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HETERO- AND HOMO-NUCLEAR BIMETALLIC RUTHENOL COMPLEXES BY DEHYDROGENATIVE METALLACYCLIZATION OF $Ru(CO)_3$(BI-1,7-CYCLOOCTADIENYL). PREPARATION AND X-RAY STRUCTURE OF $Fe(CO)_3(C_{16}H_{22})$, $RuFe(CO)_6(C_{16}H_{22})$ AND $Ru_2(CO)_6(C_{16}H_{20})$

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Summary

The reaction of $M_3(CO)_{12}$ (M = Ru, Fe) with excess bi-2,7-cyclooctadienyl ($C_{16}H_{22}$) **1** gave a mononuclear complex $M(CO)_3(1,2,1'\text{-}2'\text{-}\eta^4\text{-}C_{16}H_{22})$, **2a** (M = Ru) or **3a** (M = Fe), in good yield. Treatment of **2a** with $Fe_3(CO)_{12}$ or reaction of **3a** with $Ru_3(CO)_{12}$ gave the heterobimetallic complex $RuFe(CO)_6(C_{10}H_{22})$ consisting of a ruthenacyclopentadiene unit coordinated to an $Fe(CO)_3$ fragment, as confirmed by ^1H NMR and X-ray studies. The corresponding homobimetallic complex $Ru_2(CO)_6(C_{16}H_{22})$ was obtained from the 1 : 1 reaction of **2a** with $Ru_3(CO)_{12}$, while the direct reaction of **1** with $Ru_3(CO)_{12}$ gave $Ru_2(CO)_6(C_{16}H_{20})$ preferentially with a loss of two hydrogen atoms. The pathway for formation of these bimetallic complexes was interpreted as a dehydrogenative metallacyclization followed by hydrogen transfer.

Polyene ligands form a large variety of transition metal complexes depending on the arrangement of the double bonds. In a preceding paper, we have reported that the reaction of μ-$(CH_2)_3$-bi-1,4-pentadien-3-yl with $Ru_3(CO)_{12}$ forms $Ru(CO)[\mu$-$(CH_2)_3$-bi-1-4-η^4-1,3-pentadien-3-yl] by the proximity effect of two adjacent dienes, while bi-1,4-pentadien-3-yl bridged by a long alkylene chain gave complexes involving two $Ru(CO)_3$(1,3-pentadiene) units [1]. As an extension of these studies on the proximity-assisted formation of polyene-metal complexes, we have examined the complexation of bi-2,7-cyclooctadienyl with $Ru_3(CO)_{12}$ and $Fe_3(CO)_{12}$. Bi-2,7-cyclooctadienyl and bi-1,7-cyclooctadienyl are interesting ligands, since the four double bonds can not be in a plane due to the ring strain, which forces the $M(CO_3)$ fragment to attach in novel ways. The unique π-complexation characteristics of bi-2,7-cyclooctadienyl brings about unusual reactions. In this paper, some of these unique features are described.

The production of the mono- and/or binuclear complexes I–IV may be possible for this type of ligand. The complexes of the type I were prepared recently by Roulet

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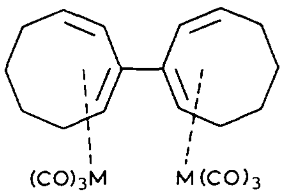

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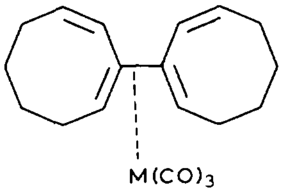

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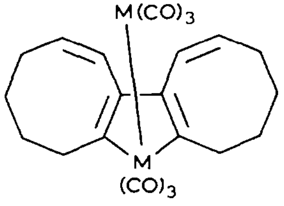

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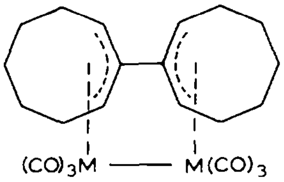


(IV)

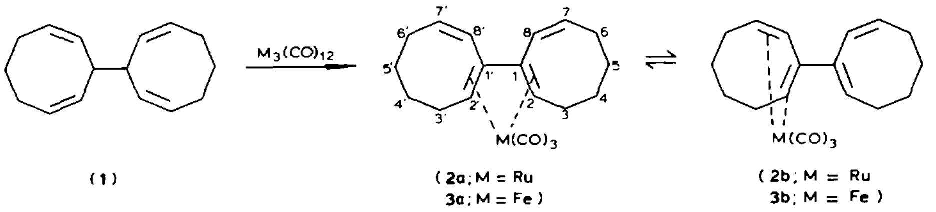
using a similar but radially disposed tetraolefinic ligand, where two $Fe(CO)_3$ fragments are complexed on the opposite faces [2]. Analogous structures are reported for $Fe_2(CO)_6$(1,4-divinyl-1,3-cyclohexadiene) [3], $Fe_2(CO)_6$(bi-2,3,5-cycloheptatrienyl) [4] and $Fe_2(CO)_6$(bi-2,3-cyclohexadienyl) [5]. Coordination of one $M(CO)_3$ group to bi-1,7-cyclooctadienyl would give the complex II. If addition or abstraction of hydrogen atoms occurs during the reaction, complexes III or IV having a M–M bond will be formed by the proximity effect of two adjacent dienes.

Results and discussion

Preparation of mononuclear ruthenium and iron complexes

The tetraene ligand, bi-2,7-cyclooctadienyl, **1**, used in this work was prepared by coupling of cyclooctadienylpotassium with $ZnCl_2$ as previously reported [6]. The 1 : 1 reaction of **1** with $Ru_3(CO)_{12}$ or $Fe_3(CO)_{12}$ in isooctane at 110–140°C for 6 h gave a product containing five or six kinds of mono- or bi-nuclear complexes as revealed by thin layer chromatography (TLC) and chemical characterization. However, when excess ligand (4 molar equivalents) was used, the production of the mononuclear ruthenium or iron complex, **2a** or **3a**, was predominant.

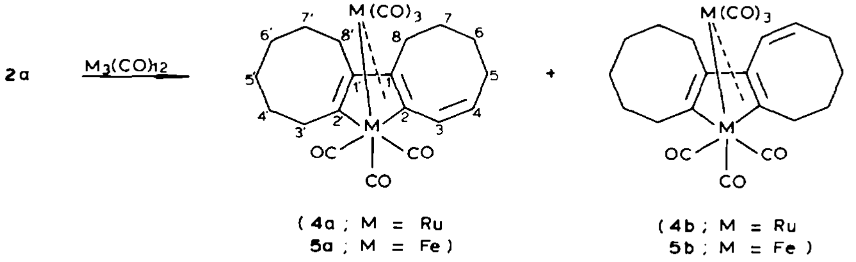
The structure of the resulting mononuclear ruthenium and iron complexes was determined to be $M(CO)_3(C_{16}H_{22})$ based on the ^1H NMR, mass, and IR spectra and elemental analysis. The ligand was converted to a conjugated tetraene system, bi-1,7-cyclooctadienyl, during the reaction by catalysis by the metal carbonyls. According to the ^1H NMR data, complexes **2a** and **3a** were not fluxional molecules, although conjugated polyene-metal complexes in many cases show the fluxional behavior in solution. If an equilibrium exists between **2a** and **2b** or **3a** and **3b** as shown in eq. 1, a simple averaged NMR spectra will be observed. NMR spectra of **2a** and **3a** recorded between 30 and −70°C revealed the absence of fluxionality. Thus, in solution **2a** and **3a** favored the 1,2,1′,2′-*tetrahapto* coordination which is the structure observed in the solid state as determined by X-ray analysis of **3a**. The non-planarity of the diene moiety composed of 7,8,1,2 or 7′,8′,1′,2′ carbon atoms may prevent the formation of **3b**. Coordination of an $Fe(CO)_3$ group to 1,2,1′,2′ atoms was also reported for $Fe(CO)_3$(bicyclooctatetraenyl) [7].



(1)

Preparation of binuclear ruthenol or ferrole complexes

The 1 : 1 reaction of **2a** with $Ru_3(CO)_{12}$ in isooctane at 120°C gave the binuclear complexes **4a**(30%) and **4b**(70%) in 80% combined yield. The iron complexes **5a**(54%) and **5b**(46%) were also obtained in 38% yield from the 1 : 3 reaction of **3a** with $Fe_3(CO)_{12}$. These complexes were separated carefully by TLC. The mass spectra of **4a–b** and **5a–b** indicate that these complexes may be formulated as $M_2(CO)_6(C_{16}H_{22})$, where M is Ru or Fe.



