Reaction of (1–3-η-Vinylcarbene)iron Complexes with Enneacarbonyldiiron. Formation of a (Ferracyclopentadiene)iron(*Fe–Fe*) Complex and a Vinylcarbenediiron(*Fe–Fe*) Complex

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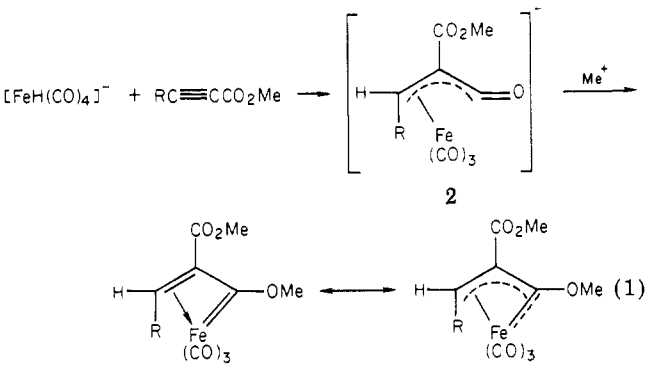
Tricarbonyl[1–3-η-1-methoxy-2-(methoxycarbonyl)prop-2-en-1-ylidene]iron (**1a**) reacts with enneacarbonyldiiron in diethyl ether at 25 °C for 2 h to give a "ferrole" derivative, tricarbonyl[2–5-η-1,1,1-tricarbonyl-5-hydroxy-2-methoxy-3-(methoxycarbonyl)ferracyclopenta-2,4-diene]iron(*Fe–Fe*) (**3**). Methylation of **3** with diazomethane gives a methoxy derivative of **3**, tricarbonyl[2–5-η-1,1,1-tricarbonyl-2,5-dimethoxy-3-(methoxycarbonyl)ferracyclopenta-2,4-diene]iron(*Fe–Fe*) (**4**). Tricarbonyl[1–3-η-*trans*-1-methoxy-2,3-bis(methoxycarbonyl)prop-2-en-1-ylidene]iron (**1b**) reacts with enneacarbonyldiiron in diethyl ether at 35 °C for 1.5 h to give hexacarbonyl-μ-[1-η^1-*anti*,2-bis(methoxycarbonyl)-3-*syn*-methoxy-η^3:η^1-allyl]-diiron(*Fe–Fe*) (**5**) by the coordination of the vinylcarbene moiety to two iron atoms: therefore **5** is regarded as a vinylcarbene dinuclear complex. The structure of **5** was determined by single-crystal X-ray diffraction study.

Since the first preparation of a transition-metal–carbene complex by E. O. Fischer in 1964,[1] much attention has been focused on the reactivities of the carbene–metal double bond especially concerning the active species in the catalytic organic reactions such as metatheses of olefins[2] or Fischer–Tropsch synthesis.[3] On the other hand, reactions of acetylenes with transition-metal complexes have led to carbene complexes[4] as well as to various organic syntheses.[5] Recently, the first (η^3-vinylcarbene)tricarbonyliron complexes, **1a** and **1b**, in which the adjacent carbene and olefin



are coordinated to one metal have been prepared by methylation of (1–3-η-acryloyl)tricarbonylferrates (**2**) derived from the reaction of acetylenes with hydridotetracarbonylferrate.[6] The highly distorted molecular structure of **1b** was revealed by X-ray analysis.[7] Complexes **1a** and **1b** are highly reactive to nucleophilic reagents such as carbon monoxide or tertiary phosphines, isocyanides, and diazomethane affording (η^4-vinylketene)-,[8] (η^4-vinylketenimine)-,[9] and (η^4-butadiene)-tricarbonyliron[10] derivatives, respectively.

