Reaction of a (π-Vinylcarbene)iron Complex with Tricarbonyl(η^4-1,5-cyclooctadiene)ruthenium. Preparation, Structure, and Reactivity of Novel (μ-Vinylcarbene)(Fe−Ru) Complexes

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[1−3-η-1-Methoxy-*anti*-2,3-bis(methoxycarbonyl)prop-2-en-1-ylidene]tricarbonyliron (**5**) reacts with $Ru(CO)_3(COD)$ to give a heterobinuclear vinylcarbene complex, [μ-(1-methoxy-*anti*-2-(methoxycarbonyl)-μ-3-(methoxycarbonyl)-1−3-η-prop-2-en-1-ylidene)]hexacarbonyl-(Fe−Ru) (**7**) in 78% yield. The complex **7** reacts with triphenylphosphine to give a substituted complex, [μ-(1-methoxy-*anti*-2-(methoxycarbonyl)-μ-3-(methoxycarbonyl)-1−3-η-prop-2-en-1-ylidene)(triphenylphosphine)]pentacarbonyl(Fe−Ru) (**8**) in 52% yield. The carbonyl group on ruthenium *trans* to the iron atom in **7** was substituted by the phosphine.

Introduction

For the past two decades, much attention has been focused on the chemistry of mononuclear **1**[1−9] and binuclear transition-metal vinylcarbene complexes **2**, (η^4-metallabutadiene)metal complexes **2′**, or η^3:η^1-allylidene complexes **2″** (Chart 1).[10−43] Especially, heterobinuclear vinylcarbene complexes[36−43] are of interest; however, methods of preparation of these complexes are

Chart 1

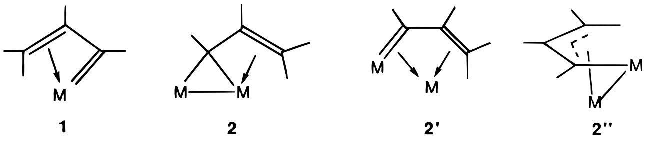

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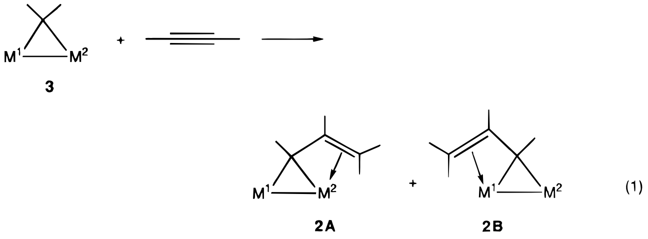
Table 1. Spectral Data for 6−8