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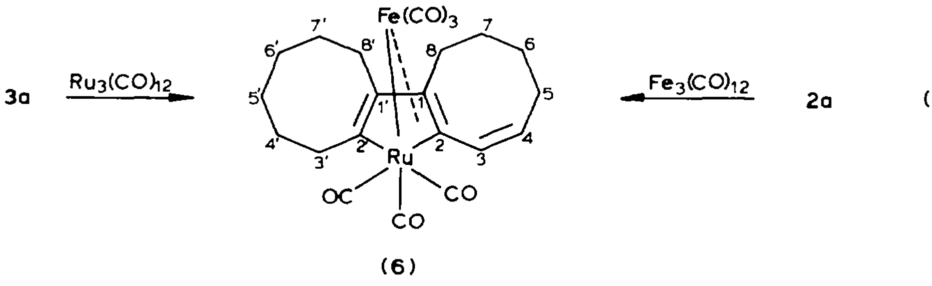
The successful synthesis of homonuclear bimetallic complexes prompted us to try the preparation of the corresponding heteronuclear complexes. The reaction of the ruthenium complex, a mixture of **4a** and **4b**, with $Fe_3(CO)_{12}$ at 120°C gave the heteronuclear complex $RuFe(CO)_6(C_{16}H_{22})$, **6**, as revealed by the mass spectrum of the reaction products, in 55% yield. The formation of homobimetallic complexes is negligible. The iron complex **3a** also gave $RuFe(CO)_6(C_{16}H_{22})$, **6**, in low yield (30%) by treatment with $Ru_3(CO)_{12}$ at 120°C. It is noteworthy that the identical heterobimetallic complex is prepared by both reactions, as revealed by the ^1H NMR, IR mass spectra of the products.

The solid state structure of **6** was solved by X-ray analysis. The molecule consists



(3)

TABLE 1

^{1}H NMR(100 MHz) AND MASS(EI) SPECTRAL DATA FOR COMPLEXES 2–7 [a]

	NMR chemical shift (δ, ppm)								mass spectrum	
	H(3)	H(4)	H(3′)	H(4′)	H(7)	H(8)	H(7′)	H(8′)	Found (M^+)	Calcd
2a	2.3(m)	1.6(m)	2.2(m)	1.6(m)	5.79(dt)	6.38(d)	5.79(dt)	6.38(d)	400	400(^{102}Ru)
					$J_{6,7} = J_{6',7'} = 6.5$, $J_{7,8} = J_{7',8'} = 11.2$ Hz					
3a	2.3(m)	1.7(m)	2.3(m)	1.7(m)	5.89(dt)	6.43(d)	5.89(dt)	6.43(d)	354	354(^{56}Fe)
					$J_{6,7} = J_{6',7'} = 7.0$, $J_{7,8} = J_{7',8'} = 11.2$ Hz					
4a	6.25(m)	6.25(m)	2.4(m)	1.7(m)	1.6(m)	2.4(m)	1.6(m)	2.3(d)	586	586(^{102}Ru)
4b	2.3(m)	1.7(m)	2.3(m)	1.7(m)	5.20(dt)	6.20(d)	1.6(m)	2.3(d)	586	586(^{102}Ru)
5a	6.05(m)	6.05(m)	2.3(m)	1.7(m)	1.6(m)	2.3(m)	1.6(m)	2.3(m)	494	494(^{56}Fe)
5b	2.3(m)	1.7(m)	2.3(m)	1.7(m)	5.45(dt)	6.25(d)	1.7(m)	2.4(m)	494	494(^{56}Fe)
6	6.05(m)	6.05(m)	2.4(m)	1.6(m)	1.6(m)	2.5(m)	1.7(m)	2.3(m)	540	540(^{56}Fe, ^{102}Ru)
7	6.14(m)	6.14(m)	2.2(m)	1.6(m)	1.6(m)	2.3(m)	5.22(dt)	6.20(d)	584	584(^{102}Ru)
							$J_{7',8'} = 11.3$ Hz			

[a] ^{1}H NMR data were collected in $CDCl_3$ at 30°C and MS data at 70 eV. The numbering system is given in eq. 1–4.

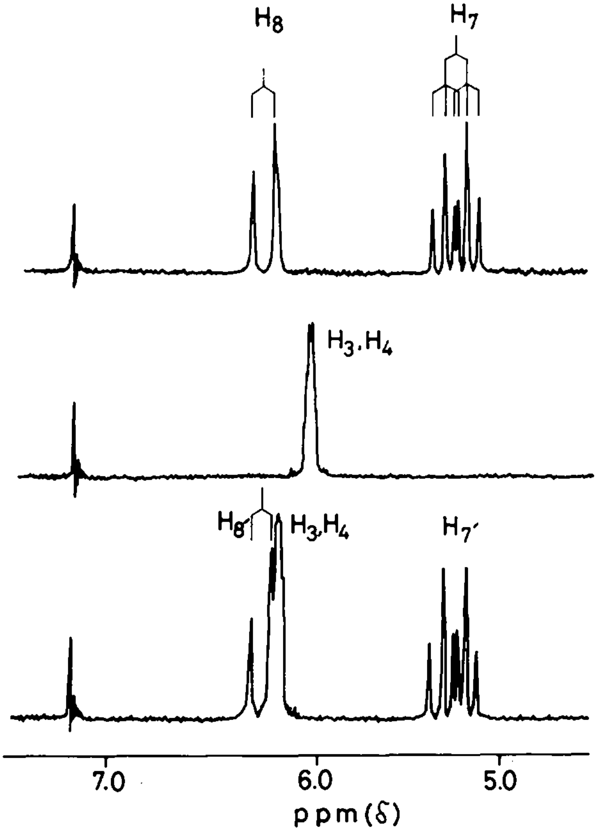


Fig. 1. ^1H NMR(100 MHz) spectra of olefinic proton signals for complexes **4b**(A), **6**(B) and **7**(C) in $CDCl_3$ at 30°C. Signal at 7.25 ppm shows the proton peak of $CHCl_3$.

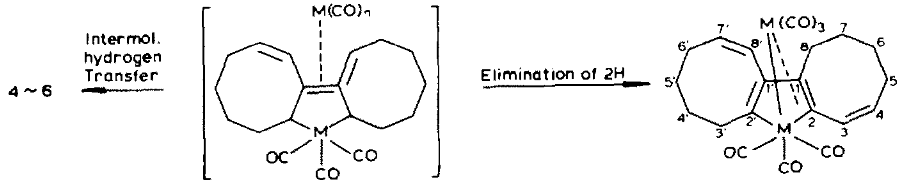
of a ruthenacyclo-2,4-pentadiene unit coordinated to $Fe(CO)_3$. The ^1H NMR assignment for complexes **2**–**6** was made based on the result of the X-ray structure determination of **6**. Complex **6** showed a simple NMR spectral pattern in the region of the olefinic H(3) and H(4) signals (Fig. 1). Complexes **4a** and **5a** also showed a similar spectral pattern (see Table 1), and therefore the proton signals were assigned to H(3), H(4) or H(3′), H(4′). The splitting pattern for the olefinic proton signals of **4b** (see Fig. 1) and **5b** were different from that of **4a** and **5a**. The observed doublet and double triplet in the NMR spectrum of **4b** were assigned to the uncoordinated olefinic protons, H(7) and H(8), because the spectra are quite similar to that of **3a**. Thus, the position of the double bond can be determined readily from the NMR spectrum pattern. The NMR data of the series of complexes are listed in Table 1.

Pathway for the formation of binuclear complexes

The process for the formation of binuclear complexes **4**–**6** from **2a** or **3a** involves dehydrogenative metallacyclization followed by intramolecular transfer of the abstracted hydrogen atoms. Two hydrogen atoms were abstracted from the *anti* position of C(2) and C(2′) atoms and were transferred to C(3), C(4) or C(7), C(8) atoms to give the complexes **4** or **5**, respectively. When the reaction of **2a** with

$Ru_3(CO)_{12}$ was carried out in the presence of two equivalents of the ligand **1**, the binuclear complex $Ru_2(CO)_6(C_{16}H_{20})$, **7**, was formed predominantly (75% yield) with loss of two hydrogen atoms. The yield of **4** was < 5% as confirmed by the mass spectrum of the products. Direct reaction of **1** with $Ru_3(CO)_{12}$ (1 : 1) also gave **7** in good yield (52%). The abstracted hydrogen was trapped by **1** and bi-2-cycloocten-1-yl was obtained in ca. 70% yield.