Scheme I

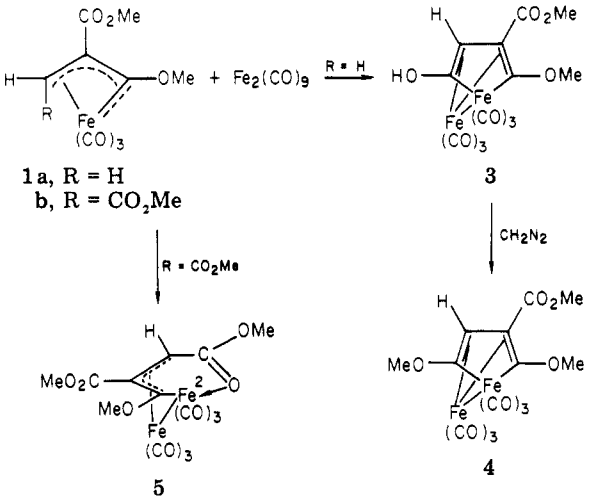


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Table I. Infrared Spectral Data (cm^{-1}, KBr)[a]

complex	carbonyl bands: metal carbonyl			carbonyl bands: ester	other bands
3	2075 s	2040 s	1990 s,br	1705 s	3250 br, ν(O-H)
4	2077 s 1987 s	2040 s	1998 s	1735 s	
5	2078 m 1995 m	2035 s 1975 s,br	2006 s	1721 m 1601 m, ν(C=O→Fe)	

[a] s = strong, m = medium, br = broad.

Table II. Hydrogen NMR Spectral Data (δ Relative to $SiMe_4$, J (Hz))[a]

complex	olefinic proton (s, 1 H)	CO_2Me (s, 3 H)	COMe (s, 3 H)	others
3[b]	5.36	3.96	3.78	5.98 (s, 1 H, OH)
4[c]	5.35	3.99	3.68 3.81	
5[b]	3.03	3.50 3.83	4.07	

[a] s = singlet, recorded at 100 MHz. [b] Solvent: CD_2Cl_2. [c] Solvent: $CDCl_3$.

This paper deals with the reaction of the η^3-vinylcarbene complexes **1a** and **1b** with enneacarbonyldiiron. The products depend upon the kinds of starting η^3-vinylcarbene complexes; a "ferrole" derivative (**3**) and an (η^3:η^1-allyl)-diiron(*Fe–Fe*) complex (**5**) were obtained in the reaction of **1a** and **1b**, respectively.

These results would shed some light on the mechanism of the formation of the "ferrole" complex by the reaction of acetylene with alkali $Fe(CO)_5$ and that of the formation of a methylene species bridged on binuclear metals from a mononuclear carbene–metal species.

Results and Discussion

Reaction of 1a with Enneacarbonyldiiron. Tricarbonyl[1-3-η-1-methoxy-2-(methoxycarbonyl)prop-2-en-1-ylidene]iron (**1a**) readily reacted with enneacarbonyldiiron in diethyl ether at 25 °C for 2 h under an argon atmosphere to give yellow crystals of **3** in 51% yield. Complex **3** is diamagnetic and stable in air for several hours. Analytical data and IR and ^1H and ^{13}C NMR spectral data of **3** are summarized in Tables I–IV. On the basis of the molecular weight, the analytical and spectral data, and its reactivity (see below), **3** has been deduced to be tricarbonyl[2-5-η-1,1,1-tricarbonyl-5-hydroxy-2-methoxy-3-(methoxycarbonyl)ferracyclopenta-2,4-diene]iron-(*Fe–Fe*) (Scheme I).

The analytical data of **3** and the molecular weight of **4** which was derived by the methylation of acidic hydroxy group in **3** (see below) with diazomethane show that **3** is a 1:1 adduct of **1a** and a "$Fe(CO)_4$" moiety. The IR spectrum of **3** (Table I) showed three strong absorptions of terminal ν(C≡O) at 2075, 2040, and 1990 (br) cm^{-1} and ester ν(C=O) at 1705 cm^{-1} as well as ν(OH) at 3250 (br) cm^{-1}. The ^1H NMR spectrum of **3** (Table II) exhibited, in addition to signals for two OMe, a signal for the olefinic proton at δ 5.36 and a hydroxylic proton at δ 5.98 which disappeared on addition of D_2O. The ^{13}C NMR spectrum of **3** (Table III) showed four resonances characteristic of a ferracyclopentadiene ring at δ 78.3 (d, J(CH) = 162 Hz, C^3 (see Table III)), 85.3 (s, C^2), 221.3, and 227.6 (s, C^1 or C^4).[11]