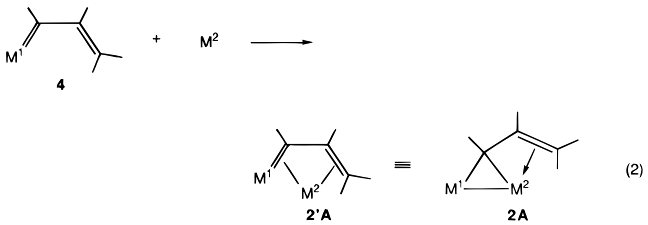
complex	IR[a] (ν/cm^{-1}; KBr disk)	^{1}H NMR[b] (δ/ppm in CDCl$_3$)	^{13}C NMR[b] (δ/ppm in CDCl$_3$)
6	2078 (m), 2035 (s), 2006 (s) 1995 (m), 1975 (s,br) (ν(C≡O)) 1721 (m, ν((C=O), ester) 1601 (m, ν(C=OFe))	4.07 (s, 3H, OMe) 3.83 (s, 3H, CO$_2$Me) 3.50 (s, 3H, CO$_2$Me) 3.03 (s, 1H, CH)	221.2 (s, *C*OMe carbene) 211.4, 209.6, 205.1 (s, Fe*C*O)[c] 186.3, 168.8 (s, *C*O$_2$Me) 82.0 (s, *C*CO$_2$Me) 63.2 (q, O*Me* J_{CH} = 145 Hz) 54.6 (q, CO$_2$Me J_{CH} = 149 Hz) 52.7 (q, CO$_2$*Me* J_{CH} = 147 Hz) 38.4 (d,*C*H J_{CH} = 161 Hz)
7	2090, 1997, 1968, 1942 (s, ν(C≡O)) 1732 (s, ν(C=O), ester) 1596 (m, ν(C=ORu))	3.94 (s, 3H, OMe) 3.84 (s, 3H, CO$_2$Me) 3.59 (s, 3H, CO$_2$Me) 3.12 (s, 1H, CH)	212.1 (s, br, Fe(*C*O)$_3$)[c] 211.0 (s, *C*OMe carbene) 196.5, 195.7, 187.7 (s, Ru(*C*O)$_3$) 188.1, 169.3 (s, *C*O$_2$Me) 81.6 (s, *C*CO$_2$Me) 63.5 (q, O*Me*, J_{CH} = 145 Hz) 54.7, 52.6 (q, CO$_2$*Me*, J_{CH} = 149 Hz) 37.1 (d, *C*H, J_{CH} = 161 Hz)
8	2029, 1992, 1951, 1938, 1919 (s, ν(C≡O)) 1731 (m, ν(C=O), ester) 1601 (m, ν(C=ORu))	7.45−7.43 (m, 15H, PPh$_3$) 3.85 (s, 3H, OMe) 3.33 (s, 3H, CO$_2$Me) 3.21 (s, 3H, CO$_2$Me) 2.80 (s, 1H, CH)	214.2 (s, br, Fe(*C*O)$_3$)[c] 210.2 (s, *C*OMe carbene) 202.5, 201.3 (d, Ru(*C*O)$_2$, J_{CP} = 5.9 Hz) 187.3, 170.9 (s, *C*O$_2$Me) 133.6−128.5 (m, PPh$_3$) 84.7 (s, *C*CO$_2$Me) 61.7 (q, O*Me*, J_{CH} = 144 Hz) 53.9 (q, CO$_2$*Me*, J_{CH} = 148 Hz) 52.5 (q, CO$_2$*Me*, J_{CH} = 149 Hz) 36.9 (d, *C*H, J_{CH} = 161 Hz)

[a] vs = very strong, s = strong, m = medium. [b] s = singlet, d = doublet, q = quartet, br = broad, m = multiplet. [c] Temperature dependence was observed. See the text.

not completely established. As for the preparation of (μ-vinylcarbene)(M^1−M^2) complexes, the following two representative methods are reported: (1) reaction of (μ-methylene)(M^1−M^2) **3** with alkynes (eq 1);[38] (2) reaction of (η^1-vinylcarbene)M^1 or 1-metallabutadiene **4** with M^2 (eq 2).[41] In the reaction of eq 1, usually a mixture of two kinds of products **2A** ((η^1-μ-methylene)M^1−(η^3-allyl)-M^2) and **2B** ((η^1-μ-methylene)M^2−(η^3-allyl)M^1) is produced.[38] In the reaction of eq 2, only **2′A** was selectively obtained.[36,41] Thus no method for selective preparation of **2B** from (η^3-C$_3$-ligand)M^1 and M^2 has been reported.

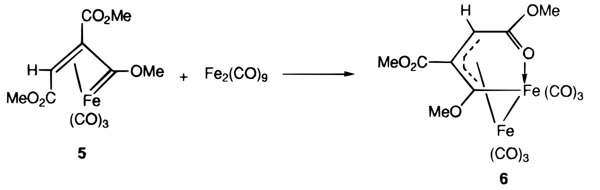


(1)



(2)

On the other hand, one of the methods to prepare a binuclear (vinylcarbene)(Fe−Fe) complex is the reaction of a mononuclear π-vinylcarbene complex with "Fe(CO)$_3$", i.e., reaction of (π-vinylcarbene)tricarbonyliron (**5**) with Fe$_2$(CO)$_9$ gives **6** (eq 3).[25] Thus, selective preparation of **2B** by the reaction of (π-vinylcarbene)iron complex with a ruthenium complex is expected (eq 4).



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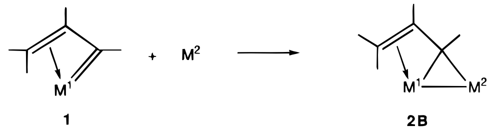

(4)

We now report structure and reactivity of a novel heterobinuclear (vinylcarbene)(Fe−Ru) complex (type **2B**) which was successfully obtained by the reaction of the (π-vinylcarbene)tricarbonyliron (**5**) with tricarbonyl(η^4-1,5-cyclooctadiene)ruthenium [Ru(CO)$_3$(COD)].

