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Synthesis of [3.3](1,1')- and [5.5](1,1')Ruthenocenophanes and Their Ferrocenoruthenocenophane Homologs

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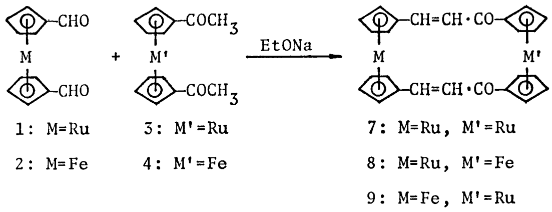
[3.3](1,1')Ruthenocenophane-2,14-diene-1,16-dione, [5.5](1,1')ruthenocenophane-2,14,17,29-tetraene-1,16-dione and their ferrocenoruthenocenophane homologs were synthesized by using an intermolecular base-catalyzed condensation.

A variety of layered compounds have been synthesized and their physical and chemical properties have been studied.[1—4] Cyclophanes in which aromatic rings are mutually stratified have been well investigated from a viewpoint of transannular π-electronic interactions. In contrast to the active interest in cyclophanes, little attention has been focused on [2.2](1,1')ferrocenophane-1,13-diyne,[5] [2.2](1,1')ferrocenophane-1,13-diene,[6] [2]paracyclo[2]paracyclo[2](1,1')ferrocenophane derivatives,[7] [3.3](1,1')ferrocenophane-1,15-diene-3,14-dione,[8] [5.5](1,1')ferrocenophanel,4,-16,19-tetraene-3,18-dione,[8] and [0]metacyclo[2]metacyclo[0](1,1')ferrocenophan-7-ene.[9] In addition, there are only a few synthetic investigations of [5]-ruthenocenophane derivatives[10] and [3]- and [4]-ruthenocenophane derivatives.[11] This paper is concerned with the synthesis of [3.3](1,1')- and [5.5](1,1')ruthenocenophanes and their ferrocenoruthenocenophane homologs, including olefinic and carbonyl groups between metallocene systems, in order to examine the transannular π-electronic interactions of the chromophores.

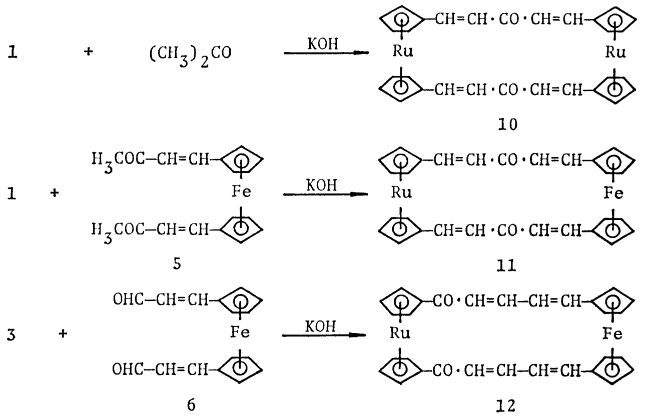
Results and Discussion

Synthesis of [3.3](1,1')Ruthenocenophane. In the presence of sodium ethoxide, the reaction of 1,1'-ruthenocenedicarbaldehyde (**1**) with 1,1'-diacetylruthenocene (**3**)[12] in ethanol gave a good yield of [3.3](1,1')ruthenocenophane-2,14-diene-1,16-dione (**7**).[13] Under the same conditions, the internal base-catalyzed condensations of **1** with 1,1'-diacetylferrocene (**4**)[17] and 1,1'-ferrocenedicarbaldehyde (**2**)[16] with **3** gave rise to the formation of [3.3](1,1')ferrocenoruthenocenophane-13,25-diene-1,12-dione (**8**)[13] and [3.3](1,1')ferrocenoruthenocenophane-2,14-diene-1,16-dione (**9**),[13] respectively (Scheme 1).



Scheme 1.

