ORGANOMETALLICS

Proximity-assisted formation of bridged iron and ruthenium carbonyl complexes of .mu.-polymethylene bis(1,3-pentadiene). Preparation and molecular structure of Ru(CO)[(.mu.-(CH2)3)(.eta.4-C5H7)2] and (.mu.-(CH2)3)[Ru(CO)3(.eta.4-C5H5)][Ru(CO)(.eta.4-C5H7)] (Ru-Ru)

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with 90% ^{13}C-enriched carbon monoxide, the autoclave was kept at 35 °C for 4 h. Then the solvent was distilled off in vacuo, and the residual solid was washed with *n*-hexane to give **6a** in 61% yield. The ^{13}C NMR of the complex showed that the 5.2% and 5.0% of ^{13}C was introduced into the 2- and 6-positions.

Reaction of 6a Labeled with ^{13}C with ^{12}CO. The benzene solution of the labeled (**6a**), which was obtained from the reaction of 2-methoxyfuran with $Fe_2(CO)_9$ under an atmosphere of 90% ^{13}C-enriched carbon monoxide, was stirred under an atmosphere of carbon monoxide (1 atm) at 35 °C for 72 h.

Reaction of 6a with $Fe_2(CO)_9$. The mixture of **6a** (133 mg, 0.5 mmol) and $Fe_2(CO)_9$ (364 mg, 1.0 mmol) in 1,2-dichloroethane (5 mL) was stirred at 70 °C for 6 h. After the evaporation of solvent, the residual oil was chromatographed on silica gel to give **5a** (36 mg, 19%) and unreacted **6a** (27 mg, 20%).

Reaction of 6a with Methanol. Complex **6a** (266 mg, 1.0 mmol) and methanol (5 mL) were placed in an autoclave under an argon atmosphere. The autoclave was charged with 50 atm of carbon monoxide and was heated at 150 °C for 4 h. Then the reaction mixture was subjected to GLC analysis, which showed the presence of 62% of **12** (based on the amount of **6a**).

Acknowledgment. We thank Prof. Y. Takegami and Dr. T. Suzuki for helpful discussions and also Prof. H. Fukami and Dr. T. Ueno for taking the GC–MS spectra.

Registry No. **5a**, 84474-43-1; **5b**, 84474-44-2; **10**, 84462-69-1; **6a**, 84462-70-4; **11**, 84507-41-5; **12**, 5164-76-1; $Fe_2(CO)_9$, 15321-51-4; $Ru_3(CO)_{12}$, 15243-33-1; 2-methoxyfuran, 25414-22-6; 2-*tert*-butoxyfuran, 32460-41-6.

Proximity-Assisted Formation of Bridged Iron and Ruthenium Carbonyl Complexes of μ-Polymethylene-Bis(1,3-pentadiene). Preparation and Molecular Structure of $Ru(CO)[(\mu\text{-}(CH_2)_3)(\eta^4\text{-}C_5H_7)_2]$ and $(\mu\text{-}(CH_2)_3)[Ru(CO)_3(\eta^4\text{-}C_5H_5)][Ru(CO)(\eta^4\text{-}C_5H_7)]$ (Ru–Ru)

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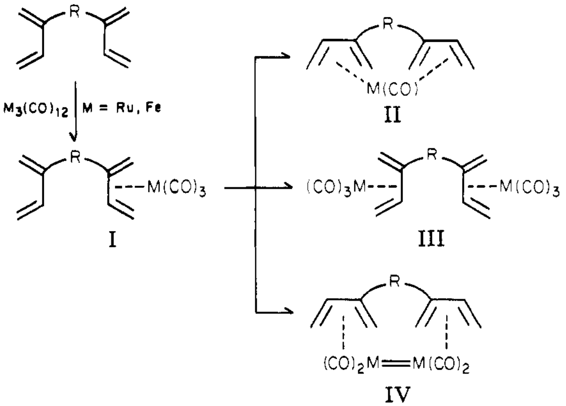
The 4:1 reaction of 3,7-divinyl-1,8-nonadiene (1) with $Ru_3(CO)_{12}$ gave mononuclear $Ru(CO)[(\mu\text{-}C_3H_6)(\eta^4\text{-}C_5H_7)_2]$ (**7a**) and binuclear $(\mu\text{-}C_3H_6)[Ru(CO)_3(\eta^4\text{-}C_5H_5)][Ru(CO)(\eta^4\text{-}C_5H_7)]$ (**8a**) in an 8:2 ratio by the proximity effect of two adjacent diene groups. Higher analogues, 3,8-divinyl-1,9-decadiene (**2**) and 3,9-divinyl-1,10-undecadiene (**3**), preferred the formation of $(\mu\text{-polymethylene})[Ru(CO)_3(\eta^4\text{-}C_5H_7)]_2$, while a linear tetraene, 1,3,7,9-decatetraene (**4**), gave $Ru(CO)_3$(bicyclo[4.2.0]2,4-octadiene) by a valence isomerization reaction with $Ru_3(CO)_{12}$. Corresponding reactions with iron carbonyls always gave the complexes $(\mu\text{-polymethylene})[Fe(CO)_3(\eta^4\text{-}C_5H_7)]_2$, irrespective of the type of tetraene ligands. The X-ray structure analysis of (3,3′-μ-trimethylene)bis(η^4-1,3-pentadiene)carbonylruthenium (**7a**) and (3,3′-μ-trimethylene)(η^4-2-methyl-1,1,1-tricarbonylruthenacyclopenta-2,4-diene)(η^4-1,3-pentadiene)monocarbonylruthenium(*Ru–Ru*) (**8a**) suggests that the former is converted to the latter through dehydrogenative metallacyclization. Crystal data for **7a**: triclinic, space group $P\bar{1}$ with $Z = 2$, $\alpha = 7.563$ (1) Å, $b = 13.132$ (1) Å, $c = 7.276$ (1) Å, $\alpha = 98.21$ (1)°, $\beta = 112.74$ (1)°, $\gamma = 81.37$ (1)°, $R_1 = 0.031$, and $R_2 = 0.042$ from the 2251 reflections. Crystal data for **8a**: monoclinic, space group $P2_1/a$ with $Z = 4$, $a = 19.265$ (3) Å, $b = 13.182$ (2) Å, $c = 7.624$ (1) Å, $\beta = 119.10$ (1)°, $R_1 = 0.051$, and $R_2 = 0.051$ from the 2140 reflections.

Multidentate ligands with chalcogen or pnicogen donor atoms in linear or cyclic arrays have played important roles in coordination chemistry. Polyolefinic carbon ligands have so far been limited to mostly cyclic ones, e.g., cyclooctatetraene,[1] bis(cyclooctatetraene),[2] etc. We have been interested in linear polyolefines because of their potential as bridging ligands between two or more metal atoms and have examined the complex formation of d^8 metals with a series of compounds containing two conjugated diene moieties connected by a polymethylene chain. Consideration of the stability of the products has led us to bind $M(CO)_3$ fragments (M = Fe, Ru) with the diene parts. The possible products are shown in eq 1.