Results and Discussion

Preparation of [μ-(1-Methoxy-*anti*-2-(methoxycarbonyl)-μ-3-(methoxy)carbonyl-1−3-η-prop-2-en-1-ylidene)]hexacarbonyl(Fe−Ru) (7). [1−3-η-1-Methoxy-*anti*-2,3-bis(methoxycarbonyl)-prop-2-ene-1-ylidene]tricarbonyliron[1] (**5**) reacted with Ru(CO)$_3$(COD)[44] to give a corresponding heterobinuclear vinylcarbene complex **7** in 78% yield (eq 5).

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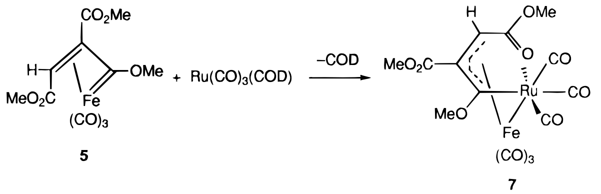
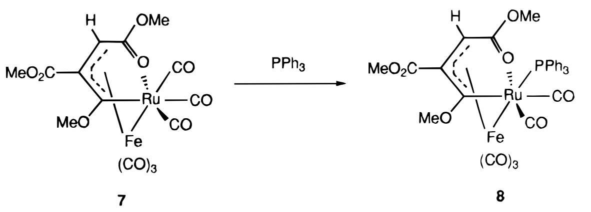


(5)

Complex **7** is an orange crystal which is stable under ambient conditions for several hours and is slowly oxidized in air. The spectral data for the complex **7** are summarized in Table 1. The IR spectrum of **7** showed ν(C=O) of the coordinated carbonyl group of ester at 1596 cm^{-1} and that of uncoordinated ester at 1732 cm^{-1}. The ^{1}H NMR spectrum of **7** showed an olefinic proton at δ 3.12 ppm. The ^{13}C NMR spectrum of **7** exhibited a characteristic signal for the olefinic carbon at δ 37.1 ppm with J_{C-H} = 161 Hz. Signals for Ru(CO)$_3$ are found as three sharp peaks at higher field,[45] δ 187.7, 195.7, and 196.5 ppm, and that for Fe(CO)$_3$ was found as a broad singlet at 212.1 ppm at 25 °C. At −60 °C this broad singlet split into three sharp signals, at 208.1, 208.5, and 219.8 ppm, showing that the Fe(CO)$_3$ group is fluxional at ambient temperature. A similar temperature dependence was observed for **6**.[25] In a comparison of the spectral data of **7** with those of **6**, which are also summarized in Table 1, **7** is deduced to be a heterobinuclear Fe−Ru vinylcarbene complex, [μ-(1-methoxy-*anti*-2-(methoxycarbonyl)-μ-3-(methoxycarbonyl)-1−3-η-prop-2-en-1-ylidene)]hexacarbonyl(Fe−Ru).

X-ray Crystal Structure of 7. The structure of **7** was confirmed by an X-ray diffraction study. The molecular geometry and atom-numbering system of **7** are shown in Figure 1, while Tables 2 and 3 summarize the results obtained. The carbene carbon (C(1)) is bridged between Fe and Ru. The C(1)−C(2)−C(3) vinylcarbene moiety coordinates to the iron as a π-allyl group. The C(1)−C(2) length of 1.401(6) Å is much shorter than C(2)−C(3) length of 1.453(6) Å. The ruthenium has a highly distorted octahedral structure; the angle Fe−Ru−C(9) was 151.7(1)°. Both the ester carbonyl group and the carbon−iron double bond of **5** coordinate to the ruthenium tricarbonyl moiety. The Fe−Ru length of 2.694(3) Å was reasonably longer than the Fe−Fe length in **6** (2.638(1) Å), and it is in the range of usual Fe−Ru lengths reported.[42,46]

Reaction of 7 with Triphenylphosphine. Complex **7** was treated with triphenylphosphine to give orange crystals of **8** in 52% yield (eq 6). Spectral data of **8** are also summarized in Table 1. The IR absorption at 1601 cm^{-1} showed that the coordinated ester group remains. The ^{13}C NMR spectrum of **8** showed two doublets at 201.3 (J_{PC} = 5.9 Hz) and 202.5 (J_{PC} = 5.9 Hz) ppm and a broad singlet at 214.2 ppm. The broad singlet split into two peaks at δ 223.2 and 209.1 (2C) at −60 °C. These spectral data strongly suggested that one of the carbonyl groups of Ru(CO)$_3$ in **7** was substituted by PPh$_3$ to form an Fe(CO)$_3$Ru(CO)$_2$(PPh$_3$) moiety. To confirm the molecular structure of **8**, X-ray analysis was performed.