Based upon these facts, a metallacyclopentene coordinated to a $M(CO)_n$ fragment was proposed as an intermediate (eq. 4). Intramolecular hydrogen transfer through

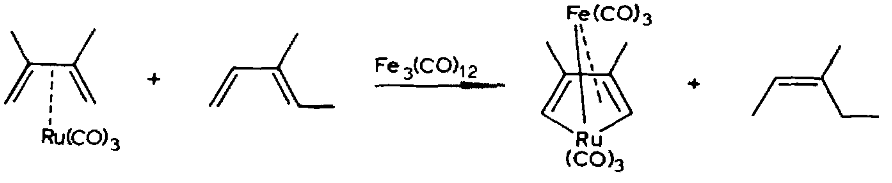


(4)

(7 , M = Ru)
(7' ; M = Fe)

$H_2M(CO)_3$ leads to complexes **4**–**6**, while intermolecular hydrogen transfer results in the production of **7**. In the reaction of the iron complex **3a** with $Fe_3(CO)_{12}$, intramolecular hydrogen transfer occurred preferentially even in the presence of two molar equivalents of bi-2,7-cyclooctadienyl and produced a mixture of **5a** and **5b** in 35% yield. Intermolecular hydrogen transfer to give **7'** is less than 5%. The metallacyclization reported for the reaction of 2,3-dimethyl-1,3-butadiene with $Os_3(CO)_{12}$ [8] and that for the reaction of isoprene with $Ru_3(CO)_{12}$ [9] may be explained by a similar process.

The application of the present reaction in the preparation of heterobimetallic complexes of simple dienes was successful. The 1 : 1 reaction of $Ru(CO)_3(\eta^4$-2,3-dimethyl-1,3-butadiene) with $Fe_3(CO)_{12}$ in hot isooctane gave the expected $RuFe(CO)_6(C_6H_8)$, **8**, in 52% yield only when a free ligand such as 3-methyl-1,3-pentadiene or 2,3-dimethyl-1,3-butadiene was added as a hydrogen acceptor (eq. 5).



(5)

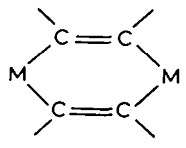
(8)

No reaction occurred without the acceptor. A diiron complex of 2,3-dimethyl-1,3-pentadiene was not obtained by this method; i.e., the reaction of $Fe_3(CO)_{12}$ with 2,3-dimethyl-1,3-pentadiene in the presence or absence of an equivalent of **3a** gave $Fe(CO)_3$(2,3-diemthyl-1,3-butadiene) as the sole product irrespective of the ratio of reactants (2 : 1, 1 : 1 and 1 : 2). However, a diruthenium complex of 2,3-dimethyl-1,3-butadiene, **9**, could be obtained in 36% yield by heating the 1 : 1 : 1 mixture of $Ru(CO)_3$(2,3-dimethyl-1,3-butadiene), **10**, 2,3-dimethyl-1,3-butadiene and $Ru_3(CO)_{12}$ to 120°C. A diruthenium complex of 3-methyl-1,3-pentadiene was also obtained in this manner. 1,3- and 1,5-Cyclooctadiene were not suitable as hydrogen acceptors, since $Ru_3(CO)_{12}$ reacts readily with these ligands to give a mixture of bimetallic and cluster complexes which is difficult to purify. Thus, a mononuclear diene-ruthenium complex or $Ru_3(CO)_{12}$ is a good starting material for the preparation of the bimetallic complexes of simple dienes. The formation of diiron complexes **5a** and **5b** is exceptional, and is presumably due to the presence of an uncoordinated olefin moiety in the molecule which accepts the abstracted hydrogen atoms.

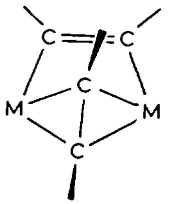
Process for double bond migration

It is evident from the X-ray and ^1H NMR studies that migration of double bonds occurred during the formation of the binuclear complexes. The conventional catalytic isomerization process can be ruled out, since the scrambling through (η^3-allyl)$RuH(CO)_3$ species generally produces a variety of isomers inconsistent with our findings [10]. No double bond migration was observed when **2a** and **3a** were heated to 140°C without addition of $M_3(CO)_{12}$.

The isomerization observed above involves a formal rotation of coordinated cyclo-3-octen-1-yne released from the bicyclooctadienyl ligand. Complete dissociation of cyclooctenyne from complexation under the reaction conditions seems improbable. Then, the rotation must take place within the framework of the binuclear complex, $[Fe(CO)_3]_2(CR)_4$, where two $Fe(CO)_3$ and four CR fragments form a 6-atomic tetracarbadimetalla cluster. An electron count of the framework orbitals indicates a preference for a pentagonalpyramidal structure (with 8 electron pairs), which is actually found. Among the 6-atom cluster family, hexagonal(A), benzvalene-type(B), and octahedral(C) clusters may be considered as possible intermediates leading to the observed isomerization. Among these, the benzvalene-type is, in our opinion, the most probable. This intermediate can result from the distortion from planarity of the metallacyclopentadiene moiety because of steric congestion at the uncoordinated olefinic hydrogens.



(A)



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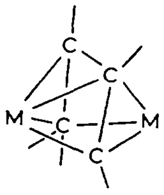
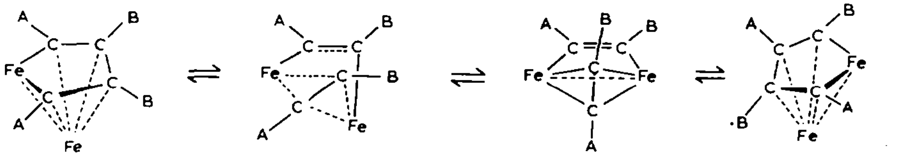


(C)

There are no reported examples of the benzvalene-type (B) structure resulting from two acetylenes and two metal atoms, but a 6-atom cluster, $[Fe(CO)_3]_2(SR)_2(CR)_2$ was found to have a structure with apical Fe atoms [11]. Examples of the octahedral carbametal clusters (C) have been found for a complex with two bulky acetylene molecules and two $Fe(CO)_2$ fragments [12] or two NbCp(CO) fragments [13]. The hexagonal structures (A) are found only in cyclic disilane derivatives and have not been reported for transition metals. Although A and C may form during the isomerization, the low-energy path probably involves the benzvalene intermediate B leading to the product. One of the possible pathways is shown in eq. 6.

There are some related isomerizations known involving bis(acetylene)/$Fe(CO)_3$

or CoCp systems. King et al., reported formation of metallacyclopentadiene from macrocyclic diacetylene and $Fe_2(CO)_9$ through a similar skeletal isomerization and


(6)

proposed an octahedral carbametal (or binuclear cyclobutadiene complex) intermediate [14]. Racemization of $(CoCp)_2(CR)_4$ at 90°C also involves a benzvalene-type intermediate, but here the metal atom assumed a different position from ours [15]. C–C bond cleavage under such mild conditions is also known for the reaction of $Ru_3(CO)_{12}$ with 1,3-cyclohexadiene [16].

X-ray structure determination of $Fe(CO)_2(C_{16}H_{22})$*, 3a*

The crystal data and the final R_1 and R_2 values for complexes **3a**, **6** and **7** are listed in Table 2. Bond distances and angles are listed in Tables 3 and 4. The molecule **3a** has a mirror plane as shown in Fig. 2. The Fe, C(9) and O(9) atoms are essentially on the mirror plane. The $Fe(CO)_3$ group is coordinated to C(1), C(2),

TABLE 2

CRYSTAL DATA AND STRUCTURE REFINEMENT FOR COMPLEXES **3a**, **6** AND **7** AT 20°C

	$C_{10}H_{22}O_3Fe$, **3a**	$C_{22}H_{22}O_6RuFe$, **6**	$C_{22}H_{20}O_6Ru_2$, **7**
space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$
crystal system	triclinic	monoclinic	monoclinic
a(Å)	9.836(2)	8.934(2)	9.945(2)
b(Å)	11.792(4)	14.801(2)	15.229(2)
c(Å)	9.152(3)	18.252(3)	16.743(5)
α(deg)	106.49(3)	90.0	90.0
β(deg)	117.52(2)	113.63(1)	118.91(1)
γ(deg)	84.54(3)	90.0	90.0
V_c(Å^3)	901.9(6)	2212.2(7)	2219.9(9)
Z	2	4	4
mol wt	354.23	539.31	582.54
D(calcd)(g/cm^3)	1.30	1.62	1.74
color	yellow	pale-yellow	pale-yellow
abs coeff(cm^{-1})	6.85	8.50	7.83
scan speed(deg min^{-1})	2.0–5.0	2.0–5.0	2.0–5.0
scan width(deg)	$0.70 + 0.69 \tan\theta$	$0.74 + 0.69 \tan\theta$	$0.72 + 0.69 \tan\theta$
bkgd time	half of the scan time	half of the scan time	half of the scan time
scan method	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
2θ limit(deg)	$3 \leq 2\theta \leq 50$	$3 \leq 2\theta \leq 50$	$3 \leq 2\theta \leq 50$
no. of total unique reflections	3095	2814	3320
no. of reflections used ($I > 3\sigma(I)$)	2722	2167	2357
final R_1	0.064	0.066	0.063
final R_2	0.086	0.075	0.069
goodness of fit	1.46	1.30	1.31