(1)

Much interest rests in how the product distribution (I–IV) depends on the number of methylene (R) between vinylidene groups, since mutual steric dispositions of the two diene units is of critical importance. In some favorable cases, the resulting polynuclear complexes may provide novel electronic or magnetic materials. The bifunctionality

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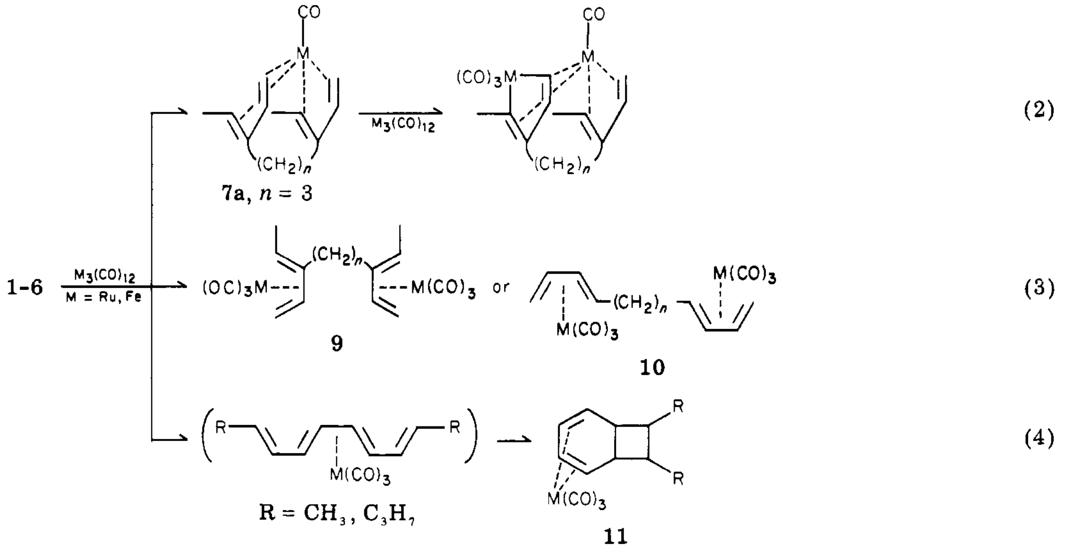
[2] Edwards, J. D.; Howard, J. A. K.; Knox, S. A. R.; Riera, V.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc.*, Dalton *Trans.* **1976**, 75.

0276-7333/83/2302-1207$01.50/0

Scheme I

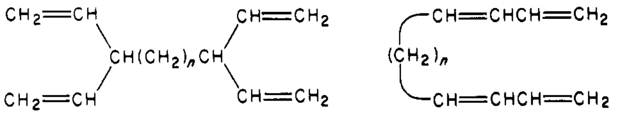


of these products implies their utility as components (pendant groups) of novel organometallic polymers with unique properties.[3] Although the chemistry of iron–diene complexes has been already established, fundamental research on ruthenium complexes is still required because of the general trend to form ill-defined cluster complexes.

This paper also reports the X-ray structure for Ru(CO)[(μ-(CH$_2$)$_3$)(η^4-diene)$_2$] and Ru$_2$(CO)$_4$(–CH=CRCR′=CH–). Ru$_2$(CO)$_4$(–CH=CRCR′=CH–) contains a ruthenacyclopentadiene which was formed from Ru(CO)[(μ-(CH$_2$)$_3$)(η^4-diene)$_2$] and Ru$_3$(CO)$_{12}$ by dehydrogenative metallacyclization.

Results and Discussion

The proximity effect of the two adjacent diene groups was examined with the six novel tetraene ligands **1–6**



1, $n = 3$
2, $n = 4$
3, $n = 5$

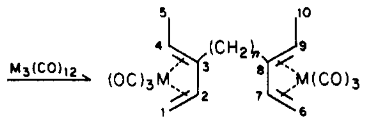
4, $n = 2$
5, $n = 5$
6, $n = 6$

linked by a polymethylene chain. These ligands were prepared by the coupling reacton of pentadienylpotassium with alkylene bromides or copper(I) chloride according to the procedure previously reported.[4] The mode of reactions of **1–6** with M$_3$(CO)$_{12}$ (M = Ru, Fe) can be classified into three categories as shown in Scheme I.

The reactions (eq 2) produce a mononuclear complex of the type M(CO)(η^4-diene)$_2$ **7** or binuclear M(CO)$_4$(η^4-diene)(η^4-metallacyclopentadiene) **8** with a M–M bond in which a metal atom coordinates to the two diene groups. Preparation of this type of ruthenium complex was first accomplished by direct reaction of tri- or tetramethylene-bridged tetraene, **1** or **2**, with Ru$_3$(CO)$_{12}$ in hot isooctane. For example, the 4:1 reaction of 3,7-divinyl-1,8-nonadiene (**1**) with Ru$_3$(CO)$_{12}$ heated in isooctane at 120 °C for 6 h gave a mixture of **7a** and **8a** in an 8:2 ratio (60% combined yield), but the products' ratio reversed to 1:9 (45% combined yield) when the reaction was carried out by using a 1:2 ratio of reactants **1** and Ru$_3$(CO)$_{12}$. The ligand **1** readily converted to a conjugated diene, 3,7-divinyl-2,7-nonadiene, during this reaction. The conversion is presumably catalyzed by ruthenium carbonyls before complexation occurs. These complexes were isolated by TLC (thin-layer chromatography), and the structure was determined by mass, IR, Raman, and NMR spectra together with the X-ray analysis as described later.

Although several related iron complexes of the type Fe(CO)(η^4-diene)$_2$ have been prepared photochemically,[5] we have not yet obtained the corresponding ruthenium complexes. Our attempts to prepare the Ru(CO)[(μ-(CH$_2$)$_n$(η^4-pentadiene)$_2$] by the photochemical reaction failed, presumably due to the inertness of triruthenium dodecarbonyl to ultravioltet light. For example, the 1:1 reaction of finely divided Ru$_3$(CO)$_{12}$ with **1** or **2** at 20–40 °C for 15 h under the ultraviolet irradiation did not gave any ruthenium complexes, but photoinduced polymerization of **1** or **2** occurred prior to the complexation. Approximately 80% of Ru$_3$(CO)$_{12}$ was recovered together with insoluble dark brown precipitates.

3,8-Divinyl-1,9-decadiene (**2**) also gave the corresponding binuclear complex **8b** in low yield (ca. 8%), when a 1:2 mixture of **2** and Ru$_3$(CO)$_{12}$ was heated to 120 °C in isooctane. A complex of the type **7a** was not obtained under these reaction conditions. The major product (90%) was the complex **9a** formulated as (μ-(CH$_2$)$_4$)[Ru(CO)$_3$(η^4-pentadiene)] (see eq 5). The 1:1 or 1:2 reaction of **3** with



(5)

9a, $n = 4$, M = Ru
b, $n = 5$, M = Ru
c, $n = 3$, M = Fe
d, $n = 4$, M = Fe
e, $n = 5$, M = Fe

Ru$_3$(CO)$_{12}$ produced the similar complex **9b** as the sole product. The corresponding reaction of **1–3** with Fe(CO)$_5$, Fe(CO)$_9$, or Fe$_3$(CO)$_{12}$ all gave the [Fe(CO)$_3$(η^4–diene)]$_2$-

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[3] (a) Yasuda, H.; Morita, Y.; Noda, I.; Sugi, K.; Nakamura, A. *J. Organomet. Chem.* **1981**, *205*, C9. (b) Carraher, C. E., Jr.; Scheats, J.; Pittman, C. U., Jr. "Organometallic Polymers"; Academic Press: New Yor, 1978. (c) Carraher, C. E. Jr., *J. Chem. Educ.* **1981**, *58*, 921.