(6)

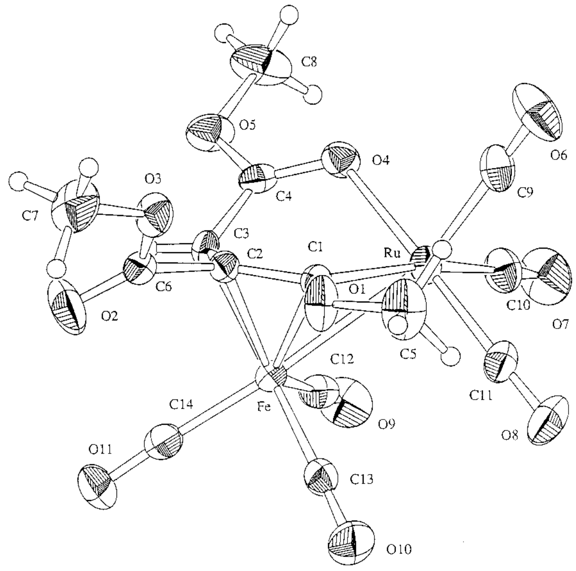


Figure 1. ORTEP view of **7**. Thermal ellipsoids are shown at the 30% probability level.

Table 2. Summary of Crystal Data, Collection Data, and Refinement of 7 and 8

	7	8
Description of Crystal		
color	orange	orange
habit	prismatic	cubic
max cryst dimens (mm)	0.20 × 0.20 × 0.30	0.20 × 0.20 × 0.20
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
Unit Cell Parameters		
a (Å)	11.01(1)	12.983(5)
b (Å)	11.11(1)	13.181(4)
c (Å)	15.066(6)	10.147(2)
α (deg)		94.34(2)
β (deg)	99.53(5)	92.59(2)
γ (deg)		64.06(2)
V (Å^3)	1817(2)	1556.8(9)
Z	4	2
formula	$C_{14}H_{10}O_{11}FeRu$	$C_{31}H_{25}O_{10}PFeRu$
fw	511.14	745.42
D_{calc} (g cm^{-3})	1.868	1.590
Data Collection		
radiation (λ, Å)	Mo $K\alpha$ (0.710 69)	
scan technique	$\omega-2\theta$	
scan width (deg)	1.63 + 0.30 tan θ	1.31 + 0.30 tan θ
$2\theta_{max}$ (deg)	50.0	55.0
no. of rflns measd	2239	7555
Structure Determination		
no. of rflns used ($I > 3\sigma(I)$)	1569	2117
no. of params varied	249	397
data/param ratio	6.30	5.33
goodness of fit	1.54	1.32
R^a	0.023	0.058
$R_w{}^a$	0.029	0.047
highest peak of resid electron density (e Å^{-3})	0.31	0.71

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$.

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Table 3. Selected Bond Lengths and Angles in Complex 7

Bond Lengths (Å)

Fe−Ru	2.694(3)	Ru−O(4)	2.135(3)
Fe−C(1)	2.178(4)	C(1)−C(2)	1.401(6)
Fe−C(2)	2.058(4)	C(2)−C(3)	1.453(6)
Fe−C(3)	2.050(5)	C(3)−C(4)	1.439(7)
Fe−C(12)	1.784(6)	C(4)−O(4)	1.229(5)
Fe−C(13)	1.771(6)	C(9)−O(6)	1.139(6)
Fe−C(14)	1.796(6)	C(10)−O(7)	1.122(6)
Ru−C(1)	2.057(4)	C(11)−O(8)	1.127(5)
Ru−C(9)	1.906(6)	C(12)−O(9)	1.146(5)
Ru−C(10)	1.980(5)	C(13)−O(10)	1.138(6)
Ru−C(11)	1.850(6)	C(14)−O(11)	1.131(6)

Bond Angles (deg)