Table III. Carbon-13 NMR Spectral Data (δ, $SiMe_4$ Internal Reference, J(^{13}C-H) (Hz))[a]

complex	C^1[f]	C^2	C^3	C^4	CO_2Me	COMe	CO_2Me	FeC≡O
3[b]	211.7[e]	85.3 (s)	78.3 (d, 162)	214.5[e]	53.0 (q, 148)	64.8 (q, 146)	168.0 (s)	210.6 (s) 211.4 (s) 211.7 (s)
4[c]	227.6 (br)	81.9 (s)	74.0 (d, 170)	221.3	52.2 (q, 148)	58.9 (q, 147) 64.3 (q, 147)	166.2 (s)	208.6 (s) 209.2 (s) 209.3 (s) 209.6 (s)
5[c]	38.4 (d, 162)	82.0 (s)	221.2 (s)		52.7 (q, 147) 54.6 (q, 149)	63.2 (q, 145)	168.8 (s) 186.3 (s)	205.1 (s)[d] 209.6 (s) 211.4 (s)

[a] At 24.0 °C. s = singlet, d = doublet, q = quartet, br = broad. [b] Solvent: MeOH-d_4. [c] Solvent: $CDCl_3$. [d] Measured at 46 °C. The temperature dependence of Fe(C≡O) is shown in Figure 1. [e] Signals of C^1 and C^4 were tentatively assigned.

[f]

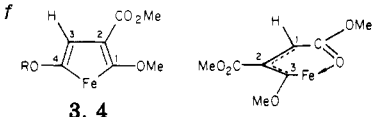

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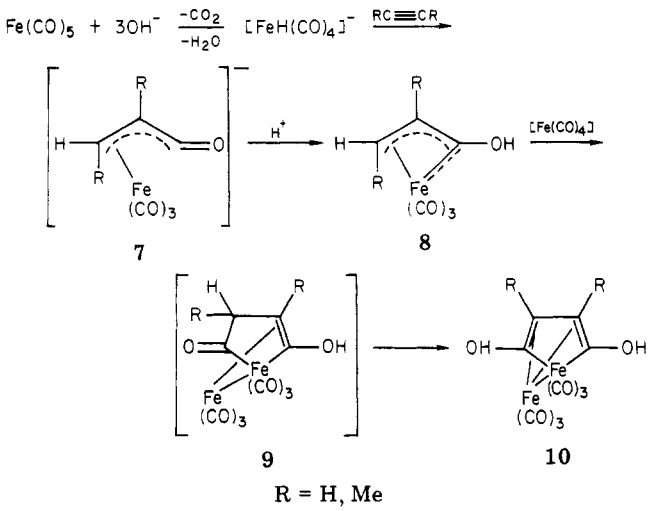
Table IV. Analytical Data

complex	yield, %	color	mol wt[a] (calcd)	Mp, θ_c/°C	% C calcd	% C found	% H calcd	% H found
3	51	yellow		144	35.81	35.63	1.84	1.66
4	64	orange	405 (450)	82	37.38	37.62	2.24	2.41
5	78	red	468 (466)	91 (dec)	36.09	36.10	2.16	2.48

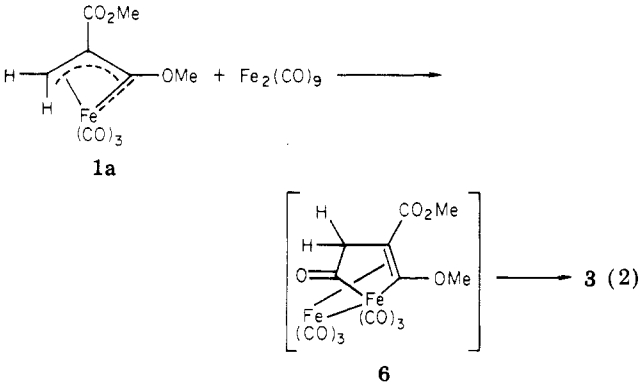
[a] Cryoscopic in benzene.