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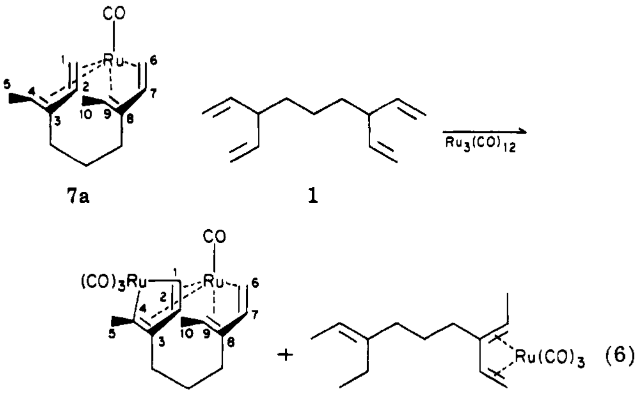
type complexes **9c–e** (eq 5) which have a structure similar to those prepared by the coupling reaction of $Fe(CO)_3(\eta^4\text{-diene})$ bearing a hydroxymethyl or halomethyl group on the diene moiety.[6]

On the basis of these facts, the formation of the ruthenium complexes **7** and **8** was interpreted by the proximity effect of the adjacent diene groups linked by an alkylene group. $Fe(CO)_3(\eta^4\text{-tetraene})$ (I) is considered as an intermediate. Molecular models suggest that the desired complex will be sterically most stable when the two diene groups are separated by a trimethylene bridge. The pentamethylene bridge seems too long to bring about the proximity controlled reaction.

Though the complexation using a ligand linked by a CH_2 or CH_2CH_2 group is important to evaulate the proximity effect, preparation of these ligands has not yet been successful. The X-ray structure of iron tricarbonyl complexes of 2,3,5,6-tetrakis(methylene)-7-oxabicyclo[2.2.1]heptane and 5,6,7,8-tetrakis(methylene)bicyclo[2.2.2]oct-2-ene[7] gave important informations on the proximity effect of the two diene groups linked by a CH_2 group, since these roof-shaped ligands can be regarded as an analogue of the CH_2-bridged tetraene (though they are doubly bridged). The Fe(CO) species can not coordinate to the two diene groups in a molecule, because the dihedral angle (115-119°) between the two diene planes dictates that the two diene moieties will not be parallel.

The binuclear ruthenium complex **8** consists of a $Ru(CO)(\eta^4\text{-diene})$ fragment coordinated to a ruthenacyclopentadiene ring system with a Ru–Ru bond. The pathway for the formation of **8** from **7** may be interpreted by dehydrogenative metallacyclization of **7** (eq 6), because heating



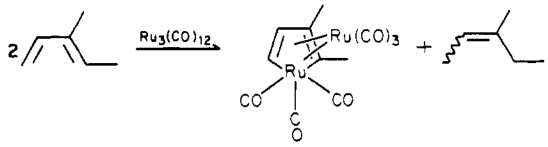
7a **1**

8a **12a** (6)

of a 1:1:1 mixture of **1**, **7a**, and $Ru_3(CO)_{12}$ to 120 °C for 10 h resulted in the formation of **8a** in 30–50% yield together with the hydrogenated species **12a** in 40% yield. We can discount the possibility that complex **8** arose from the direct reaction of **7** with $Ru_3(CO)_{12}$, because **7a** was inert to ruthenium carbonyls in hot isooctane (80% of **7a** was recovered).

Complex **8a** is the first example for binuclear ruthenium complexes consisting of metallacyclopentadiene and M(CO)(diene) groups. A related iron complex, $Fe_2(CO)_4(C_6H_5C_2C_6H_4C_2C_6H_5)_2$, was obtained by the photochemical reaction of *o*-bis(phenylethynyl)benzene with $Fe(CO)_5$.[8] The iron complex consists of an Fe(CO)(cyclobutadiene) fragment coordinated to a ferracyclopentadiene ring through an *o*-phenylene bridge. The corresponding reaction of *o*-bis((trimethylsilyl)ethynyl)benzene with $Fe_2(CO)_9$, however, did not give these types of complexes but gave a conventional tricarbonyl ferracyclopentadiene coordinated with an $Fe(CO)_3$ fragment.[9]

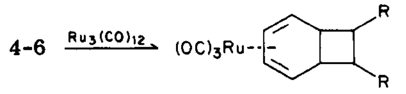
We have examined the reaction of 3-methyl-1,3-pentadiene as the model for the reaction given in eq 6, but neither the complex corresponding to **8a** nor Ru(CO)(3-methyl-1,3-pentadiene)$_2$ was formed. From the resulting solution, a binuclear complex shown in eq 7 was isolated



(7)

in 50% yield in addition to 3-methyl-2-pentene. Similar ruthena- and osmacyclopentadienes were already known.[10] Thus, complexation to lead to **7a** and **8a** is unique for trimethylene-bridged bis(diene) ligands.

Linear tetraenes such as **4–6** gave tricarbonyl(bicyclic diene)ruthenium **11a–c** in good yield by reaction with $Ru_3(CO)_{12}$ in hot isooctane as confirmed by the mass and the ^1H NMR spectra (eq 8). The cyclization is interpreted

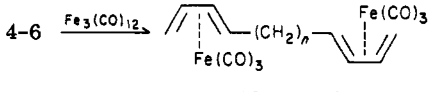


(8)

11a, R = CH_3
b, R = C_3H_7
c, R = C_3H_7 or C_4H_9

as ruthenium carbonyl catalyzed isomerization of **4–6** to conjugated tetraenes followed by ring closure. Such a ring closure is well-known for 2,4,6,8-decatetraene which was converted to bicyclo[4.2.0]2,4-octadiene via cycloocta-1,3,5-triene by the conrotatory valence isomerization.[11] An intermediate in the reaction (eq 8) may be $Ru(CO)_3$(linear conjugated tetraene) which is similar to $Fe(CO)_3$(1,8-disubstituted octatetraene).[12] The ^1H NMR spectra of the resulting complexes are very close to that of bicyclooctadiene complexes of Fe and Ru prepared from cycloocta-1,3,5-triene.[13] The stereochemistry of the ring closure is not clear at present.

In contrast to ruthenium carbonyls, iron carbonyls such as $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ produced solely complexes **10a–c** by reaction with the linear tetraenes. Coordination of an $Fe(CO)_3$ fragment occurred prior to isomerization.



(9)

10a, n = 2
b, n = 5
c, n = 6

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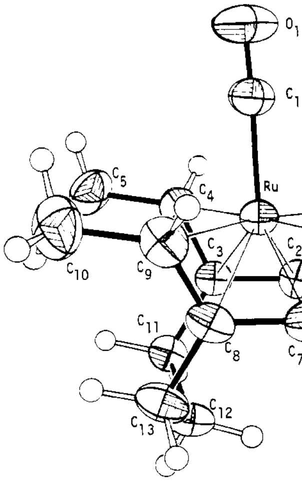

Figure 1. An ORTEP drawing of $Ru(CO)[(\mu\text{-}C_3H_6)(\eta^4\text{-}C_5H_7)_2]$ (**7a**). The notation is consistent with the tables.