Ru−Fe−C(1)	48.5(1)	O(4)−Ru−C(10)	86.3(2)
Ru−Fe−C(2)	77.2(1)	O(4)−Ru−C(11)	174.1(2)
Ru−Fe−C(3)	82.3(2)	C(1)−Ru−C(9)	99.5(2)
Ru−Fe−C(12)	80.6(2)	C(1)−Ru−C(10)	162.4(2)
Ru−Fe−C(13)	96.0(2)	C(1)−Ru−C(11)	94.9(2)
Ru−Fe−C(14)	175.1(2)	C(9)−Ru−C(10)	97.4(2)
C(1)−Fe−C(2)	38.5(2)	C(9)−Ru−C(11)	93.7(2)
C(1)−Fe−C(3)	70.9(2)	C(10)−Ru−C(11)	88.9(2)
C(1)−Fe−C(12)	128.8(2)	Ru−O(4)−C(4)	116.9(3)
C(1)−Fe−C(13)	92.7(2)	Ru−C(1)−Fe	78.9(2)
C(1)−Fe−C(14)	129.5(2)	Ru−C(1)−O(1)	129.1(3)
C(2)−Fe−C(3)	41.4(2)	Ru−C(1)−C(2)	119.6(3)
C(2)−Fe−C(12)	138.1(2)	Fe−C(1)−O(1)	125.8(3)
C(2)−Fe−C(13)	118.4(2)	Fe−C(1)−C(2)	66.1(2)
C(2)−Fe−C(14)	99.0(2)	O(1)−C(1)−C(2)	111.3(4)
C(3)−Fe−C(12)	100.8(2)	Fe−C(2)−C(1)	75.4(2)
C(3)−Fe−C(13)	159.7(2)	Fe−C(2)−C(3)	69.0(2)
C(3)−Fe−C(14)	92.8(2)	Fe−C(2)−C(6)	126.9(3)
C(12)−Fe−C(13)	98.8(2)	C(1)−C(2)−C(3)	118.8(4)
C(12)−Fe−C(14)	100.7(2)	C(1)−C(2)−C(6)	125.1(4)
C(13)−Fe−C(14)	88.5(2)	C(3)−C(2)−C(6)	116.1(4)
Fe−Ru−O(4)	85.39(9)	Fe−C(3)−C(2)	69.6(3)
Fe−Ru−C(1)	52.5(1)	Fe−C(3)−C(4)	114.3(4)
Fe−Ru−C(9)	151.7(1)	C(2)−C(3)−C(4)	121.2(4)
Fe−Ru−C(10)	110.2(1)	O(4)−C(4)−O(5)	120.3(4)
Fe−Ru−C(11)	93.1(2)	O(4)−C(4)−C(3)	125.3(4)
O(4)−Ru−C(1)	88.8(2)	O(5)−C(4)−C(3)	114.5(5)
O(4)−Ru−C(9)	90.3(2)		

Table 4. Selected Bond Lengths and Angles in Complex 8

Bond Lengths (Å)

Fe−Ru	2.714(2)	Ru−O(4)	2.128(8)
Fe−C(1)	2.20(1)	C(1)−C(2)	1.43(2)
Fe−C(2)	2.04(1)	C(2)−C(3)	1.46(2)
Fe−C(3)	2.07(1)	C(3)−C(4)	1.44(2)
Fe−C(11)	1.78(2)	C(4)−O(4)	1.24(1)
Fe−C(12)	1.72(2)	C(9)−O(6)	1.17(1)
Fe−C(13)	1.75(2)	C(10)−O(7)	1.12(1)
Ru−C(1)	2.06(1)	C(11)−O(8)	1.15(2)
Ru−C(9)	1.89(1)	C(12)−O(9)	1.16(1)
Ru−C(10)	1.86(1)	C(13)−O(10)	1.17(2)
Ru−P(1)	2.373(4)		

Bond Angles (deg)