TABLE 3

SELECTED BOND LENGTHS (Å) WITH e.s.d.'s FOR COMPLEXES **3a**, **6** AND **7**

	$C_{19}H_{22}O_3Fe$, **3a**	$C_{22}H_{22}O_6RuM$, **6** (M = Fe)	$C_{22}H_{20}O_6RuM$ [a] **7** (M = Ru)
Ru–M		2.630(2)	2.706(2)
Ru–C(1)		2.975(14)	2.972(19)
Ru–C(1′)		2.978(15)	2.989(15)
Ru–C(2)		2.068(16)	2.115(18)
Ru–C(2′)		2.097(15)	2.030(16)
M–C(1)	2.070(8)	2.177(14)	2.283(19)
M–C(1′)	2.073(8)	2.171(16)	2.269(15)
M–C(2)	2.113(9)	2.125(16)	2.236(18)
M–C(2′)	2.113(8)	2.142(16)	2.194(16)
M–C(9)	1.770(10)	1.780(18)	1.912(18)
M–C(10)	1.797(10)	1.768(17)	1.910(20)
M–C(11)	1.784(9)	1.758(16)	1.889(17)
Ru–C(9)		2.564(18)	2.667(18)
Ru–C(12)		1.876(18)	1.888(20)
Ru–C(13)		1.958(19)	1.951(18)
Ru–C(14)		1.976(20)	1.963(16)
C(1)–C(1′)	1.430(11)	1.446(21)	1.410(24)
C(1)–C(2)	1.429(12)	1.395(21)	1.414(26)
C(1′)–C(2′)	1.424(11)	1.386(22)	1.458(22)
C(2)–C(3)	1.545(14)	1.517(22)	1.506(29)
C(2′)–C(3′)	1.541(13)	1.482(24)	1.525(25)
C(3)–C(4)	1.520(15)	1.428(28)	1.413(36)
C(3′)–C(4′)	1.534(14)	1.468(26)	1.505(33)
C(1)–C(8)	1.516(12)	1.526(22)	1.553(28)
C(1′)–C(8′)	1.553(12)	1.530(31)	1.544(24)
C(7)–C(8)	1.405(14)	1.536(28)	1.522(33)
C(7′)–C(8′)	1.422(14)	1.506(35)	1.429(29)

[a] M is given as Ru(2) and Ru as Ru(1) in Fig. 4.

C(1′), C(2′) atoms. The arrangement of three CO groups relative to the carbocyclic ligand is similar to those reported for $Fe(CO)_3$(butadiene) [17] and $Fe(CO)_3$(cyclohexadiene) [18]. The bond lengths of C(1′)–C(1), C(1)–C(2) and C(1′)–C(2′) are equal within experimental error as shown in Table 3. The Fe–C(1) and Fe–C(1′) bond lengths are a little shorter than the Fe–C(2) and Fe–C(2′) bond lengths and are in agreement with the reported data for $Fe(CO)_3$(diene). The four carbon atoms in each cyclooctadiene, C(8), C(1), C(2), C(3) and C(8′)C(1′), C(2′)C(3′) are nearly planar, and the two cyclooctadienyl groups are bent away from the $Fe(CO)_3$ group. The fractional atomic coordinates with e.s.d.'s are given in Table 6 in the Experimental section.

X-ray structure determination of $FeRu(CO)_6(C_{16}H_{20})$, **6**

The structure of **6** is shown in Fig. 3, and important distances and angles are listed in Tables 3 and 4. The molecule is composed of a 1,1,1-tricarbonyl(ruthenacyclo-2,4-pentadiene)unit coordinated to an $Fe(CO)_3$ group. The Ru–Fe bond length (2.63 Å) is similar to the Ru–Fe (2.66 ± 0.1 Å) [19] and is less than the Ru–Ru (2.82 ± 0.1 Å) bond distances [20] reported so far. The bond distances of

TABLE 4

SELECTED BOND ANGLES (°) WITH e.s.d.'s FOR COMPLEXES **3a**, **6** AND **7**

	3a[M(1) = Fe]	**6**[M(1) = Fe, M(2) = Ru]	**7**[M(1) = M(2) = Ru]
M(1)-C(1)-C(2)	71.6(5)	69.1(8)	69.9(10)
M(1)-C(1')-C(2')	71.6(4)	70.1(9)	68.1(8)
M(1)-C(2)-C(1)	68.4(4)	73.1(9)	73.6(10)
M(1)-C(2')-C(1')	68.6(4)	72.4(9)	73.7(8)
M(1)-C(1)-C(1')	69.9(4)	70.4(8)	71.4(9)
M(1)-C(1')-C(1)	69.7(4)	70.8(8)	72.5(9)
M(2)-C(1)-C(2)		38.2(8)	40.8(9)
M(2)-C(1')-C(2')		39.3(9)	37.2(7)
M(2)-C(2)-C(1)		117.1(11)	113.2(12)
M(2)-C(2')-C(1')		116.0(11)	116.9(11)
M(2)-M(1)-C(1)		75.8(4)	72.5(4)
M(2)-M(1)-C(1')		76.0(4)	73.2(3)
M(1)-M(2)-C(2)		52.1(4)	53.5(4)
M(1)-M(2)-C(2')		52.4(4)	52.8(4)
C(1)-C(2)-C(3)	121.8(8)	120.4(13)	120.8(16)
C(1')-C(2')-C(3')	122.0(7)	122.0(14)	115.4(14)
C(2)-C(3)-C(4)	113.1(8)	119.9(15)	119.8(19)
C(2')-C(3')-C(4')	112.0(8)	122.9(15)	116.1(17)
C(3)-C(4)-C(5)	115.8(9)	129.8(19)	118.7(24)
C(3')-C(4')-C(5')	114.7(9)	123.4(20)	117.8(23)
C(6)-C(7)-C(8)	113.7(9)	119.1(17)	120.7(22)
C(6')-C(7')-C(8')	120.0(9)	120.0(20)	125.3(25)
C(7)-C(8)-C(1)	113.1(8)	109.4(14)	111.9(17)
C(7')-C(8')-C(1')	112.4(8)	112.5(19)	117.1(16)
C(8)-C(1)-C(2)	121.1(8)	124.4(13)	123.3(16)
C(8')-C(1')-C(2')	122.2(7)	123.1(15)	123.9(14)
C(2)-C(1)-C(1')	115.9(7)	113.7(13)	117.0(15)
C(2')-C(1')-C(1)	115.0(7)	114.7(14)	112.4(14)
M(1)-C(9)-O(9)	176.0(9)	164.6(16)	166.0(16)

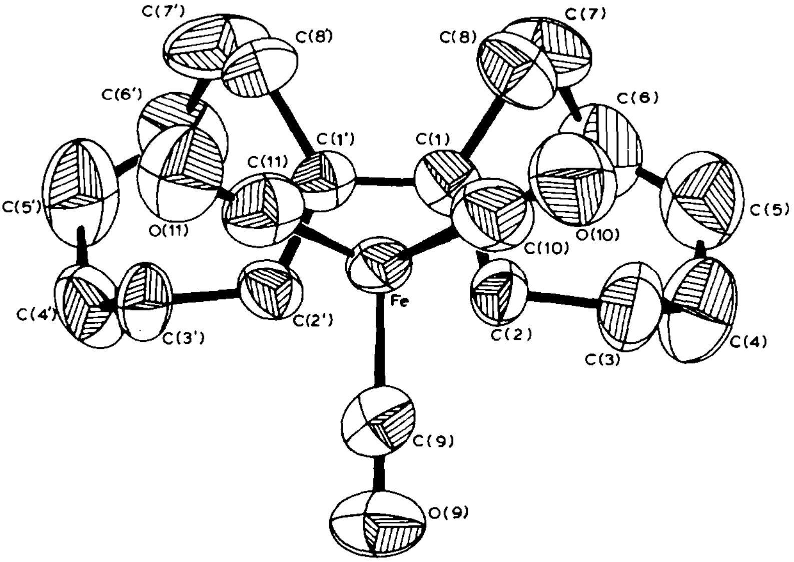


Fig. 2. ORTEP drawing of $Fe(CO)_3(C_{16}H_{22})$, **3a**, showing the numbering system.

TABLE 5

IR AND RAMAN CO STRETCHING VIBRATIONS FOR COMPLEXES 2-3 AND 5-7 [a]

Complex	IR (hexane solution, cm^{-1})			Raman (single crystal, cm^{-1})		
2a	2055s	1990wvs	1983(sh)	2060s	1980vs	1975s
3a	2041s	1975vs	1969(sh)	2030s	1965vs	1950s
5a	2060m	2020vs	1985s	2060vs	2020w	1990vs
	1975m	1940w		1980s	1970m	1915w
6	2080m	2030vs	2000s	2075vs	2025w	2000vs
	1990m	1985w	1925w	1985s	1975m	1900w
7	2085m	2035vs	1995s	2075vs	2030w	2000vs
	1985m	1970w	1960(sh)	1990s	1940m	

[a] Spectral data were collected at 25°C.