Table I. Selected Bond Lengths (Å) with Esd's for Complexes 7a and 8a

	7a	8a
Ru_1-Ru_2		2.720 (1)
Ru_1-C_1	2.209 (5)	2.235 (10)
Ru_1-C_2	2.155 (6)	2.223 (10)
Ru_1-C_3	2.178 (5)	2.239 (9)
Ru_1-C_4	2.251 (6)	2.245 (9)
Ru_1-C_5	3.355 (8)	3.397 (11)
Ru_1-C_6	2.225 (6)	2.223 (13)
Ru_1-C_7	2.158 (6)	2.157 (13)
Ru_1-C_8	2.178 (5)	2.174 (10)
Ru_1-C_9	2.263 (6)	2.244 (13)
Ru_1-C_{10}	3.377 (7)	3.304 (15)
Ru_1-C_{14}	1.903 (7)	1.905 (12)
Ru_2-C_{14}		2.736 (12)
Ru_2-C_1		2.073 (10)
Ru_2-C_2		2.941 (10)
Ru_2-C_3		2.981 (9)
Ru_2-C_4		2.117 (9)
C_1-C_2	1.419 (9)	1.391 (14)
C_2-C_3	1.419 (8)	1.401 (14)
C_3-C_4	1.404 (8)	1.403 (13)
C_6-C_7	1.403 (8)	1.441 (18)
C_7-C_8	1.423 (7)	1.401 (16)
C_8-C_9	1.407 (8)	1.443 (16)
C_4-C_5	1.512 (10)	1.494 (14)
C_9-C_{10}	1.506 (9)	1.456 (20)
C_3-C_{11}	1.527 (8)	1.541 (14)
C_{11}-C_{12}	1.526 (9)	1.523 (15)
C_{12}-C_{13}	1.537 (8)	1.539 (15)
C_8-C_{13}	1.516 (7)	1.648 (15)
C_1-C_6	3.419 (9)	3.501 (16)
C_4-C_9	3.599 (8)	3.585 (16)
C_2-C_7	3.145 (8)	3.152 (16)
C_3-C_8	3.158 (7)	3.257 (15)

Molecular Structure of 7a. A perspective drawing of the molecule $Ru(CO)[(\mu\text{-}(CH_2)_3)(\eta^4\text{-}C_5H_7)_2]$ (**7a**) is shown in figure 1. Selected bond lengths and bond angles are listed in Tables I and II. The central ruthenium atom is pentacoordinated, with one carbonyl and four double bonds of the two diene groups approximating a square pyramid; i.e., the carbonyl carbon (C_{14}) lies at the axial position and two sets of four carbon atoms (C_1,C_4,C_6,C_9 and C_2,C_3,C_7,C_8) at the basal positions. This arrangement corresponds well with the structure observed for $Fe(CO)(\eta^4\text{-butadiene})_2$[14a] and $Fe(CO)(\eta^4\text{-cyclohexadiene})_2$.[14b]

Table II. Selected Bond Angles (deg) with Esd's for Complexes 7a and 8a

	7a	8a
Ru_1-C_1-C_2	69.0 (4)	71.4 (6)
Ru_1-C_2-C_1	73.1 (4)	72.3 (6)
Ru_1-C_3-C_4	74.4 (3)	72.0 (5)
Ru_1-C_4-C_3	68.7 (3)	71.5 (5)
Ru_1-C_6-C_7	68.8 (3)	68.3 (7)
Ru_1-C_7-C_6	74.0 (3)	73.3 (7)
Ru_1-C_8-C_9	74.9 (3)	73.6 (7)
Ru_1-C_9-C_8	68.2 (3)	68.3 (6)
Ru_2-C_1-C_2		114.8 (7)
Ru_2-C_4-C_3		114.2 (7)
C_1-Ru_1-C_4	76.6 (2)	71.9 (4)
C_6-Ru_1-C_9	76.5 (2)	78.1 (5)
C_1-Ru_2-C_4		77.7 (4)
C_1-Ru_1-C_6	100.9 (2)	103.5 (4)
C_4-Ru_1-C_9	105.7 (2)	106.0 (4)
C_1-C_2-C_3	120.5 (5)	117.4 (9)
C_2-C_3-C_4	116.3 (6)	114.8 (9)
C_3-C_4-C_5	124.5 (6)	123.8 (9)
C_6-C_7-C_8	121.1 (5)	120.9 (11)
C_7-C_8-C_9	116.6 (5)	117.8 (10)
C_8-C_9-C_{10}	124.5 (5)	123.7 (11)
C_2-C_3-C_{11}	119.4 (5)	119.9 (9)
C_4-C_3-C_{11}	124.2 (5)	125.2 (9)
C_7-C_8-C_{13}	119.9 (5)	121.8 (10)
C_9-C_8-C_{13}	123.4 (5)	120.3 (9)
C_3-C_{11}-C_{12}	116.5 (5)	114.6 (8)
C_{11}-C_{12}-C_{13}	113.9 (5)	114.0 (9)
C_{12}-C_{13}-C_8	115.7 (5)	116.4 (9)

Two 1,3-pentadiene units formed by carbon atoms C_1–C_5 or C_6–C_9 are both planar. Deviation of each atoms from the plane is within 0.01 Å. The dihedral angle between the two 1,3-pentadiene planes is 17.1°, larger than the value of 6.5° reported for Fe(CO)(butadiene)(1,3-cyclohexadiene).[14] Larger covalent radius of Ru atom compared to Fe atom probably accounts for the observed expansion of the dihedral angle. Though the bond angles around the three sp^3-carbon atoms (C_{11}, C_{12}, C_{13}) slightly deviate from the idealized value, the observed values indicate that the dihedral angle is little affected by the linkage between the two pentadiene units. Two methyl groups at the diene termini occupy the syn position with respect to the $(CH_2)_3$ chain and are pushed out of the diene plane. The C–C bond distances and bond angles around the carbon atoms of C_1, C_2, C_3, and C_4 are nearly equal to those of C_6, C_7, C_8, and C_9. The bond lengths between Ru and the terminal carbon atoms (Ru–C_1, Ru–C_4, Ru–C_6, Ru–C_9) are longer than those between Ru and the central carbon atoms (Ru–C_2, Ru–C_3, Ru–C_7, Ru–C_8) in accord with the relative bond distances observed for $Fe(CO)_3(\eta^4\text{-butadiene})$[15] and $Fe(CO)(\eta^4\text{-butadiene})_2$.[14a]

Molecular Structure of 8a. The molecule has a asymmetric structure as shown in Figure 2. The selected bond lengths and the bond angles are listed in tables I and II. The molecule consists of a $Ru(CO)(\eta^4\text{-diene})$ fragment coordinated to a ruthenacyclopentadiene ring system. The central Ru_1 is bonded with two atoms (C_{14} and Ru_2) and coordinated by four double bonds. The square-based pyramidal core which is made up of the carbonyl carbon atom (C_{14}) and the C_2, C_3, C_7, and C_8 atoms in the diene moieties shows the similar configuration to that observed for the parent complex **7a** but deviates substantially from the idealized geometry because the Ru_1–C_2 and Ru_1–C_3 bond distances are longer than the Ru_1–C_7 and Ru_1–C_8 distances.

The four carbon atoms of the 1,3-pentadiene unit (C_1–C_4) are in a plane (see supplementary material). The C_6, C_7, C_8, and C_9 atoms in a ruthenole ring are also coplanar. The dihedral angle between the two planes is 17.5°,

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[14] (a) Whiting, D. A. *Cryst. Struct. Commun.* **1972**, *1*, 379. (b) Kruger, C.; Tsay, Y. H. *J. Organomet. Chem.* **1971**, *33*, 59. (c) Bassi, I. W.; Scormaglia, R. *Ibid.* **1972**, *37*, 353.

[15] Mills, O. S.; Robinson, G. *Acta Crystalogr.* **1963**, *16*, 758.