Synthesis of [5.5](1,1')Ruthenocenophane. In the presence of KOH, the base-catalyzed condensation of **1** with acetone led to the formation of [5.5](1,1')ruthenocenophane-2,14,17,29-tetraene-1,16-dione (**10**).[13] In the same manner, the reactions of **1** with 1,1'-bis(2-acetylvinyl)ferrocene (**5**)[18] and of **3** with 1,1'-bis(2-formylvinyl)ferrocene (**6**)[18] also gave [5.5](1,1')ferrocenoruthenocenophane-2,14,17,29-tetraene-1,16-dione (**11**)[13] and [5.5](1,1')ferrocenoruthenocenophane-2,4,16,18-tetraene-1,20-dione (**12**),[13] respectively (Sceheme 2).



Scheme 2.

Characterization and Spectral Data. The structures of the phane compounds **7**—**12** and the other compounds were determined on the basis of IR, ^{1}H NMR, and mass spectra and elemental analyses. The ^{1}H NMR spectral data of the phane compounds **7**—**12** are summarized in Table 1. The coupling constants of doublets for olefinic protons in **7**—**12** are 15 or 16 Hz, except for the case of **12**. On the other hand, the IR spectral data of olefinic linkages in **7**—**12** exhibit two bands at *ca.* 1600 and 960 cm^{-1} (Table 2). The J values in the ^{1}H NMR spectra and the IR spectral data support the conclusion that the olefinic protons occupy a *trans* position relative to each other. The ^{1}H NMR signal of the olefinic protons in **7** (δ, 6.34 and 6.91 ppm) is shifted upfield by about 0.37 ppm, as compared with that of the reference compound, 1,3-diruthenocenyl-2-propen-1-one (**13**) (δ, 6.71 and 7.29 ppm) (Fig. 1). The upfield shift of the olefinic protons in **7** should be due to the magnetic anisotropy of the other olefinic bond. Similarly, the protons of the olefinic bonds in **8**, **9**, **10**, **11**, and **12** are shifted somewhat upfield, as compared with the positions of the reference compounds, 1-ferrocenyl-3-ruthenocenyl-2-propen-1-one (**14**), 3-ferrocenyl-1-ruthenocenyl-2-propen-1-one (**15**), 1,5-diruthenocenyl-1,4-pentadien-3-one (**16**), 1-ferrocenyl-5-ruthenocenyl-1,4-

Table 1. ^{1}H NMR spectral data of phane compounds (**7**—**12**) and the reference compounds (**13**—**18**) (δ)[a]

Compound	Olefinic proton	Cp ring proton
7	6.34 (d,[c] J=16 Hz) 6.91 (d, J=16 Hz)	4.76 (t)[d] 4.84 (t) 5.12 (t) 5.37 (t)
8	6.29 (d, J=16 Hz) 6.80 (d, J=16 Hz)	4.55 (t) 4.80 (t) 5.03 (t) 5.10 (t)
9	6.48 (d, J=15 Hz) 7.06 (d, J=15 Hz)	4.48 (t) 4.76 (t) 4.80 (t) 4.91 (t)
10	6.14 (d, J=16 Hz) 6.73 (d, J=16 Hz)	4.80 (t) 5.04 (t)
11[f]	6.05 (d, J=16 Hz) 6.17 (d, J=16 Hz) 7.05 (d, J=16 Hz) 7.21 (d, J=16 Hz)	4.45 (t) 4.54 (t) 4.77 (t) 4.89 (t)
12	6.3—7.1 (m)[e] 7.19 (d, J=15 Hz)	4.44 (t) 4.47 (t) 4.92 (t) 5.28 (t)
13	6.71 (d, J=16 Hz) 7.29 (d, J=16 Hz)	4.55 (s)[b] 4.57 (s) 4.77 (t) 4.87 (t) 5.13 (t) 5.20 (t)
14	6.91 (d, J=15 Hz) 7.39 (d, J=15 Hz)	4.17 (s) 4.56 (s) 4.61 (t) 4.79 (t) 4.92 (t) 5.21 (s)
15	6.77 (d, J=16 Hz) 7.44 (d, J=16 Hz(	4.16 (s) 4.51 (t) 4.60 (s) 4.76 (t) 4.89 (t) 5.28 (t)
16	6.63 (d, J=16 Hz) 7.39 (d, J=16 Hz)	4.57 (s) 4.77 (t) 5.07 (t)
17[f]	6.54 (d, J=16 Hz) 6.55 (d, J=16 Hz) 7.49 (d, J=16 Hz) 7.59 (d, J=16 Hz)	4.17 (s) 4.47 (t) 4.56 (s) 4.73 (t) 4.93 (t)
18	6.8—7.2 (m) 7.30 (d, J=15 Hz)	4.16 (s) 4.42 (t) 4.58 (t) 4.61 (s) 4.87 (t) 5.18 (t)