Ru–C(1), Ru–C(1′), Ru–C(2) and Ru–C(2′) are a little longer than the corresponding Fe–C lengths in ferracyclopentadiene complexes [21]. A semibridged CO is observed between C(9) and the Ru(2) atom, and the Ru–C distance (2.56 Å) is comparable to the reported semibridged Fe–C bond lengths (2.37–2.80 Å) [21]. It is clear from the bond distances that a double bond exists between C(3)–C(4) in line with the ^{1}H NMR results. The dihedral angle between C(2)–C(3) and C(4)–C(5) bonds is 50.9°, a value comparable to that (52.6°) between C(6)–C(7) and C(8)–C(1) bonds observed in **3a**. Fractional atomic coordinates are given in Table 7.

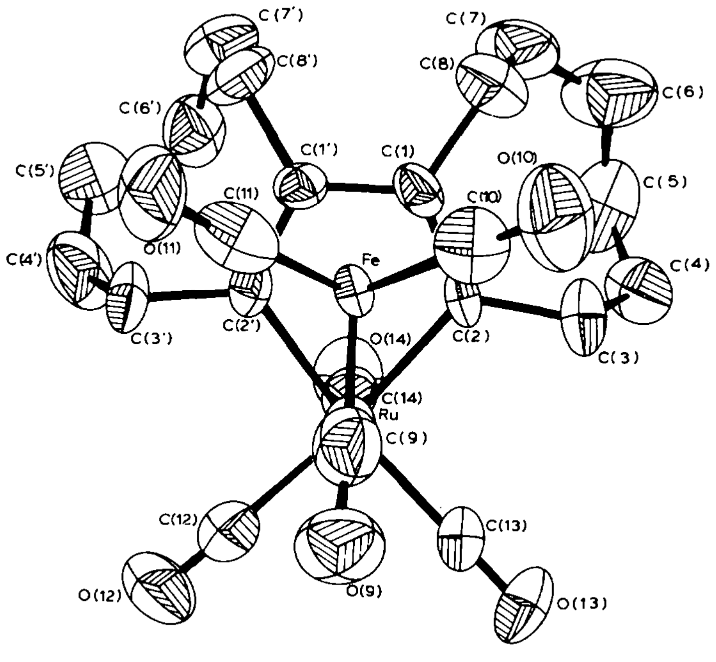


Fig. 3. ORTEP drawing of $RuFe(CO)_6(C_{16}H_{22})$, **6**.

TABLE 6

FINAL FRACTIONAL ATOMIC COORDINATES AND ANISOTROPIC THERMAL PARAMETERS WITH e.s.d.'s IN $Fe(CO)_3(C_{16}H_{22})$, **3a** [a]

	x	*y*	*z*	*β*(11)
Fe	0.31952(10)	0.22549(8)	0.84614(11)	0.0094(1)
C(9)	0.2160(8)	0.0928(6)	0.7931(9)	0.0129(10)
O(9)	0.1509(7)	0.0045(5)	0.7510(9)	0.0217(11)
C(10)	0.4529(8)	0.2445(6)	1.0677(9)	0.0145(11)
O(10)	0.5368(7)	0.2560(6)	1.2082(7)	0.0231(11)
C(11)	0.2016(8)	0.3367(6)	0.9000(9)	0.0143(10)
O(11)	0.1254(7)	0.4076(5)	0.9351(7)	0.0218(10)
C(1)	0.4793(7)	0.2492(5)	0.7684(7)	0.0084(8)
C(2)	0.4684(7)	0.1263(6)	0.7546(8)	0.0115(9)
C(3)	0.6034(9)	0.0631(7)	0.8690(10)	0.0168(12)
C(4)	0.7083(11)	0.0081(9)	0.7896(13)	0.0155(15)
C(5)	0.8153(12)	0.0925(11)	0.7940(16)	0.0158(17)
C(6)	0.7304(12)	0.1777(12)	0.6757(14)	0.0180(19)
C(7)	0.7162(10)	0.3087(9)	0.7721(12)	0.0136(13)
C(8)	0.6323(8)	0.3179(7)	0.8712(9)	0.0093(6)
C(1')	0.3388(7)	0.3013(5)	0.6777(7)	0.0103(8)
C(2')	0.2070(7)	0.2225(5)	0.5846(7)	0.0088(8)
C(3')	0.0434(7)	0.2666(7)	0.5014(9)	0.0090(9)
C(4')	−0.0057(9)	0.2699(8)	0.3174(10)	0.0146(12)
C(5')	0.0643(12)	0.3765(10)	0.3028(12)	0.0263(18)
C(6')	0.2338(12)	0.3724(10)	0.3591(11)	0.0183(18)
C(7')	0.3317(11)	0.4531(7)	0.5354(10)	0.0196(16)
C(8')	0.3294(8)	0.4341(6)	0.6808(8)	0.0153(11)

[a] The form of the thermal ellipsoid is $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

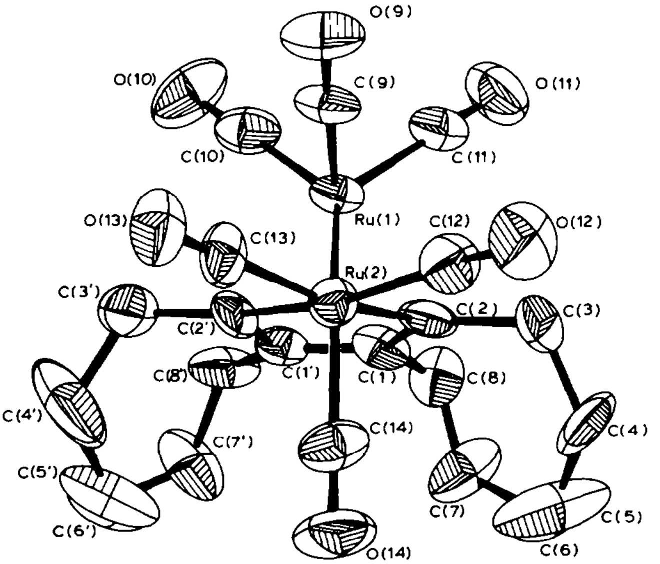


Fig. 4. ORTEP drawing of $Ru_2(CO)_6(C_{16}H_{20})$, 7.

$\beta(22)$	$\beta(33)$	$\beta(12)$	$\beta(13)$	$\beta(23)$
0.0057(1)	0.0105(1)	−0.0007(1)	0.0085(2)	0.0043(1)
0.0086(6)	0.0176(14)	−0.0009(13)	0.0105(20)	0.0091(16)
0.0101(6)	0.0359(16)	−0.0110(13)	0.0189(22)	0.0119(16)
0.0091(6)	0.0141(12)	0.0007(14)	0.0059(15)	0.0126(20)
0.0151(7)	0.0134(9)	−0.0008(14)	0.0067(16)	0.0070(13)
0.0084(6)	0.0143(12)	0.0009(13)	0.0151(19)	0.0063(14)
0.0120(6)	0.0252(12)	0.0107(13)	0.0305(19)	0.0086(14)
0.0067(5)	0.0109(10)	−0.0013(10)	0.0082(15)	0.0025(12)
0.0069(5)	0.0148(11)	0.0051(11)	0.0120(17)	0.0066(13)
0.0105(8)	0.0198(15)	0.0130(16)	0.0127(22)	0.0099(18)
0.0105(10)	0.0214(21)	0.0082(20)	0.0190(30)	0.0073(24)
0.0126(15)	0.0273(31)	0.0054(26)	0.0230(40)	0.0055(35)
0.0157(17)	0.0236(26)	0.0002(28)	0.0260(39)	0.0076(34)
0.0103(10)	0.0226(21)	−0.0036(9)	0.0195(28)	0.0038(24)
0.0093(8)	0.0144(13)	−0.0054(13)	0.0068(18)	0.0017(16)
0.0060(5)	0.0096(9)	−0.0013(10)	0.0093(15)	0.0029(11)
0.0076(5)	0.0112(10)	−0.0001(10)	0.0067(15)	0.0059(12)
0.0107(7)	0.0153(12)	0.0029(13)	0.0038(17)	0.0090(15)
0.0133(9)	0.0157(14)	0.0016(16)	0.0033(21)	0.0140(19)
0.0194(12)	0.0205(18)	0.0078(24)	0.0126(30)	0.0218(26)
0.0126(12)	0.0170(16)	−0.0008(24)	0.0182(29)	0.0104(23)
0.0082(7)	0.0155(15)	−0.0022(18)	0.0168(26)	0.0076(17)
0.0060(5)	0.0154(11)	−0.0003(12)	0.0151(19)	0.0035(13)

X-ray structure determination of $Ru_2(CO)_6(C_{16}H_{22})$, 7

The ORTEP drawing of $Ru_2(CO)_6(C_{16}H_{22})$, **7**, is shown in Fig. 4. The molecule involves a ruthenacyclopentadiene group. The geometry of **7** is essentially the same as that of **6**. The Ru–Ru bond distance (2.71 Å) is a little shorter than the sum of the covalent radius (1.41 Å) of Ru^0 obtained from X-ray studies on ruthenium cluster compounds [20]. The Ru(1)–C(1), Ru(1)–C(2), Ru(1)–C(1′), and Ru(1)–C(2′) distances are longer than the corrresponding distances observed for **6**. Double bonds exist between C(1)–C(2), C(1′)–C(2′), C(3)–C(4), and C(7′)–C(8′) as expected from the ^1H NMR spectrum. Accurate bond lengths and bond angles around C(5′) and C(6′) are not available due to the rather large thermal parameters for these atoms. The fractional atomic coordinates are listed in Table 8.