Table III. ^{1}H NMR Data for Complexes **7a**, **8a**, **9a**, and **9d**[a]

	chemical shift, δ			coupling constant, Hz		
complex	H_1,$H_{1'}$ (H_6,$H_{6'}$)	H_2 (H_7)	H_4 (H_9)	$J_{1,1'}$ ($J_{6,6'}$)	$J_{1,2}$ ($J_{6,7}$)	$J_{4,5}$ ($J_{9,10}$)
7a	0.35 (anti) 1.46 (syn)	4.19	0.99	2.8	9.7	6.2
8a	0.30 (anti) 1.58 (syn)	5.21	1.30 diene unit	2.8	8.0	6.0
	6.38	6.90	2.42 ruthenole ring		6.1	
9a	0.27 (anti) 1.56 (syn)	5.24	1.21	3.6	6.2	6.1
9d	0.20 (anti) 1.62 (syn)	5.15	0.97	2.8	9.6	6.1

[a] Data were collected at 100 MHz in $CDCl_3$ at 30 °C. The numbering system for **9a** and **9d** is given in eq 5 and that for **7a** and **8a** in eq 6. H_1 and H_6 are protons at the anti position with respect to H_2 and H_7, respectively, and $H_{1'}$ and $H_{6'}$ are the protons at the syn position.

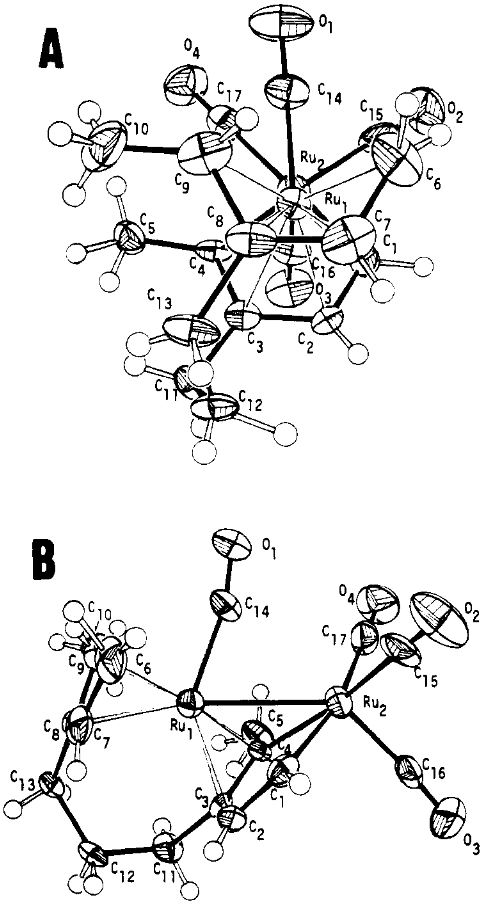

Figure 2. ORTEP drawings of (μ-C_3H_6)[Ru(CO)$_3$(η^4-C_5H_5)][Ru(CO)(η^4-C_5H_7)] (**8a**): (A) viewed down approximately along the Ru–Ru axis; (b) perpendicular to the Ru–Ru bond.

which is very close to the corresponding angle of 17.1° observed for **7a**. The two methyl groups at the diene termini and the trimethylene chain are oriented in essentially the same manner as the corresponding carbon atoms of **7a**.

The bond distances between Ru_1 and each of the four carbon atoms in the ruthenacyclopentadiene are all identical within their standard deviations, but, for the diene system (C_6–C_9), the bond distances between Ru_1 and the two terminal carbon atoms (C_6 and C_9) are 0.05–0.09 Å longer than those between Ru_1 and the two central atoms (C_7 and C_8). The C–C bond distances in the ruthenacyclopentadiene moiety are all comparable.

Table IV. Frequencies of Carbonyl Stretching Vibration for Complexes **7a**, **8a**, **9a**, and **9d**[a]

	IR, cm^{-1}		Raman, cm^{-1}	
	M(CO)$_3$	M(CO)	M(CO)$_3$	M(CO)
7a		1985		1965
8a	2050		2045	
	2000	1985	1980	1965
	1995		1975	
9a	2060		2050	
	1995		1985	
	1985		1975	
9d	2050		2030	
	1970		1965	
	1965		1955	

[a] IR data were collected with hexane solution and the Raman data in the solid state (single crystals).

Ru_2 atoms is π bonded with three CO groups and σ bonded with C_1, C_2, and Ru_1 atoms to assume a 17-electron structure (Ru_1 has 19 electrons). The carbonyl carbon atom (C_{14}) attached to the Ru_1 is semibridging to the Ru_2 atom. The Ru_2–C_{14} distance (2.736 Å) is larger than that (2.0814 Å) reported for a (μ-methylcarbyne)ruthenium complex, [Ru_2(CO)(μ-CO){μ-η^1,η^3-C(Me)C(Me)CH_2}(η-C_5H_5)$_2$].[16] The Ru–Ru bond distance (2.720 Å) is identical with that of 2.719 Å observed for above-mentioned μ-methylcarbyne complex[16] but shorter than those (2.777–2.992 Å) observed for the cluster complexes $Ru_3(CO)_8(C_8H_6)$,[17] $Ru_3(CO)_{12}$,[18] and $Ru_3H_3(CO)_9(\mu_3\text{-CMe})$.[19]

NMR Spectra of Complexes 7a and 8a. NMR spectral data for complexes **7a** and **8a** are given in Table III. The data for a tetramethylene-bridged binuclear ruthenium complex **9a** and a binuclear iron–diene complex **9d** are also given for comparison. Proton signals of H_2 and H_7 which are bonded to the C_2 and C_7 carbon atoms of the diene moiety in **7a** appeared at a significantly higher field (4.2 ppm) than the corresponding protons of **9a** and **9d** (5.1–5.2 ppm), indicating that H_2 (H_7) of **7a** is present in a magnetically shielded zone. This trend has also been found in Fe(CO)(butadiene)$_2$ (4.27 ppm) and Fe(CO)(isoprene)$_2$ (3.90 ppm).[5] The chemical shift difference between anti protons (H_1, H_6) at the diene termini and H_2 (H_7) at the central carbons of **7a** is 3.84 ppm and that between syn protons ($H_{1'}$, $H_{6'}$) and H_2 (H_7) is 2.73 ppm. These values are comparable to those (3.3–4.3 (syn) and 2.8–3.2 (anti) ppm, respectively) reported for Fe(CO)$_3$(butadiene)$_2$ and Fe(CO)$_3$(isoprene)$_2$.[5a,b] However, deshielding (1.02 ppm) at the H_7 position was observed when **7a** was converted into **8a**. This deshielding is due to the

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(18) Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2655.

(19) Sheldrick, G. M.; Yesinowski, J. P. *J. Chem. Soc., Chem. Commun.* **1975**, 873.

extensive delocalization of electrons on the ruthenole ring of **8a**. Both the H_1 and H_2 signals of **8a** appeared in the same region as those of simple ferrole or ruthenole complexes.

IR, Raman, and Mass Spectra of Complexes 7a and 8a. The IR and Raman CO stretching vibrations of **7a**, **8a**, **9a**, and **9d** are given in Table IV. Complex **7a** showed one IR- and Raman-active absorption which is readily assigned to Ru(CO). Complex **8a** also showed the Ru(CO) absorption in the samge region. Three absorptions bands assigned to $Ru(CO)_3$ vibrations of **8a** are shifted to wavelengths 5–10 cm^{-1} higher than those of the $Ru(CO)_3$ abosorptions observed for **9a**. The Fe analogue generally absorbed at higher wavelengths than the Ru analogues as was observed between **9a** and **9d**.