a) In DMSO-d_6 except where indicated otherwise. b) Singlet. c) Doublet. d) Triplet. e) Multiplet. f) In $CDCl_3$.

Table 2. IR spectral data of phane compounds (**7**—**12**) and the reference compounds (**13**—**18**)

Compound	$\tilde{\nu}$(-HC=CH-)/cm^{-1}	$\tilde{\nu}$($>$C=O)/cm^{-1}
7	1591, 961	1651
8	1591, 959	1655
9	1592, 972	1659
10	1587, 968	1610
11	1560, 982	1655
12	1580, 960	1645
13	1586, 965	1652
14	1574, 975	1642
15	1585, 966	1649
16	1562, 978	1610
17	1575, 986	1626
18	1585, 1002	1650

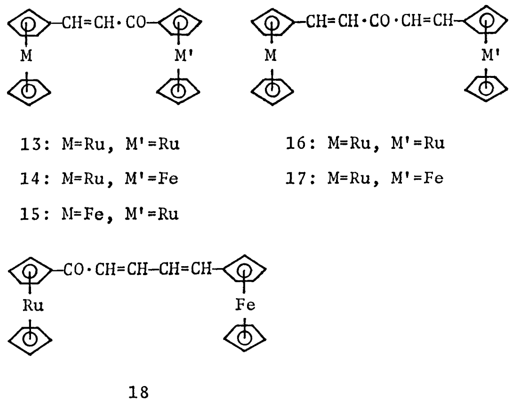


Fig. 1.

pentadien-3-one (**17**), and 5-ferrocenyl-1-ruthenocenyl-2,4-pentadien-1-one (**18**), respectively (see Table 1). These upfield shifts may also be caused by the magnetic anisotropy of the other olefinic group.

The electronic spectra of phane compounds **7**, **10**, and **12** and the reference compounds **13**, **16**, and **18** in chloroform are shown in Figs. 2—4. The electronic spectra of d^6 metallocenes have been thoroughly studied.[14] It is well known that the bathochromic and hyperchromic shifts of absorption bands of metallocenes are caused by the conjugations of the olefinic and carbonyl groups with cyclopentadienyl rings.[15] Thus, the absorption bands of **13**, **16**, and **18** in the 400 and 500 nm regions correspond to the spin-allowed d-d transitions of ruthenocene and ferrocene, respectively. The intense bands of **13**, **16**, and **18** at *ca.* 300 nm are associated with the charge transfer

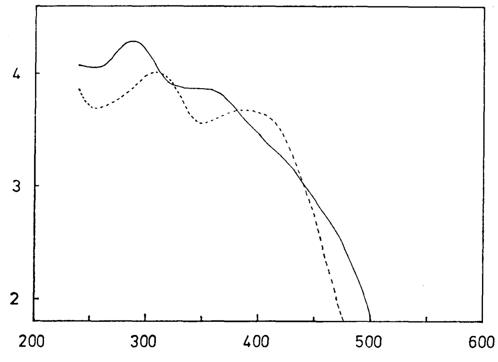


Fig. 2. The electronic spectra of phane compound **7** (——) and the reference compound **13** (----) in chloroform.