Conformation of cyclooctadienyl ring in 3a, 6 and 7

^1H NMR studies have revealed an unsymmetrical distorted boat-chair conformation for *cis*-cyclooctene [22] and an irregular form for *cis,cis*-1,3-cyclooctadiene [23]. The solid state structures of cyclooctene, cyclooctadiene and their metal complexes have not been well elucidated.

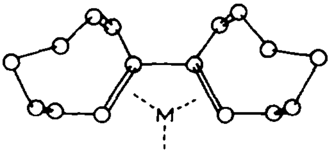
The present X-ray work showed that all of the cyclooctene and cyclooctadiene units involved in **3a**, **6** and **7** assumed the twisted boat-chair form. There is

TABLE 7

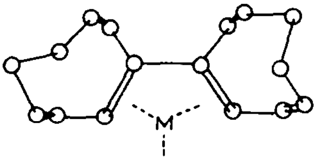
FRACTIONAL ATOMIC COORDINATES AND ANISOTROPIC THERMAL PARAMETERS WITH e.s.d.'s IN $RuFe(CO)_6(C_{16}H_{22})$, **6**

	x	y	z	$\beta(11)$
Ru	0.17041(14)	0.15814(8)	0.15501(6)	0.0163(2)
Fe	−0.03323(20)	0.25195(12)	0.19676(10)	0.0083(2)
C(9)	−0.1222(19)	0.1492(12)	0.1474(10)	0.0191(30)
O(9)	−0.2122(14)	0.0898(8)	0.1161(8)	0.0213(22)
C(10)	−0.0923(16)	0.2438(11)	0.1276(9)	0.0096(22)
O(10)	−0.1312(15)	0.2348(9)	0.3296(7)	0.0277(26)
C(11)	−0.1970(18)	0.3250(11)	0.1420(9)	0.0147(26)
O(11)	−0.3006(14)	0.3761(9)	0.1061(7)	0.0202(22)
C(12)	0.3845(20)	0.1748(10)	0.1627(9)	0.0228(32)
O(12)	0.5130(13)	0.1877(9)	0.1679(8)	0.0158(20)
C(13)	0.1979(20)	0.0321(10)	0.1914(9)	0.0253(34)
O(13)	0.2173(18)	−0.0404(8)	0.2110(7)	0.0454(37)
C(14)	0.0801(22)	0.1209(10)	0.0413(9)	0.0301(40)
O(14)	0.0279(18)	0.1028(9)	−0.0232(7)	0.0451(37)
C(1)	0.1480(15)	0.3508(9)	0.1972(7)	0.0129(21)
C(2)	0.1061(16)	0.2929(9)	0.1315(7)	0.0149(24)
C(3)	0.0412(18)	0.3307(10)	0.0470(8)	0.0182(27)
C(4)	0.1502(27)	0.3741(15)	0.0183(10)	0.0390(52)
C(5)	0.2700(23)	0.4469(13)	0.0547(11)	0.0261(40)
C(6)	0.3709(22)	0.4487(12)	0.1423(10)	0.0248(37)
C(7)	0.2862(24)	0.4957(12)	0.1899(12)	0.0302(43)
C(8)	0.1301(19)	0.4536(9)	0.1915(10)	0.0203(30)
C(1′)	0.2059(16)	0.3043(10)	0.2734(7)	0.0133(23)
C(2′)	0.2126(15)	0.2109(9)	0.2684(7)	0.0135(22)
C(3′)	0.2742(18)	0.1525(12)	0.3407(8)	0.0178(27)
C(4′)	0.4467(20)	0.1504(12)	0.3969(10)	0.0196(31)
C(5′)	0.5607(22)	0.2284(15)	0.4098(13)	0.0177(33)
C(6′)	0.5452(30)	0.3131(16)	0.4481(15)	0.0320(52)
C(7′)	0.4249(25)	0.3795(14)	0.3929(12)	0.0352(51)
C(8′)	0.2466(20)	0.3548(12)	0.3524(9)	0.0222(32)

essentially a mirror symmetry for the ligand of complex **3a**, with the mirror plane passing through the center of the C(1)–C(1′) bond. In contrast to the above, there is no mirror symmetry for the ligand of **6**. This difference is responsible for the uncoordinated double bonds present at different positions; i.e., double bonds are between C(7)–C(8) for **3a** and C(3)–C(4) for **6**.



Ligand part of 3a



Ligand part of 6

$\beta(22)$	$\beta(33)$	$\beta(12)$	$\beta(13)$	$\beta(23)$
0.0039(1)	0.0027(1)	0.0001(1)	0.0047(1)	0.0004(1)
0.0031(1)	0.0015(1)	0.0001(3)	0.0023(2)	0.0003(2)
0.0064(10)	0.0045(7)	0.0020(30)	0.0044(23)	0.0021(14)
0.0066(7)	0.0068(6)	−0.0051(21)	0.0065(20)	−0.0011(11)
0.0066(10)	0.0049(7)	−0.0040(25)	0.0051(20)	−0.0001(14)
0.0098(9)	0.0049(6)	−0.0022(25)	0.0145(20)	0.0021(12)
0.0067(10)	0.0054(7)	−0.0030(26)	0.0074(22)	−0.0027(13)
0.0090(8)	0.0051(5)	0.0114(22)	0.0019(18)	0.0024(11)
0.0037(8)	0.0049(7)	0.0033(25)	0.0092(25)	0.0014(12)
0.0108(9)	0.0075(6)	0.0052(23)	0.0113(20)	0.0020(13)
0.0048(8)	0.0027(5)	−0.0009(27)	0.0045(23)	0.0015(11)
0.0047(6)	0.0049(5)	0.0036(25)	0.0043(24)	0.0047(10)
0.0046(8)	0.0040(7)	−0.0037(30)	0.0083(27)	0.0004(12)
0.0093(9)	0.0032(4)	−0.0091(31)	0.0102(22)	−0.0038(11)
0.0032(6)	0.0030(5)	0.0034(20)	0.0046(17)	−0.0004(9)
0.0034(6)	0.0022(5)	0.0045(20)	0.0018(17)	0.0015(9)
0.0056(8)	0.0029(5)	0.0077(26)	0.0049(20)	0.0046(12)
0.0106(15)	0.0033(7)	−0.0101(45)	0.0135(32)	0.0009(16)
0.0077(12)	0.0065(9)	−0.0098(36)	0.0106(33)	0.0007(18)
0.0071(11)	0.0051(8)	−0.0046(34)	0.0103(29)	0.0015(16)
0.0052(9)	0.0062(9)	−0.0040(33)	0.0114(34)	−0.0005(15)
0.0028(7)	0.0053(7)	0.0015(23)	0.0061(25)	0.0001(11)
0.0051(7)	0.0021(5)	−0.0043(21)	0.0026(17)	−0.0014(10)
0.0051(7)	0.0014(4)	0.0004(20)	0.0044(16)	0.0013(9)
0.0080(10)	0.0029(5)	0.0042(29)	0.0068(21)	0.0038(13)
0.0068(10)	0.0045(7)	0.0107(31)	0.0006(24)	0.0001(14)
0.0104(15)	0.0088(12)	0.0031(37)	0.0120(33)	0.0041(22)
0.0093(16)	0.0103(15)	0.0026(46)	0.0030(4)	−0.0041(25)
0.0069(12)	0.0053(9)	0.0033(39)	−0.0081(34)	−0.0039(17)
0.0071(10)	0.0037(6)	−0.0051(31)	0.0069(24)	−0.0043(14)