Ru−Fe−C(1)	48.1(3)	P(1)−Ru−C(9)	94.5(4)
Ru−Fe−C(2)	77.7(4)	P(1)−Ru−C(10)	100.0(4)
Ru−Fe−C(3)	83.1(3)	O(4)−Ru−C(1)	87.7(4)
Ru−Fe−C(11)	76.7(5)	O(4)−Ru−C(9)	89.7(5)
Ru−Fe−C(12)	96.0(5)	O(4)−Ru−C(10)	173.5(5)
Ru−Fe−C(13)	173.4(6)	C(1)−Ru−C(9)	164.4(5)
C(1)−Fe−C(2)	39.1(4)	C(1)−Ru−C(10)	96.0(5)
C(1)−Fe−C(3)	71.5(5)	C(9)−Ru−C(10)	85.3(6)
C(1)−Fe−C(11)	124.7(6)	Ru−O(4)−C(4)	119.3(9)
C(1)−Fe−C(12)	91.0(6)	Ru−C(1)−Fe	79.2(5)
C(1)−Fe−C(13)	133.6(6)	Ru−C(1)−O(1)	131.5(8)
C(2)−Fe−C(3)	41.5(5)	Ru−C(1)−C(2)	119.5(10)
C(2)−Fe−C(11)	137.4(6)	Fe−C(1)−O(1)	126.8(8)
C(2)−Fe−C(12)	116.1(7)	Fe−C(1)−C(2)	64.4(7)
C(2)−Fe−C(13)	100.9(6)	O(1)−C(1)−C(2)	108(1)
C(3)−Fe−C(11)	101.8(6)	Fe−C(2)−C(1)	76.5(8)
C(3)−Fe−C(12)	157.4(7)	Fe−C(2)−C(3)	70.4(8)
C(3)−Fe−C(13)	91.6(6)	Fe−C(2)−C(6)	126(1)
C(11)−Fe−C(12)	100.0(7)	C(1)−C(2)−C(3)	119(1)
C(11)−Fe−C(13)	100.6(7)	C(1)−C(2)−C(6)	123(1)
C(12)−Fe−C(13)	90.5(7)	C(3)−C(2)−C(6)	116(1)
Fe−Ru−P(1)	151.4(1)	Fe−C(3)−C(2)	68.1(8)
Fe−Ru−O(4)	84.3(2)	Fe−C(3)−C(4)	113.5(9)
Fe−Ru−C(1)	52.7(4)	C(2)−C(3)−C(4)	121(1)
Fe−Ru−C(9)	111.7(4)	O(4)−C(4)−O(5)	120(1)
Fe−Ru−C(10)	93.6(4)	O(4)−C(4)−C(3)	123(1)
P(1)−Ru−O(4)	84.4(2)	O(5)−C(4)−C(3)	115(1)
P(1)−Ru−C(1)	100.6(4)		

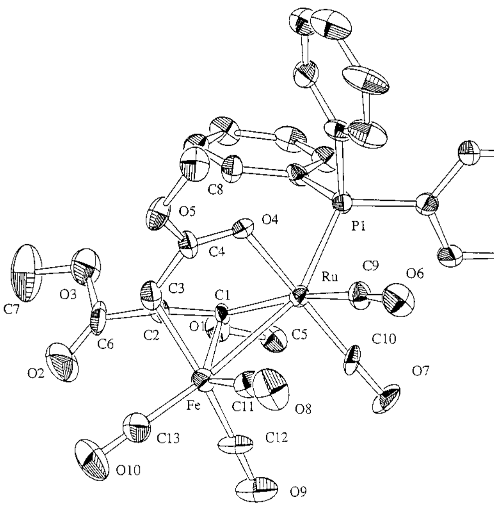
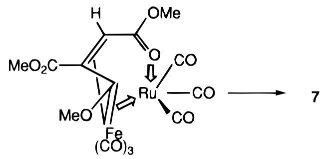


Figure 2. ORTEP view of **8**. Thermal ellipsoids are shown at the 30% probability level.

X-ray Crystal Structure of 8. The molecular geometry and atom-numbering system of **8** are shown in Figure 2, while Tables 2 and 4 summarize the results obtained. The ruthenium has again a distorted octahedral structure; the bond angle Fe−Ru−P(1) was 151.4(1)°. The Fe−Ru length of 2.714(2) Å was reasonably longer than that in **7** (2.694(3) Å). The carbonyl group on the ruthenium *trans* to the iron in **7** (C(9)≡O(6)) was substituted by triphenylphosphine. This trans effect of $Fe(CO)_3$ group was already reported for the reaction of $[Fe(CO)_3SR]_2$ (R = Me, Et) with phosphines.[47]