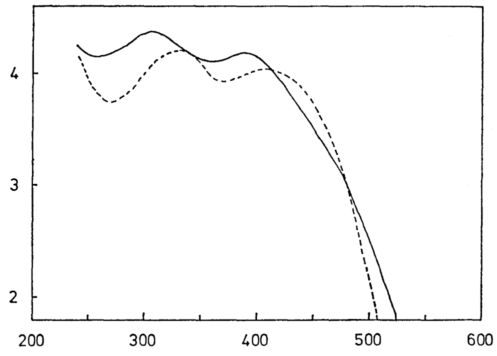


Fig. 3. The electronic spectra of phane compound **10** (——) and the reference compound **16** (----) in chloroform.

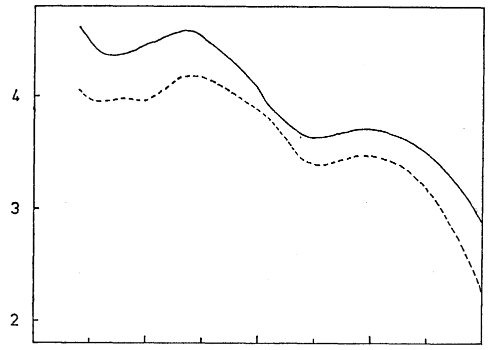


Fig. 4. The electronic spectra of phane compound **12** (——) and the reference compound **18** (----) in chloroform.

transitions between metal and ligand. The electronic spectra of **7** and **10** show new shoulder bands at longer wavelengths and the broadening of absorption curves, and the absorption bands of charge transfer and d-d transitions are located at shorter wavelengths and the intensity increases, as compared with the spectra of **13** and **16**. On the other hand, three bands of **12** are located at similar positions to the bands of **18**, and the intensity of **12** is much higher than those of **18**.

Experimental

Measurements. The ^{1}H NMR spectra were obtained with a JEOL JNM-FX 100 spectrometer (100 MHz) at 26 °C. 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.

Materials. All the melting points are uncorrected. The following compounds were synthesized by the methods described in the literature: 1,1′-ruthenocenedicarboxylic acid,[12] 1,1′-ferrocenedicarbaldehyde (**2**),[16] 1,1′-diacetylruthenocene (**3**),[12] 1,1′-diacetylferrocene (**4**),[17] 1,1′-bis(2-acetylvinyl)ferrocene (**5**),[18] and 1,1′-bis(2-formylvinyl)ferrocene (**6**).[18]

Dimethyl 1,1′-Ruthenocenedicarboxylate. A methanol solution (120 ml) containing 1,1′-ruthenocenedicarboxylic acid (3.8 g, 11.9 mmol) and concentrated sulfuric acid (0.30 ml) was refluxed for 20 h under a nitrogen atmosphere. After the mixture was poured into water, the solution was extracted by chloroform. The chloroform extract was washed by saturated sodium hydrogencarbonate, water and brine, and then dried over anhydrous sodium sulfate. After purification by column-chromatography (silica gel–chloroform), 4.0 g (98%) of this compound was obtained; mp 165—167 °C (chloroform). ^{1}H NMR ($CDCl_3$): δ 3.74 (6H, s, $-COOCH_3$), 4.73 (4H, t, J=1.8 Hz, Rc ring protons), 5.17 ppm (4H, t, J=1.8 Hz, Rc ring protons). IR (KBr): 1709 cm^{-1} ($-COOCH_3$). MS: *m/e* 347 (M^+) and 101 (Ru^+). Found: C, 48.59; H, 4.32%. Calcd for $C_{14}H_{14}O_4Ru$: C, 48.41; H, 4.06%.