IR and Raman spectral studies

Five depolarized ($5A'$) and two polarized ($2A''$) IR- and Raman-active vibrations are expected to exist for **5a**, **6** and **7**, since these complexes have a common $(CO)_3M-M(CO)_3$ unit. One of the vibrations is assignable to the M–M vibration. The expected six CO stretching vibrations were observed in the IR(hexane solution) and Raman(crystalline state) spectra of **5a**, **6** and **7** as listed in Table 5 (data for **2a** and **3a** are also given for comparison). The lowest frequency is assigned to the semi-bridged CO vibration, since bridged or semi-bridged CO groups generally absorb in this region. The $M(CO)_n$ stretching frequency increased in the order $Fe_2(CO)_6 > RuFe(CO)_6 > Ru_2(CO)_6$. The M–M vibrations for **5a**, **6** and **7** were observed in the Raman spectra at 190, 185 and 173 cm^{-1}, respectively. Approximate M–M force constants calculated by neglecting the ligands are 0.59 (Fe–Fe) 0.72 (Ru–Fe) and 0.89 mdyn/Å (Ru–Ru). The values increased with increasing atomic

TABLE 8

FINAL FRACTIONAL ATOMIC COORDINATES AND ANISOTROPIC THERMAL PARAMETERS IN $Ru_2(CO)_6(C_{16}H_{20})$, 7

	x	*y*	*z*	$\beta(11)$
Ru(1)	0.41426(11)	0.22090(7)	0.23620(8)	0.0082(1)
Ru(2)	0.36606(11)	0.07339(7)	0.13577(8)	0.0076(1)
C(9)	0.2143(15)	0.2192(12)	0.1315(8)	0.0092(18)
O(9)	0.0953(12)	0.2344(9)	0.0764(8)	0.0122(16)
C(10)	0.3432(16)	0.2491(11)	0.3208(12)	0.0111(21)
O(10)	0.3084(15)	0.2645(9)	0.3732(9)	0.0215(22)
C(11)	0.4567(16)	0.3398(11)	0.2250(10)	0.0100(20)
O(11)	0.4865(16)	0.4104(7)	0.2153(9)	0.0297(27)
C(12)	0.4789(17)	−0.0276(10)	0.1392(12)	0.0119(22)
O(12)	0.5499(16)	−0.0856(8)	0.1432(10)	0.0296(27)
C(13)	0.1840(15)	0.0091(10)	0.1181(11)	0.0078(17)
O(13)	0.0828(13)	−0.0301(9)	0.1102(10)	0.0117(16)
C(14)	0.2757(15)	0.0989(9)	0.0049(10)	0.0090(18)
O(14)	0.2282(12)	0.1145(8)	−0.0669(7)	0.0170(18)
C(1)	0.6490(14)	0.1683(9)	0.2660(11)	0.0069(16)
C(2)	0.5459(15)	0.1650(10)	0.1711(10)	0.0087(18)
C(3)	0.5840(17)	0.2061(10)	0.1078(12)	0.0130(22)
C(4)	0.6866(22)	0.1615(19)	0.0794(14)	0.0147(28)
C(5)	0.8243(22)	0.1082(17)	0.1544(18)	0.0157(31)
C(6)	0.9433(24)	0.1587(15)	0.2248(19)	0.0183(34)
C(7)	0.9330(18)	0.1724(16)	0.3106(14)	0.0080(21)
C(8)	0.7944(14)	0.2232(11)	0.3086(13)	0.0052(16)
C(1′)	0.6037(13)	0.1254(9)	0.3239(9)	0.0049(14)
C(2′)	0.4557(14)	0.0816(9)	0.2733(10)	0.0085(17)
C(3′)	0.4012(16)	0.0316(12)	0.3314(11)	0.0100(20)
C(4′)	0.4554(22)	−0.0618(12)	0.3543(16)	0.0205(32)
C(5′)	0.6258(24)	−0.0778(14)	0.4070(20)	0.0184(34)
C(6′)	0.7450(38)	−0.0376(26)	0.4746(28)	0.0121(48)
C(6″)	0.7606(44)	−0.0341(29)	0.4202(27)	0.0204(66)
C(7′)	0.7975(21)	0.0522(14)	0.4712(13)	0.0200(32)
C(8′)	0.6994(18)	0.1258(12)	0.4292(10)	0.0140(23)

number in line with the trend reported for $(CO)_5MRe(CO)_5^-$ (M = Cr, Mo, W) [24] and $[M_2(CO)_{10}]$ (M = Mn, Tc, Re) [25].

Experimental

All the reactions were carried out under an argon atmosphere. $Ru_3(CO)_{12}$ (Strem Chem.) was used without further purification. $Fe_3(CO)_{12}$ was prepared from $Fe(CO)_5$ according to the known method [26]. Separation of the product was made by thin-layer chromatography (TLC) on silica gel plates (Merck, Kieselgel 60-F_{254}. 20 × 20 cm^2, thickness 1.0 mm) using hexane as an eluent. ^1H NMR spectra were recorded on a Varian XL-100 instrument. Mass spectra (EI) were recorded on a JEOL-OISG-2 spectrometer. IR spectra were obtained on a Hitachi EPI-2 spectrometer and Raman spectra on a JASCO R-800 Raman spectrophotometer equipped with a He-Ar laser source at a normal power of 50 mW. Elemental analysis was

$\beta(22)$	$\beta(33)$	$\beta(12)$	$\beta(13)$	$\beta(23)$
0.0032(1)	0.0053(1)	0.0003(1)	0.0061(1)	−0.0010(1)
0.0030(1)	0.0046(1)	−0.0007(1)	0.0053(1)	−0.0004(1)
0.0061(9)	0.0040(8)	0.0044(22)	0.0026(19)	−0.0004(14)
0.0076(8)	0.0071(8)	0.0075(19)	0.0012(18)	−0.0011(12)
0.0056(9)	0.0069(10)	0.0084(22)	0.0093(25)	0.0036(15)
0.0091(9)	0.0078(8)	0.0076(23)	0.0184(23)	0.0017(14)
0.0056(9)	0.0038(8)	0.0021(21)	0.0008(20)	−0.0019(13)
0.0017(5)	0.0094(9)	−0.0038(18)	0.0082(25)	0.0001(10)
0.0034(8)	0.0071(11)	0.0010(21)	0.0041(25)	−0.0001(14)
0.0041(6)	0.0011(10)	0.0110(22)	0.0186(28)	0.0008(13)
0.0043(8)	0.0059(9)	−0.0010(19)	0.0044(20)	0.0024(13)
0.0085(9)	0.0098(9)	−0.0058(20)	0.0086(21)	0.0024(14)
0.0040(7)	0.0042(7)	−0.0070(18)	0.0040(19)	−0.0003(11)
0.0063(7)	0.0041(6)	−0.0030(18)	0.0063(16)	0.0011(10)
0.0023(6)	0.0074(10)	−0.0009(16)	0.0077(21)	−0.0020(12)
0.0047(7)	0.0055(9)	0.0020(18)	0.0093(21)	0.0013(13)
0.0032(7)	0.0073(10)	−0.0009(20)	0.0096(25)	−0.0001(14)
0.0188(25)	0.0055(9)	0.0080(44)	0.0114(31)	−0.0002(27)
0.0111(18)	0.0157(22)	−0.0016(37)	0.0208(45)	−0.0123(33)
0.0078(14)	0.0156(22)	−0.0030(35)	0.0218(47)	−0.0053(28)
0.0127(18)	0.0069(12)	−0.0036(30)	0.0059(26)	−0.0027(22)
0.0030(7)	0.0106(13)	−0.0007(18)	0.0053(23)	−0.0007(16)
0.0042(7)	0.0032(6)	−0.0001(6)	0.0007(15)	−0.0010(11)
0.0031(6)	0.0060(8)	0.0019(17)	0.0092(20)	−0.0014(12)
0.0067(10)	0.0055(9)	0.0006(23)	0.0082(23)	0.0015(15)
0.0038(9)	0.0142(18)	0.0025(27)	0.0191(41)	0.0095(21)
0.0036(10)	0.0190(26)	0.0059(32)	−0.0016(47)	−0.0004(27)
0.0066(23)	0.0083(26)	0.0056(53)	0.0052(58)	0.0036(38)
0.0083(27)	0.0066(24)	0.0069(68)	0.0118(67)	0.0035(40)
0.0061(12)	0.0060(11)	−0.0025(31)	−0.0012(30)	0.0014(17)
0.0062(10)	0.0034(8)	−0.0034(25)	0.0023(21)	−0.0009(14)

carried out with a Yanagimoto Model MT-2 CHN analyzer. X-ray data were collected with a Rigaku rotating-anode type four-circle automated diffractometer at 40 kV, 200 mA.