The mass spectrum of **7a** showed a number of parent peaks (M^+ 303, 304, 305, 306, and 308) reflecting the ruthenium isotopes. The distribution of M^+ (11.6, 13.6, 18.0, 31.6, 17.3%, respectively) is in good accord with the natural abundance of ruthenium isotopes. The spectrum of **8a** also showed several parent peaks (M^+ 484, 486, 488, 490, and 494) as expected from the natural abundance of ruthenium isotopes. Progressive loss of carbon monoxide from the parent peak to give $M^+ - CO$, $M^+ - 2CO$, and $M^+ - 3CO$ species was observed for **8a**. However, the loss of $C_2H_6 + 2H_2$ from $M^+ - 3CO$ was preferred over the formation of the $M^+ - 4CO$ fragment. Similar behavior was observed for **7a**. The intensity ratio of the $M^+ - CO$ to $M^+ - (C_2H_6 + 2H_2)$ peaks was ca. 2:3 when the spectrum was run at 75 eV. A loss of hydrogen may give the metal carbide cation which is often observed in the mass spectra of metal carbonyl complexes.[20]

Experimental Section

All the reactions were carried out under argon atmosphere in a thick-walled glass tube fitted with a pressure release. $Ru_3(CO)_{12}$ (Strem Chem.) was used without further purification. $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ were prepared from $Fe(CO)_5$ (Strem Chem.). Separation and isolation of the complexes were made by thin-layer chromatography with silica gel plates (Merck, Kieselgel 60F254, 20 × 20 cm^2). NMR spectra were recorded on a Varian XL-100 instrument with a VFT-100-620L Fourier transform accessory. IR spectra were obtained on a Hitachi EPI-2 spectrometer and Raman spectra on a JASCO R-800 Laser-Raman spectrophotometer. Mass spectra (EI) were recorded on a JEOL-OISG-2 spectrometer. Elemental analysis were carried out with a Yanagimoto Model MT-2 CHN analyzer.

Preparation of Tetraene Ligands 1–6. All the tetraenes used in this work were prepared by the reaction of pentadienylpotassium with dibromoalkanes or by the homocoupling of pentadienylpotassium with CuCl as previously reported.[4] The separation of the isomers was carried out with a preparative gas chromatograph, and the samples were distilled after being dried over calcium hydride.

Preparation of Complexes 7a and 8a. A mixture of 3,7-divinyl-1,8-nonadiene (**1**; 0.35 g, 2.0 mmol) and $Ru_3(CO)_{12}$ (0.32 g, 0.50 mmol) in isooctane (15 mL) was heated to 140 °C for 6–10 h in a sealed tube. The color of the solution changed from deep red to pale yellow. The solution was cooled, filtered, and evaporated to dryness. The short-path distillation at 120 °C (1 mmHg) gave $Ru(CO)_3(C_{13}H_{22})$ (**12a**) as a yellow oil (0.06 g, 0.16 mmol). The residue was separated into two components with TLC plates by using *n*-hexane as eluent. $Ru(CO)(C_{13}H_{20})$ (**7a**) was obtained from the upper pale yellow band (R_f 0.41) in 49% yield (0.22 g, 0.7 mmol) and $Ru_2(CO)_4(C_{13}H_{18})$ (**8a**) from the lower pale yellow band (R_f 0.21) in 12% yield (0.05 g, 0.13 mmol) based on $Ru_3(CO)_{12}$. Single crystals for X-ray diffraction studies of **7a** and **8a** were obtained by recrystallization from *n*-hexane at −20 °c.

Complex **7a**: mass spectrum *m/e* 305 (M^+, ^{101}Ru). Anal. Calcd for $C_{14}H_{20}ORu$: C, 55.06; H, 6.60. Found: C, 54.95; H, 6.50.

Complex **8a**: mass spectrum, *m/e* 488 (M^+, ^{101}Ru). Anal. Calcd for $C_{17}H_{18}O_4Ru_2$: C, 41.80; H, 3.71. Found: C, 41.51, H, 3.65.

Complex **12a**: mass spectrum, *m/e* 363 (M^+, ^{101}Ru). Anal. Calcd for $C_{16}H_{22}O_3Ru$: C, 52.89; H, 6.10. Found: C, 51.92; H, 5.88.

Preparation of Complexes 8b and 9a. A mixture of 3,8-divinyl-1,9-decadiene (**2**; 0.28 g, 1.5 mmol) and $Ru_3(CO)_{12}$ (0.32 g, 0.5 mmol) in isooctane (20 mL) was heated to 130 °C for 10 h in a sealed glass tube. After filtration, the solution was distilled at 100 °C (0.5 mmHg) to give the hydrogenated complex **12b** (0.5 g) as yellow oil, and the residue was washed with *n*-hexane at −78 °C to remove polymeric hydrocarbon. The residue was dissolved into a minimum amount of *n*-hexane and purified by recrystallization. The white crystalline solid was separated into two components **8b** and **9a** by TLC in essentially the same way as described for **7a** and **8a**. The R_f values for **8b** and **9a** are 0.18 and 0.39 and the yields are 8% (0.05 g) and 45% (0.19 g), respectively, based on $Ru_3(CO)_{12}$. The numbering system follows eq 4 and 5.

Complex **8b**: ^1H NMR ($CDCl_3$) δ 6.38 (d, *J* = 6 Hz, H_1), 6.90 (d, *J* = 6 Hz, H_2), 0.26 (d of d, *J* = 3 and 6 Hz, anti H_6) 1.56 (d of d, *J* = 3 and 6 Hz, syn H_6), 5.21 (t, *J* = 6 Hz, H_7), 1.22 (q, *J* = 6 Hz, H_9), 1.56 (d, *J* = 6 Hz, CH_3), 2.5 (m, H_{11}, H_{14}), 1.7 (m, H_{12}, H_{13}); mass spectrum, *m/e* 502 (M^+, ^{101}Ru). Anal. Calcd for $C_{18}H_{20}O_4Ru_2$: C, 43.03; H, 4.01. Found: C; 42.33; H, 3.74.

Complex **9a**: ^1H NMR ($CDCl_3$) δ 0.27 (d of d, *J* = 3 Hz, anti H_1, H_6), 1.56 (d of d, *J* = 6 Hz, syn H_1, H_6), 5.24 (d of d, *J* = 6 Hz, H_2, H_7) 1.21 (q, H_4, H_9), 1.56 (d, H_5, H_{10}), 2.5 (m, H_{11}, H_{14}), 1.64 (m, H_{12}, H_{13}); mass spectrum, *m/e* 560 (M^+, ^{101}Ru). Anal. Calcd. for $C_{20}H_{22}O_6$ Ru_2: C, 42.86; H, 3.96. Found: C, 42.83; H, 3.96.

Complex **12b**: ^1H NMR ($CDCl_3$) δ 0.30 (d of d, *J* = Hz, anti H_1), 1.60 (d of d, *J* = 7 Hz, syn H_1), 5.24 (t, H_2), 1.26 (q, *J* = 6 Hz, H_4), 5.17 (m, CH═CH), 2.3–2.9 (m, CH_2), 1.60 (d, CH_3); mass spectrum, *m/e* 375 (M^+, ^{101}Ru). Anal. Calcd for $C_{17}H_{23}O_3Ru$: C, 54.24; H, 6.16. Found: C, 54.01; H, 5.98.

Preparation of Iron Complexes 9c–e. The reaction of ligands **1–3** (1.5 mmol) with $Fe_3(CO)_{12}$ (1.5 g, 30 mmol) was carried out at 120 °C in isooctane (30 mL) in a sealed tube fitted with a condenser and a pressure release. After separation of black precipitates by filtration, the solution was evaporated to dryness and the products were separated by TLC. Complexes **9c** and **9d** were obtained as yellow crystals, and **9e** was obtained as a yellow oil. Yields were 75–85% based on ligands.