1,1′-Bis(hydroxymethyl)ruthenocene. A solution of dimethyl 1,1′-ruthenocenedicarboxylate (2.7 g, 7.78 mmol) in benzene (150 ml) was added dropwise to a mixture of lithium aluminum hydride (0.65 g) in ether (150 ml). After the solution was refluxed for 4 h under a nitrogen atmosphere, the excess lithium aluminum hydride was decomposed with a small amount of cold water. The resulting mixture was extracted with chloroform. The chloroform extract was dried over anhydrous sodium sulfate. The removal of chloroform yielded 2.2 g (98%) of this compound; mp 125—127 °C (chloroform). ^{1}H NMR ($CDCl_3$): δ 1.80 (4H, br-s, $-CH_2-$), 4.16 (2H, br-s, $-OH$), 4.58 (4H, t, J=1.8 Hz, Rc ring protons), and 4.71 ppm (4H, t, J=1.8 Hz, Rc ring protons). IR (KBr): 3176 cm^{-1} ($-OH$). MS: *m/e* 291 (M^+) and 101 (Ru^+). Found: C, 49.99; H, 4.42%. Calcd for $C_{12}H_{14}O_2Ru$: C, 49.48; H, 4.84%.

*1,1′-Ruthenocenedicarbaldehyde (**1**).* A solution of 1,1′-bis(hydroxymethyl)ruthenocene (1.5 g, 5.15 mmol) and active manganese dioxide (12 g) in chloroform (100 ml) was shaken for 24 h at room temperature. After filtration of active manganese dioxide, the removal of chloroform left 1.0 g (70%) of **1**; mp 235 °C (dec) (hexane–dichloromethane). ^{1}H NMR ($CDCl_3$): δ 4.94 (4H, t, J=1.8 Hz, Rc ring protons), 5.18 (4H, t, J=1.8 Hz, Rc ring protons), and 9.71 ppm (2H, s, $-CHO$). IR (KBr): 1655 cm^{-1} ($-CHO$). MS: *m/e* 287 (M^+) and 101 (Ru^+). Found: C, 50.44; H, 3.28%. Calcd for $C_{12}H_{10}O_2Ru$: C, 50.17; H, 3.51%.

General Procedure for an Intermolecular Base-catalyzed Condensation.

*[3.3](1,1′)Ruthenocenophane-2,14-diene-1,16-dione (**7**).* A mixture of **1** (1.0 g, 3.48 mmol), **3** (1.1 g, 3.48 mmol), and sodium (0.5 g) in ethanol (100 ml) was stirred at 60 °C for 6 h under a nitrogen atmosphere. After the crude product was filtered off, washed with water, ethanol, and

Table 3. Analysis and property of phane compounds (**7**—**12**) and the reference compounds (**13**—**18**)

Compound	
7	mp>300 °C (chloroform). Found: C, 55.46; H, 3.77%. Calcd for $C_{26}H_{20}O_2Ru_2$: C, 55.12; H, 3.56%. MS: *m/e* 566 (M^+) and 101 (Ru^+).
8	mp 270 °C (dec) (chloroform). Found: C, 60.14; H, 3.52%. Calcd for $C_{26}H_{20}O_2RuFe$: C, 59.90; H, 3.87%. MS: *m/e* 521 (M^+), 101 (Ru^+), and 56 (Fe^+).
9	mp 280 °C (dec) (chloroform). Found: C, 59.34; H, 3.56%. Calcd for $C_{26}H_{20}O_2RuFe$: C, 59.90; H, 3.87%. MS: *m/e* 521 (M^+), 101 (Ru^+), and 56 (Fe^+).
10	mp 287 °C (dec) (chloroform). Found: C, 58.52; H, 3.56%. Calcd for $C_{30}H_{24}O_2Ru_2$: C, 58.24; H, 3.91%. MS: *m/e* 619 (M^+) and 101 (Ru^+).
11	mp 118—120 °C (chloroform). Found: C, 62.44; H, 3.97%. Calcd for $C_{30}H_{24}O_2RuFe$: C, 62.84; H, 4.22%. MS: *m/e* 573 (M^+), 101 (Ru^+), and 56 (Fe^+).
12	mp 270 °C (dec) (chloroform). Found: C, 62.27; H, 4.86%. Calcd for $C_{30}H_{24}O_2RuFe$: C, 62.84; H, 4.22%. MS: *m/e* 577 (M^+), 101 (Ru^+), and 56 (Fe^+).
13	mp 255—258 °C (hexane-chloroform). Found: C, 53.64; H, 3.79%. Calcd for $C_{23}H_{20}ORu_2$: C, 53.69; H, 3.92%. MS: *m/e* 514 (M^+) and 101 (Ru^+).
14	mp 257—259 °C (hexane-chloroform). Found: C, 58.42; H, 4.11%. Calcd for $C_{23}H_{20}ORuFe$: C, 58.86; H, 4.30%. MS: *m/e* 469 (M^+), 101 (Ru^+), and 56 (Fe^+).
15	mp 218—220 °C (hexane-chloroform). Found: C, 58.74; H, 4.45%. Calcd for $C_{23}H_{20}ORuFe$: C, 58.86; H, 4.30%. MS: *m/e* 469 (M^+), 101 (Ru^+), and 56 (Fe^+).
16	mp 131—134 °C (chloroform-ether). Found: C, 55.84; H, 3.82%. Calcd for $C_{25}H_{22}ORu_2$: C, 55.55; H, 4.10%. MS: *m/e* 540 (M^+) and 101 (Ru^+).
17	mp 214—217 °C (chloroform). Found: C, 59.18; H, 4.13%. Calcd for $C_{25}H_{22}ORuFe$: C, 60.62; H, 4.48%. MS: *m/e* 495 (M^+), 101 (Ru^+), and 56 (Fe^+).
18	mp 195—196 °C (hexane-dichloromethane). Found: C, 60.26; H, 4.87%. Calcd for $C_{25}H_{22}ORuFe$: C, 60.62; H, 4.48%. MS: *m/e* 495 (M^+), 101 (Ru^+), and 56 (Fe^+).