Mechanism of Formation of 7. The mechanism of formation of **7** would be similar to that of the formation of **6** by the reaction of **5** with $Fe_2(CO)_9$ (eq 7). The



(7)

mononuclear vinylcarbene complex **5** coordinates to the $Ru(CO)_3$ moiety which is generated by the dissociation of 1,5-cyclooctadiene from $Ru(COD)(CO)_3$. The coordination of a metal−carbon double bond to another metal complex has been well examined by Stone.[43]

General Discussion. As for the preparation of the homobinuclear vinylcarbene complex, the following representative methods are reported: (1) reaction of a binuclear carbonyl complex with cyclopropene derivatives;[13] (2) reaction of a binuclear (μ-methylene)M_2 complex with acetylenes;[22] (3) reaction of a (μ-acetylene)M_2 complex with diazomethane;[23] (4) reaction of a mononuclear η^1-vinylcarbene complex with metal carbonyls;[33,36] (5) activation of a C−H bond of an η^3-allyl ligand.[30]

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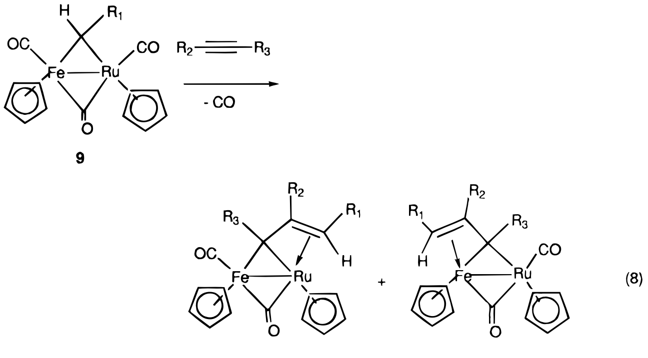
(47) deBeer, J. A.; Haines, R. J.; Greatrex, R; Greenwood, N. N. *J. Chem. Soc. A* **1971**, 3271.

One of the methods for the preparation of a heterobinuclear Fe−Ru vinylcarbene or a η^3:η^1-allylidene complex is the reaction of (μ-methylene)(Fe−Ru) complex (**9**) with acetylenes reported by Knox and co-workers (eq 8).[38] The selectivity of this reaction for **10a** and **10b** depends upon the alkynes and pure **10b** could not be formed by this method.

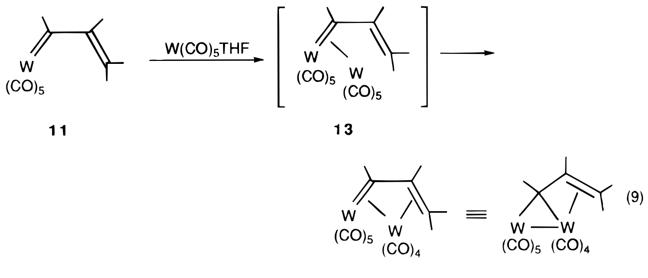


9

(8)

10a **10b**

Reaction of 1-tungstenabutadiene (**11**) with unsaturated M^{2}Ln gives an η^3:η^1-allylidene(M^2−W) complex.[36,41] In this reaction, complex **13** is supposed to be a key intermediate to give **12**.[36] Thus by this method, only a complex of type **2A** is formed (eq 9).



11 **13**

(9)

12

The present results showed that the reaction in eq 4 provides a novel method for the preparation of heterobinuclear vinylcarbene complexes of type **2B**. In this reaction no transmetalated complex **2A** was formed at all. The reaction was selective in contrast to the reaction shown by eq 1. The reaction of **5** with other COD-coordinated complexes such as RuCp*(COD)Cl was attempted and gave a very complicated mixture of several complexes. Preparation of an Fe−Ru binuclear vinylcarbene complex by the reaction of **5** with $Ru_3(CO)_{12}$ was attempted; however, no isolable product was obtained probably because of the unsuccessful generation of a $Ru(CO)_3$ moiety.

In conclusion, the reaction of a (π-vinylcarbene)M^1 complex with M^2 provides a novel method for the selective preparation of **2B**.