Complex **9c**: ^1H NMR ($CDCl_3$) δ 0.18 (d of d, *J* = 2 Hz, anti H_1, H_6), 1.57 (d of d, syn H_1, H_6), 5.09 (d of d, H_2, H_7) 1.00 (H_4, H_9), 1.6–2.9 (m, CH_2), 1.46 (d, CH_3); mass spectrum, *m/e* 456 (M^+, ^{101}Ru). Anal. Calcd for $C_{19}H_{20}O_6Fe_2$: C, 50.03, H, 4.42. Found: C, 50.28; H, 4.57.

Complex **9d**: ^1H NMR ($CDCl_3$) δ 0.20 (d of d, anti H_1, H_6), 1.62 (d of d, syn H_1, H_6), 5.15 (d of d, H_2, H_7), 0.97 (q, H_4H_9), 1.6–2.7 (m, CH_2), 1.48 (d, CH_3); mass spectrum, *m/e* 470 (M^+, ^{101}Ru). Anal. Cald for $C_{20}H_{22}O_6Fe_2$: C, 51.10; H, 4.72. Found: C, 51.44; H, 4.79.

Complex **9e**: ^1H NMR ($CDCl_3$) δ 0.20 (d of d, anti H_1, H_6), 1.62 (d of d, syn H_1, H_6), 5.15 (d of d, H_2, H_7), 0.97 (q, H_4, H_9), 1.7–2.7 (m, CH_2), 1.50 (d, CH_3); mass spectrum, *m/e* 484 (M^+, ^{101}Ru).

Preparation and characterization of **10a–c** was done in essentially the same way as described for **9c–e**.

Preparation of Bicyclic Complex 11a. An isooctane solution (15 mL) containing $Ru_3(CO)_{12}$ (0.32 g, 0.5 mmol) and 1,3,7,9–decatetraene (0.2 g, 1.5 mmol) was heated to 140 °C. The color of the solution changed from deep red to pale-yellow. After the usual workup, the products were distilled at 140 °C (1 mmHg) to give the complex **11a** as a yellow oil in 70% yield: ^1H NMR $(CDCl)_3$, δ 5.6(m, 2H), 3.5(m, 2H), 25(m, 2H), 1.7(m, 2H), 1.6(d 6H). Anal. Calcd for $C_{13}H_{14}O_3Ru$: C, 48.89; H, 4.42. Found, C, 49.25; H, 4.68; mass spectrum, m/e 320(M^+, ^{101}Ru).

X-ray Data Collection. Complexes **7a** and **8a** were prepared as described above and a suitable crystal was mounted on a glass fiber attached to the brass pin of a goniometer. Diffraction data were collected on a Rigaku rotating anode-type automated four-circle diffractometer using Mo Kα radiation at 20 ± 2 °C. Final unit cell parameters were determined from a least-squares fit of angular settings of 40 strong reflections in the range $31 < 2\theta < 43$ for **7a** and 18 reflections in the range $22 < 2\theta < 34$ for

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(20) Charalambous, J. "Mass Spectrometry of Metal Compounds"; Butterworths: London, 1975; p 118.

Table V. Crystal Data and Data Collection Parameters

	$Ru(CO)(C_{13}H_{20})$ (**7a**)	$Ru_2(CO)_4(C_{13}H_{18})$ (**8a**)
color	pale yellow	pale yellow
formula	$RuC_{14}H_{20}O$	$Ru_2C_{17}H_{18}O_4$
mol wt	305.4	488.5
cryst size	0.21 × 0.23 × 0.15	0.25 × 0.22 × 0.20
space group	$P\bar{1}$	$P2_1/a$
a, Å	7.564 (1)	19.265 (3)
b, Å	13.133 (1)	13.182 (2)
c, Å	7.277 (1)	7.625 (1)
α, deg	98.22 (1)	90
β, deg	112.75 (1)	119.10 (1)
γ, deg	81.37 (1)	90
V, Å^3	656.1 (1)	1691.8 (6)
Z	2	4
D_{calcd}, g cm^{-3}	1.55	1.93
Laue symmetry	triclinic	monoclinic
systematic absences		$0k0$, $k = 2n + 1$, $h0l$, $h = 2n + 1$
μ(Mo Kα), cm^{-1}	7.42	9.18
radiation	graphite-monochromatized Mo Kα ($\lambda = 0.7107$ Å)	
scan type	$\omega/2\theta$	$\omega/2\theta$
scan width, deg	1.5 + 0.35 tan θ	1.5 + 0.35 tan θ
bkgd (total):scan ratio	1:1	1:1
decay of stds	<2%	<2%
collection range, deg	5–50	5–50
total unique reflctn	2952	2621
unique data with $I > 3\sigma(I)$	2251	2140
final R_1 value	0.031	0.051
final R_2 value	0.042	0.051

Table VI. Atomic Fractional Coordinates, Their Standard Deviations, and Thermal Parameters for Non-Hydrogen Atoms of $Ru(CO)(C_{13}H_{20})$ (7a)

atom	x	y	z	B(eq),[a] Å^2
Ru	0.63387 (5)	0.22385 (3)	0.23482 (5)	2.510
C(14)	0.4458 (8)	0.3239 (4)	0.2877 (9)	4.06
O(14)	0.3375 (8)	0.3851 (4)	0.3221 (9)	7.7
C(1)	0.4327 (8)	0.1600 (5)	−0.0566 (7)	3.95
C(2)	0.6277 (7)	0.1384 (4)	−0.0434 (6)	3.24
C(3)	0.7449 (7)	0.2209 (4)	−0.0013 (6)	2.89
C(4)	0.6551 (8)	0.3215 (4)	0.0149 (7)	3.55
C(5)	0.7583 (10)	0.4179 (5)	0.0713 (10)	5.5
C(6)	0.6265 (8)	0.1129 (4)	0.4357 (7)	3.56
C(7)	0.8041 (7)	0.0994 (4)	0.4110 (6)	2.81
C(8)	0.9188 (6)	0.1836 (4)	0.4568 (6)	2.52
C(9)	0.8501 (7)	0.2781 (4)	0.5372 (6)	3.12
C(10)	0.9462 (9)	0.3760 (5)	0.5873 (8)	4.77
C(11)	0.9582 (8)	0.1957 (5)	0.0341 (7)	3.74
C(12)	1.0750 (7)	0.1224 (4)	0.1946 (7)	3.49
C(13)	1.0991 (7)	0.1699 (4)	0.4082 (7)	3.05

[a] Given in the form of $\exp[-B((\sin\theta)/\lambda)^2]$.

Table VII. Atomic Fractional Coordinates, Their Standard Deviations, and Thermal Parameters for Non-Hydrogen Atoms of $Ru_2(CO)_4(C_{13}H_{18})$ (8a)