Preparation of bicyclo-2,7-octadienyl, 1

The ligand **1** was synthesized according to the method previously reported [6]. A THF solution (50 ml) of cyclooctadienylpotassium (1.5 g, 10 mmol), which was prepared by direct metalation of 1,3-cyclooctadiene in THF/NEt_3, was added to anhydrous zinc chloride (2.9 g, 21 mmol) dissolved in THF (20 ml) at −20°C. The mixture was heated to 40°C for 3 h to complete the coupling reaction. After quenching with water (1.0 mol) and removal of THF by flash distillation, the resulting bicyclo-2,7-octadienyl was extracted with pentane (100 ml) and purified by distillation (98°C/10^{-1} mmHg). The distillate contained bi-2,7-cyclooctadienyl (85–95%) and 1,3-cyclooctadienyl-2,7-cyclooctadiene (5–15%). Bi-2,7-

cyclooctadienyl could be separated from the isomers by thin layer chromatography on Kieselgel plates using hexane as an eluent (R_f values for bi-2,7-cyclooctadienyl and 1,3-cyclooctadienyl-2,7-cyclooctadiene are 0.70 and 0.64, respectively).

Preparation of mononuclear complexes 2a and 3a

A mixture of bicyclo-2,7-octadiene (2.2 g, 10 mmol) and $Ru_3(CO)_{12}$ (1.9 g, 3 mmol) in isooctane (30 mol) was heated to 140°C for 6 h in a thick-walled glass tube fitted with a pressure release to give a homogeneous pale yellow solution. After filtration, the solution was condensed to 2 ml. Colorless crystals of $Ru(CO)_3$(bicyclo-1,7-octadienyl), **2a**, were obtained in 80% yield by cooling the solution to −20°C. The complex was purified by recrystallization from hexane.

Anal. Found: C, 57.29; H, 5.56. Calcd for $C_{19}H_{22}O_3Ru$: C, 57.13; H, 5.55%.

The corresponding iron complex **3a** was prepared from $Fe_3(CO)_{12}$ (1.5 g, 3 mmol) and bi-2,7-cyclooctadienyl (8 mmol) and isolated as yellow crystals in essentially the same way as described for **2a** except for the reaction temperature (110°C). Typical yield is 65% based on bi-2,7-cyclooctadienyl.

Anal. Found: C, 64.67, H, 6.76. Calcd for $C_{19}H_{22}O_3Fe$: C, 64.42; H, 6.26%.

Preparation of diruthenium complexes 4a and 4b

A mixture of $Ru(CO)_3(C_{16}H_{22})$, **2a**, (0.8 g, 2.0 mmol) and $Ru_3(CO)_{12}$ (1.3 g, 2.0 mmol) was heated to 140°C for 6 h in isooctane (30 ml). After removal of unreacted $Ru_3(CO)_{12}$ and dark-brown precipitates by filtration at 25°C, the solution was evaporated to dryness in vacuo. The residue was dissolved in a minimum amount of hexane, and chromatographic separation was made on TLC plates to give $Ru_2(CO)_6(C_{16}H_{22})$, **4a**, (65%) and **4b** (35%) in 80% combined yield. The R_f values were 0.44 and 0.41, respectively.

Anal. Found: C, 45.50; H, 3.51. Calcd for $C_{22}H_{22}O_6Ru_2$, **4a**: C, 45.20, H, 3.79%.

Anal. Found: C, 45.35, H. 3.68. Calcd for $C_{22}H_{22}O_6Ru_2$, **4b**: C, 45.20; H, 3.79%.

Preparation of diruthenium complex 7

A mixture of bicyclo-2,7-octadienyl(0.4 g, 2 mmol) and $Ru_3(CO)_{12}$ (1.3 g, 2 mmol) in isooctane (30 ml) was stirred at 140°C for 6 h. Purification of the reaction product on TLC plates gave $Ru(CO)_3(C_{16}H_{22})$, **2a** (12%), $Ru_2(CO)_6(C_{16}H_{20})$, **7** (65%), **4a** (12%) and **4b** (11%) in 80% combined yield. The R_f values for **2a** and **7** were 0.50 and 0.36, respectively.

Anal. Found: C, 45.70; H, 3.79. Calcd for $C_{22}H_{20}O_6Ru_2$, **7**: C, 45.36, H, 3.46%.

Preparation of diiron complexes 5a and 5b

A mixture of **3a** (0.7 g, 2 mmol) and $Fe_3(CO)_{12}$(3 g, 6 mmol) in isooctane (30 ml) was heated to 120°C for 6 h. After the usual work up, the resulting complexes were separated on TLC plates. A mixture of **5a** (54%) and **5b** (46%) was obtained in 38% combined yield. Their R_f values are 0.43 and 0.40, respectively. The direct reaction of $Fe_3(CO)_{12}$(3 mmol) with bi-2,7-cyclooctadienyl (2 mmol) also gave **5a** (8% yield) and **5b** (7% yield).

Anal. Found: C, 53.46; H, 4.49. Calcd for $C_{22}H_{22}O_6Fe_2$, **5a**: C, 53.48; H, 4.69%.

Anal. Found: C, 53.55; H, 4.56. Calcd for $C_{22}H_{22}O_6Fe_2$, **5b**: C, 53.48; H, 4.49%.

Preparation of hetero bimetallic complex 6

A mixture of **3a** (0.7 g, 2 mmol) and $Ru_3(CO)_{12}$(1.3 g, 2 mmol) in isooctane (30 ml) was stirred at 140°C for 4 h. After filtration, the solution was condensed to 2 ml and cooled to −20°C to induce crystallization. $RuFe(CO)_6(C_{16}H_{22})$, **6**, was obtained as pale yellow crystals in 55% yield based on **3a**. The reaction of **2a** (2 mmol) with $Fe_3(CO)_{12}$(4 mmol) at 120°C for 10 h also gave **6** in 30% yield. The sample was purified by TLC (R_f, 0.42).

Anal. Found: C, 49.76; H, 4.30. Calcd for $C_{22}H_{22}O_6RuFe$: C, 48.99; H, 4.11%.

Preparation of $RuFe(CO)_6(C_6H_8)$, 8

2.3-Dimethyl-1,3-butadiene(0.4 ml. 4 mmol) was added to $Ru_3(CO)_{12}$(0.7 g, 1 mmol) dispersed in isooctane(10 ml) and the mixture was stirred at 120°C for 5 h. The resulting complexes were separated on Kieselgel plates to give $Ru(CO)_3$(2,3-dimethyl-1,3-butadiene), **10**, in 42% yield together with $Ru_2(CO)_6(C_6H_8)$ in 15% yield. R_f values were 0.58 and 0.35, respectively. To an isooctane soluton(8 ml) of **10**(0.3 g, 1 mmol) was added a mixture of $Fe_3(CO)_{12}$(2 g, 4 mmol) and 3-methyl-1,3-pentadiene (0.15 ml, 1 mmol). After heating the mixture to 120°C for 10 h, the solution was filtered and condensed. The products were separated by thin layer chromatography to give $RuFe(CO)_6(C_6H_8)$ in 52% yield. R_f value 0.39. ^1H NMR($CDCl_3$), δ 6.48(s,H), 1,29 ppm (s, CH_3). mass spectrum(EI), 406(M^+), Calcd 406(^{102}Ru, ^{56}Fe).

Anal. Found: C, 35.01; H, 1.75. Calcd for $C_{12}H_8O_6RuFe$, **8**: C, 35.58; H, 1.99%. Complex **9** was characterized as follows. ^1H NMR($CDCl_3$) δ 6.82(s, H), 1.36 ppm (s, CH_3); mass spectrum(EI), 452(M^+), Calcd 452(^{102}Ru).

Anal. Found: C, 31.55; H, 1.68. Calcd for $C_{12}H_8O_6Ru_2$, **9**; C, 32.01; H, 1.79%.

X-ray data collections and structure determination of 3a, 6 and 7

Single crystals of **3a** (0.3 × 0.3 × 0.3 mm), **6** (0.3 × 0.2 × 0.2 mm) and **7** (0.2 × 0.2 × 0.2 mm) were obtained by recrystallization from hexane at −20°C. A crystal was glued to a glass fiber attached to the brass pin of a goniometer head, and then intensity measurement was carried out. Their space groups were determined from preliminary Weissenberg and precession photographs and are listed in Table 2. The data were collected by the ω—2θ scan technique for **3a**, **6** and **7** using Mo-K_α radiation monochromated with a graphite crystal (λ 0.7107 Å). Intensity data were corrected for Lorentz and polarization effects and merged to a unique set of reflections. Corrections for absorption were found to be unnecessary. No intensity decay was observed for all the monitor reflections (3 every 120 min).

The structure were solved by the heavy-atom procedure. The iron and ruthenium atom positions were located from a three-dimensional Patterson synthesis, and all remaining non-hydrogen atoms were located by successive density difference Fourier synthesis. The structure was refined by the block-diagonal squares (HBLS-V) [27] with anisotropic thermal parameters for all non-hydrogen atoms. Further refinement with isotropic thermal parameters for hydrogen atoms was not tried. Final discrepancy factors, $R_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$ and $R_2 = (\Sigma w(|Fo| - |Fc|)^2/\Sigma wFo^2)^{1/2}$ where $w = 1/\sigma^2(Fo)$, are listed in Table 2.

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