1669 (C=O). $\lambda_{max}(\varepsilon)$: 248 (10400) and 351 (1090). MS: 313 (M^+, 57), 284 ([M−CHO]$^+$, 100), 270 ([M−CH_2CHO]$^+$, 22), and 256 ([M−CH_2CH_2CHO]$^+$, 33). Found: C, 57.13; H, 5.10%. Calcd for $C_{15}H_{16}ORu$: C, 57.49; H, 5.15%.

The second band eluted with hexane-ethyl acetate (5:1) yielded **9** (1.3 g, 79%), deep yellow needles, mp 90—91 °C (hexane-ethyl acetate). ^{1}H NMR: δ=1.5—1.7 (4H, m, H(2) and H(3) of bridged -CH_2-), 2,2—2.5 (4H, m, H(1) and H(4) of bridged -CH_2-), 4.59 (3H, m, Cp), 4.74(1H, m, Cp), 4.90, (1H, m, Cp), 4.96 (1H, m, Cp), 5.14 (1H, s, Cp), and 9.63 (1H, s, -CHO). IR: 1669 (C=O). $\lambda_{max}(\varepsilon)$: 257 (13300) and 359 (2060). MS: (M^+, 91), 284 ([M−CHO]$^+$, 100), 270 ([M−CH_2CHO]$^+$, 16), and 256 ([M−CH_2CH_2CHO]$^+$, 31). Found: C, 57.75; H, 5.20%. Calcd for $C_{15}H_{16}ORu$: C, 57.49; H, 5.15%.

7-(2-Carboxyvinyl)[4](1,1′)ruthenocenophane (10). The aldehyde **9** (1.9 g, 6.1 mmol) was treated with malonic acid (1.3 g, 12 mmol) and piperidine (0.27 g) in dry pyridine (30 ml) at 100 °C for 3 h. The cooled solution was extracted with chloroform. The extract was washed with dil HCl and water, and then extracted with a 2 M NaOH solution. Acidification of the aqueous layer with dil HCl gave the precipitate of **10** (1.9 g, 88%), pale orange prisms, mp 189—190 °C (EtOH). ^{1}H NMR: δ=1.4—1.7 (4H, m, H(2) and H(3) of bridged -CH_2-), 2.2—2.4 (4H, m, H(1) and H(4) of bridged -CH_2-), 4.29 (1H, m, Cp), 4.56 (2H, m, Cp), 4.71 (1H, m, Cp), 4.76 (2H, d, J=1.0 Hz, Cp), 4.93 (1H, s, Cp), 5.90 and 7.50 (2H, an AX system, J=15.6 Hz, *trans* olefinic protons). IR: 1666 (C=O) and 1611 (C=C). $\lambda_{max}(\varepsilon)$: 287 (18800) and 354 (4800). MS: 355 (M^+, 100), 310 ([M−CO_2-H]$^+$, 45), and 284 ([M−CH=$CHCO_2H$]$^+$, 39). Found: C, 57.37; H, 5.59%. Calcd for $C_{17}H_{18}O_2Ru$: C, 57.45; H, 5.10%.

7-(2-Carboxyethyl)[4](1,1′)ruthenocenophane (11). Hydrogenation of **10** (4.0 g, 11 mmol) over PtO_2 (50 mg) in ethanol (500 ml) gave **11** (4.0 g, 99%), pale yellow prisms, mp 128—129 °C (EtOH). ^{1}H NMR: δ=1.4—1.6 (4H, m, H(2) and H(3) of bridged -CH_2-), 2.2—2.4 (4H, m, H(1) and H(4) of bridged -CH_2-), 2.49(4H, s, -CH_2- of -CH_2CH_2-CO_2H), 4.31 (1H, m, Cp), 4.42 (1H, m, Cp), 4.5—4.6 (4H, m, Cp), and 4.63 (1H, m, Cp). IR: 1701 (C=O). $\lambda_{max}(\varepsilon)$: 313 (312). MS: 357 ($M^+$, 14), 312([M−$CO_2H$]$^+$, 41), 298 ([M−$CH_2CO_2H$]$^+$, 83), and 284 ([M−$CH_2CH_2CO_2H$]$^+$, 100). Found: C, 56.80; H, 5.67%. Calcd for $C_{17}H_{20}O_2Ru$: C, 57.13; H, 5.64%.