atom	x	y	z	B(eq),[a] Å^2
Ru(1)	0.21894 (5)	0.17463 (8)	0.83589 (13)	2.38
Ru(2)	0.35174 (5)	0.18430 (8)	0.79660 (14)	2.80
C(14)	0.2960 (7)	0.2605 (10)	1.0380 (19)	3.4
O(1)	0.3307 (5)	0.3145 (9)	1.1656 (14)	5.3
C(15)	0.3807 (7)	0.1397 (11)	0.6098 (19)	3.4
O(2)	0.3935 (6)	0.1069 (9)	0.4899 (15)	5.4
C(16)	0.4450 (7)	0.1278 (10)	1.033 (2)	3.9
O(3)	0.4966 (6)	0.0914 (9)	1.1647 (16)	6.6
C(17)	0.3943 (6)	0.3212 (11)	0.8242 (18)	3.5
O(4)	0.4197 (6)	0.4010 (8)	0.8412 (16)	5.5
C(1)	0.2872 (7)	0.0550 (9)	0.7765 (16)	2.6
C(2)	0.2091 (6)	0.0553 (8)	0.6189 (17)	2.3
C(3)	0.1805 (7)	0.1458 (9)	0.5120 (16)	2.3
C(8)	0.0967 (6)	0.1911 (10)	0.7727 (17)	2.9
C(7)	0.1295 (8)	0.1029 (11)	0.886 (3)	3.7
C(6)	0.2005 (8)	0.1078 (12)	1.077 (2)	4.3
C(4)	0.2353 (6)	0.2261 (9)	0.5776 (16)	2.1
C(5)	0.2191 (6)	0.3274 (10)	0.4771 (17)	3.3
C(9)	0.1350 (7)	0.2863 (10)	0.856 (2)	3.6
C(10)	0.1116 (8)	0.3826 (11)	0.750 (3)	4.7
C(11)	0.0931 (6)	0.1538 (9)	0.3458 (17)	2.8
C(12)	0.0330 (6)	0.1167 (10)	0.4069 (18)	2.9
C(13)	0.0247 (6)	0.1866 (11)	0.5577 (16)	3.1

[a] Given in the form of $\exp[-B((\sin\theta)/\lambda)^2]$.

8a. The crystallographic and data collection details are given in Table V. The observed data were corrected for Lorentz and polarization effects, but no absorption correction was applied to the intensity data, which might limit the accuracy of the present structure analysis.

Solution and Refinement of the Structure. (A) Complex 7a. The structure of **7a** was solved by the conventional heavy-atom technique. The position of a Ru atom was obtained from a Patterson synthesis. Subsequent refinements and difference Fourier calculations led to the location of all other 15 non-hydrogen atoms. The choice of $P\bar{1}$ was confirmed by the successful refinment of the structure. The model was refined by block-diagonal least squares using the HBLS-V program.[21] All the non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms with the isotropic thermal parameters. More cycles of refinement led to final values of $R_1 = \sum(|F_o| - |F_c|/\sum|F_o| = 0.031$ and $R_2 = \{\sum w(|F_o| - |F_c|)^2/ \sum w|F_o|^2\}^{1/2} = 0.042$ with the weight given by $w = 1/\sigma^2(F_o)$. A final difference map had a background electron density level of 0.3 e/Å^3 with no peak higher than 0.5 e/Å^3. The final fractional coordinates are given in Table VI. The final values of the thermal parameters are given in the supplementary materials.

(B) Complex 8a. The structure of **8a** was solved by the straightforward application of the direct method program MULTAN-78.[22] An E map based upon the 500 reflections with the heighest value of $|E|$ revealed the two ruthenium atoms. Difference electron density maps revealed the rest of 21 non-hydrogen atoms. The model was refined by a block-diagonal least squares (HBLS-V).[21] All of the non-hydrogen atoms were refined with anisotropic thermal parameters and all of the hydrogen atoms with isotropic thermal parameters. In the least squares refinement, the function

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(21) Ashida, T. The Universal Crystallographic Computing System-Osaka, The Computation Center of Osaka University, 1979, pp 53–59.

(22) Main, P.; Hull, S. E.; Lessinger, L; Germain, G.; Dechlercq, J. P.; Woolfson, M. M. "Multan-78 Crystallographic Program System", University of York, England and Louvain, Belgium, 1978.

minimized was $\sum w(|F_o| - |F_c|)$ with the weight, w, assigned as $1/\sigma^2(F_o)$. The final discrepancy factors are $R_1 = 0.051$ and $R_2 = 0.051$. A final difference Fourier map was featureless with the highest residual electron equal to 0.25 e/Å^3. The final fractional coordinates are given in Table VII and the final values of the thermal parameters in the supplementary material.

Acknowledgment. The X-ray structure analysis was done in the Crystallographic Research Center, Osaka University. We are very grateful to Prof. N. Yasuoka of the Research Center for his valuable advice throughout the X-ray work and to Dr. W. E. Rhine of the University of Dayton Research Institute for suggestions regarding the manuscript.

Registry No. **7a**, 86238-29-1; **8a**, 86238-30-4; **8b**, 86238-31-5; **9a**, 86217-14-3; **9c**, 86217-17-6; **9d**, 86217-15-4; **9e**, 86238-32-6; **11a**, 86217-18-7; **12a**, 86217-16-5.

Supplementary Material Available: Tables of structure factors, anisotropic thermal parameters, and H atom parameters (with esd's), and deviations from the plane of the pentadiene or ruthenacyclic ring (18 pages). Ordering information is given on any current masthead page.

([2.2]Paracyclophane)iron(II) Complexes. Synthesis and Intramolecular Charge-Transfer Interactions

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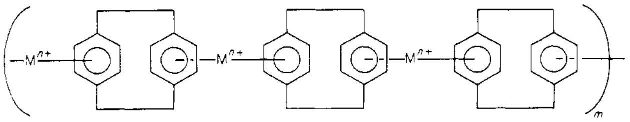
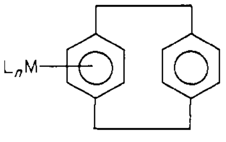
As part of a project designed to examine synthetic routes to organometallic polymers based on [2.2]-paracyclophanes, a number of new bis(arene)iron(II) salts have been prepared from [2.2]paracyclophanes, employing a modification of the Fischer–Hafner synthesis. These include the parent complex 4 ($M = Fe^{2+}$), the bis(tetramethyl[2.2]paracyclophane)iron(II) bis(hexafluorophosphate) complexes **6** and **11b**, and the bis(octamethyl[2.2]paracyclophane)iron(II) bis(hexafluorophosphate) complex **11a**. The electronic spectra of **11a,b** in the region of 400–600 nm show significantly enhanced absorption compared with the spectrum of bis(hexamethylbenzene)iron bis(hexafluorophosphate). This is assigned to charge-transfer interactions between the complexed and noncomplexed aromatic rings in the paracyclophane complexes. An attempt to extend complexation in **11a** by treatment with tris(acetone)(*p*-cymene)ruthenium(II) dication led to disruption of the arene–iron bond and the formation of the (*p*-cymene)([2.2]paracyclophane)ruthenium(II) salt **17**.

Although a number of bis(arene)iron(II) and ruthenium(II) complexes are known,[1] none derived from a paracyclophane had until recently been described.[2] Our interest in these substances and their transition-metal congeners derived from their possible use as monomeric components in the construction of multilayered or columnar organometallic polymers of general structure 1. Such polymers might be expected to exhibit unique properties of electrical conduction, since physical data,[3] chemical reactivity studies,[4] and theoretical analyses[5] all suggest extensive through space orbital interaction between the aromatic rings of [2.2]paracyclophane. The combination of such interactions and those associated with metal–ring bonding should provide a macromolecular framework with extensive orbital delocalization leading to band formation.

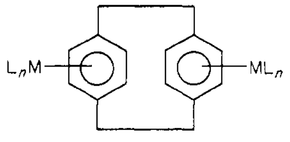


1

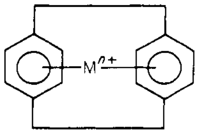
Of the three general classes of (paracyclophane)metal complexes 2, 3, and 4, those of type 4 seemed to us best suited for elaboration to oligomeric or polymeric structures such as 1. A number of complexes of structure 2[6] are known, and one of structure 3[7] has been reported, but none



2a



2b



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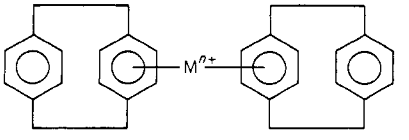

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