Experimental Section

All manipulations were performed under a dry argon atmosphere with standard Schlenk techniques. 1,2-Dichloroethane was distilled from $CaCl_2$; diethyl ether was distilled from benzophenone ketyl; *n*-hexane and benzene were distilled from sodium. The (π-vinylcarbene)iron complex **5**[1] and tricarbonyl(1,5-cyclooctadiene)ruthenium[44] were prepared by the literature method. Other reagents were used as obtained from commercial sources. Melting points were determined under air on a Yanagimoto micro melting point apparatus. Infrared spectra were recorded on a Shimadzu FTIR-8100 spectrometer and calibrated with a polystyrene standard. Elemental analyses were carried out at the Microanalysis Center of Kyoto University. ^{1}H and ^{13}C NMR spectra were obtained on a JEOL GSX-270 or a JEOL EX-400 spectrometer. Spectral data for the products are summarized in Table 1.

Reaction of 5 with Tricarbonyl(1,5-cyclooctadiene)ruthenium. To a solution of **5** (1.81 g, 5.56 mmol) in benzene (15 mL) was added a benzene solution (10 mL) of tricarbonyl(1,5-cyclooctadiene)ruthenium (2.01 g, 6.87 mmol) slowly at 0 °C, and then the mixture was stirred at room temperature for 8 h. After the solvent was evaporated in vacuo, the residue was extracted with 1,2-dichloroethane (10 mL), and the extract was chromatographed on silica gel (eluent, *n*-hexane and then benzene). A yellow orange band with benzene eluent was collected. Crystallization of the orange oil from diethyl ether at −78 °C gave orange crystals of a heterobinuclear μ-vinylcarbene complex **7** (2.22 g, 4.35 mmol, 78%).

7: Orange crystals, mp 108.0−110.0 °C. Anal. Calcd for $C_{14}H_{10}O_{11}FeRu$: C, 32.90; H, 1.97. Found: C, 33.08; H, 2.06.

Reaction of 7 with Triphenylphosphine. The heterobinuclear μ-vinylcarbene complex **7** (0.083 g, 0.16 mmol) and triphenylphosphine (0.045 g, 0.17 mmol) were dissolved in 1,2-dichloroethane (4 mL) at room temperature, and the mixture was stirred for 4 h. After the solvent was evaporated in vacuo, recrystallization of the residue from a mixture of diethyl ether and 1,2-dichloroethane (3:1) at −78 °C gave orange crystals of **8** (0.062 g, 0.084 mmol, 52%).

8: Orange crystals, mp 118.5−120.5 °C (dec). Anal. Calcd for $C_{31}H_{25}O_{10}PFeRu$: C, 49.95; H, 3.38. Found: C, 49.42; H, 3.35.

X-ray Structure Determinations of 7 and 8. The crystal data and experimental details for **7** and **8** are summarized in Table 1. Diffraction data were obtained with a Rigaku AFC-7R. The reflection intensities were monitored by three standard reflections at every 150 mesurements. No decay correction was applied. Reflection data were corrected for Lorentz and polarization effects. Azimuthal scans of several reflections indicated no need for an absorption correction.

The structures were solved by direct methods using SHELX86[48] and refined anisotropically for non-hydrogen atoms by full-matrix least-squares calculations. Atomic scattering factors and anomalous dispersion terms were taken from the literature.[49] No hydrogen atoms were refined except for one hydrogen on C(3) of **7**, which was refined isotropically. The final R and R_w values were 0.023 and 0.029 for **7** and 0.058 and 0.047 for **8**, respectively. The calculations were performed on an IRIS Indigo computer by using the program system teXsan.[50]

The final atomic parameters for non-hydrogen atoms for **7** and **8** are given in the Supporting Information, and selected bond lengths and angles are summarized in Tables 3 and 4, respectively.

Supporting Information Available: Text describing X-ray procedures, tables of X-ray data, positional and thermal parameters, and bond distances and angles, and an ORTEP diagram (45 pages). Ordering information is given on any current masthead page.

OM960904M

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(48) SHELX86: Sheldrick, G. M. *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Oxford University Press: Oxford, U.K., 1985; pp 175−189.

(49) (a) Cromer, D. T.; Waber, G. T. *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, U.K., 1974; Vol. IV. (b) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781. (c) Creagh, D. C.; McAuley, W. J. *International Tables for X-Ray Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Boston, MA, 1992; Vol. C. (d) Creagh, D. C., Hubbell, J. H. *International Tables for X-Ray Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Boston, MA, 1992; Vol. C.

(50) teXsan: Crystal Structure Analysis Package, Molecular Structure Corp., 1985, 1992.