ether, and then dried, 1.6 g (80%) of **7** was obtained.

[5.5](1,1')Ruthenocenophane-2,14,17,29-tetraene-1,16-dione (10). A mixture of **1** (2.0 g, 6.96 mmol), acetone (0.2 g, 3.48 mmol), and potassium hydroxide (3.5 g) in ethanol (100 ml) was heated at 60 °C for 6 h under a nitrogen atmosphere. After the crude product was filtered off, washed with water, ethanol, and ether, and then dried, 1.6 g (75%) of **10** was yielded.

The yields of phane compounds **8**, **9**, **11**, and **12** were 78, 80, 75, and 79%, respectively.

1,3-Diruthenocenyl-2-propen-1-one (13). A solution of formylruthenocene[11] (1.0 g, 3.86 mmol), acetylruthenocene[16] (1.05 g, 3.86 mmol), and sodium (0.5 g) in ethanol (50 ml) was stirred at 60 °C for 6 h under a nitrogen atmosphere. After the crude product was filtered off, washed with water, ethanol, and ether, and then dried, 1.6 g (81%) of **13** was obtained.

1,5-Diruthenocenyl-1,4-pentadien-3-one (16). A mixture of formylruthenocene[11] (1.0 g, 3.86 mmol), acetone (0.11 g, 1.93 mmol), and potassium hydroxide (1.9 g) in ethanol (50 ml) was heated at 60 °C for 6 h under a nitrogen atmosphere. After the crude product was filtered off, washed with water, ethanol, and ether, and then dried, 1.4 g (66%) of **16** was yielded.

1-Ferrocenyl-3-ruthenocenyl-2-propen-1-one (**14**) and 3-ferrocenyl-1-ruthenocenyl-2-propen-1-one (**15**) were prepared in 69 and 70% yields from formylruthenocene[11] and acetylferrocene[19] and from formylferrocene[20] and acetylruthenocene[16] under the same conditions as **13**, respectively. 1-Ferrocenyl-5-ruthenocenyl-1,4-pentadien-3-one (**17**) and 5-ferrocenyl-1-ruthenocenyl-2,4-pentadien-1-one (**18**) were prepared in 62 and 60% yields from formylruthenocene[11] and (2-acetylvinyl)ferrocene[18] and from acetylruthenocene[16] and (2-formylvinyl)ferrocene[18] under the same conditions as **16**, respectively.

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