[4](1,1′)[3](3,3′)Ruthenocenophan-16-one (12). A mixture of **11** (5.0 g, 14 mmol) and $(CF_3CO)_2O$ (15 g, 0.70 mol) in dry cyclohexane (500 ml) was refluxed for 2 weeks. The cooled mixture was poured into saturated aq $NaHCO_3$ and extracted with ether. The residue was chromatographed over silica gel with benzene-ethyl acetate(1:1) to give **12** (3.8 g, 80%), yellow prisms, mp 139—140 °C (hexane-ethyl acetate). ^{1}H NMR: δ=1.4—1.6 (4H, m, H(2) and H(3) of bridged -CH_2-), 2.1—2.4 (4H, m, H(1) and H(4) of bridged -CH_2-), 2.87 (4H, bs, H(17) and H(18) of bridged -CH_2-), 4.57 (1H, dd, J=1.2 and 2.0 Hz, Cp), 4.82 (1H, dd, J=1.2 and 2.1 Hz, Cp), 4.93 (1H, dd, J=2.4 and 4.9 Hz, Cp), 4.94 (1H, dd, J=2.4 and 4.8 Hz, Cp), 5.20 (1H, t, J=1.0 Hz, Cp), and 5.28 (1H, t, J=1.1 Hz, Cp). $\lambda_{max}(\varepsilon)$: 259 (4840) and 333^{sh} (787). MS: 339 (M^+, 100), 311 ([M−CO]$^+$, 100), 297 ([M−CH_2-CO]$^+$, 48), and 283 ([M−CH_2CH_2CO]$^+$, 69). Found: C, 60.00; H, 5.24%. Calcd for $C_{17}H_{18}ORu$: C, 60.16; H, 5.35%.

[4](1,1′)[3](3,3′)Ruthenocenophane (13). A suspension of **12** (0.50 g, 1.5 mmol), $LiAlH_4$ (0.17 g, 4.4 mmol), and $AlCl_3$ (0.88 g, 6.64 mmol) in dry THF (50 ml) was refluxed for 3 h. After the excess reagent was decomposed with moist THF and water, the products were extracted with ether. The residue was chromatographed over silica gel with benzene to yield **13** (0.35 g, 72%), pale yellow needles, mp 40—41 °C (benzene). ^{1}H NMR: δ=1.3—1.7 (10H, m, bridged -CH_2-), 1.8—2.3 (4H, m, bridged -CH_2-), 4.33 (2H, dd, J= 1.2 and 2.0 Hz, Cp), 4.52 (2H, s, H(9) and H(15) of Cp), and 4.68 (2H, dd, J=1.2 and 2.1 Hz, Cp). $\lambda_{max}(\varepsilon)$: 266^{sh} (645) and 319 (606). MS: 325 (M^+, 100) and 297 ([M−CH_2CH_2]$^+$, 87). Found: C, 62.43; H, 6.16%. Calcd for $C_{17}H_{20}Ru$: C, 62.75; H, 6.19%.

[4](1,1′)[4](3,3′)Ruthenocenophan-2-one (14). To a solution of **12** (2.5 g, 7.4 mmol) in methanol (100 ml) and ether (150 ml), CH_2N_2 (0.37 mol) in ether (500 ml) was

added. The resulting solution was stirred at 0 °C for 10 h in the dark, and then evaporated. The residue was chromatographed over silica gel with benzene–ethyl acetate as eluent. The first band eluted with benzene–ethyl acetate (10:1) yielded **14** (2.2 g, 83%), pale orange prisms, mp 118—119 °C (hexane–ethyl acetate). ^{1}H NMR: δ=1.4—1.6 (4H, m, H(17) and H(18) of bridged $-CH_2-$), 2.1—2.3 (4H, m, H(16) and H(19) of bridged $-CH_2-$), 2.5—2.6 (2H, m, H(4) of bridged $-CH_2-$), 2.7—2.9 (2H, m, H(3) of bridged $-CH_2-$), 3.16 (2H, s, H(1) of bridged $-CH_2-$), 4.50 (2H, dd, J=1.2 and 2.3 Hz, Cp), 4.58 (2H, dd, J=1.2 and 2.3 Hz, Cp), and 4.78 (2H, s, H(9) and H(15) of Cp). IR: 1686 (C=O). $\lambda_{max}(\varepsilon)$: 280^{sh} (1490). MS: 353 (M^+, 98), 325 ([M−CO]$^+$, 100), 311 [M−CH_2CO]$^+$, 47), and 297 ([M−CH_2CH_2CO]$^+$, 85). Found: C, 61.43; H, 5.79%. Calcd for $C_{18}H_{20}ORu$: C, 61.17; H, 5.70%.

The second band eluted with benzene–ethyl acetate (1:20) yielded a small amount of [4](1,1′)[4](3,3′)ruthenocenophan-1-one, which was not isolated in the pure state.

[4](1,1′)[4](3,3′)Ruthenocenophane (15). A mixture of **14** (1.0 g, 2.8 mmol), $LiAlH_4$ (0.32 g, 8.4 mmol), and $AlCl_3$ (1.7 g, 13 mmol) in dry THF (100 ml) was refluxed for 5 h, and then extracted with ether. The residue was chromatographed over silica gel with benzene–ethyl acetate (20:1) to yield **15** (0.72 g, 75%), pale yellow needles, mp 94—95 °C (petroleum ether). $\lambda_{max}(\varepsilon)$: 280^{sh} (292) and 309 (260). MS: 339 (M^+, 100) and 311 ([M−CH_2CH_2]$^+$, 66). Found: C, 63.76; H, 6.58%. Calcd for $C_{18}H_{22}Ru$: C, 63.69; H, 6.53%.

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