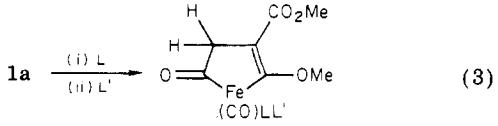
Scheme II



Treatment of **3** with diazomethane in diethyl ether under nitrogen at room temperature gave orange crystals of **4** in 64% yield. Following observations show that **4** is tricarbonyl[2-5-η-1,1,1-tricarbonyl-2,5-dimethoxy-3-(methoxycarbonyl)ferracyclopenta-2,4-diene]iron(*Fe–Fe*) derived from the methylation of the hydroxyl group in **3** by diazomethane. (i) In the IR spectrum of **4**, the absorption of ν(OH) at 3250 cm^{-1} in **3** disappeared. (ii) In the ^{1}H NMR spectrum of **4**, the signal for the hydroxyl proton in **3** disappeared and a new signal for a methoxy group appeared at δ 3.81 in addition to those for the two methoxy groups. (iii) The ^{13}C NMR spectrum of **4** also exhibited the signal of the introduced methoxy carbon at δ 58.9 (q, J(CH) = 147 Hz) in addition to those of the ferracyclopentadiene ring.

The formation of **3** by the reaction of **1a** with $Fe_2(CO)_9$ may be rationalized as follows. The attack of the "Fe(CO)$_4$" moiety on **1a** would induce the insertion of a carbon monoxide into methylene carbon–iron bond of **1a** to give an intermediate, **6**, (2-3-η-ferracyclopentenone)tricarbonyliron(*Fe–Fe*). The keto–enol isomerization would give the product **3** (eq 2). Analogous formation of a ferracyclopentenone complex by the insertion of a carbon monoxide into a methylene–iron bond in **1a** has been observed in the reaction of **1a** with tertiary phosphines and/or carbon monoxide (L or L′) (eq 3).[8,12]





(3)

On the other hand, the ferrole complex **10** (Scheme II) similar to **3** was prepared by the reaction of acetylene with alkali solution of $Fe(CO)_5$[13] and the structure of which was determined by X-ray diffraction.[14] However, the mechanism of the formation of **10** has never been revealed. Taking into account that **1a** is prepared by the methylation of **2** derived from the reaction of the acetylene with [FeH(CO)$_4$]$^-$ (eq 1), the present result strongly suggests that the mechanism for the formation of **10** is as follows. Acetylene first reacts with [FeH(CO)$_4$]$^-$ derived from the reaction of alkali with $Fe(CO)_5$ to give (η^3-acryloyl)ferrate (**7**), protonation of which by the protic solvents may give an η^3-vinylhydroxycarbene complex **8**. It is reasonable to explain that **8** then reacts with "Fe(CO)$_4$" which exists in the reaction solution[15] to give the ferrole complex **10** via **9** in a manner similar to **3** being formed from **1a**. Alternatively, it is strongly suggested that this duplicate carbonylation of acetylene affording **10** would proceed via an η^3-vinylcarbene complex.

Reaction of 1b with Enneacarbonyldiiron. Tricarbonyl[1-3-η-*trans*-1-methoxy-2,3-bis(methoxycarbonyl)prop-2-en-1-ylidene]iron (**1b**) reacted with $Fe_2(CO)_9$ in diethyl ether at 35 °C under an argon atmosphere to give red crystals of **5** in 78% yield. Complex **5** is diamagnetic and stable in air for several hours. The structure of **5** was determined by X-ray analysis (see below) to be hexacarbonyl-μ-[1-η^1-*anti*,2-bis(methoxycarbonyl)-3-*syn*-methoxy-η^3:η^1-allyl]-diiron(*Fe–Fe*) (Scheme I) which was fully consistent with the analytical and spectral data. The IR spectrum of **5** (Table I) showed five strong terminal ν(C≡O) absorptions in the 1975–2075-cm^{-1} region in addition to those of ester ν(C=O) at 1721 cm^{-1} and ester ν(C=O) coordinated to iron atom at 1601 cm^{-1}.[16] The ^{1}H NMR spectrum of **5** (Table II) showed a signal of an olefinic proton at a high field [δ 3.03 (s)] in addition to those of the methoxy groups. The ^{13}C NMR spectrum of **5** exhibited the resonances of two olefinic carbons at δ 38.4 (d, J(CH) = 162 Hz) and 82.0 (s), and a singlet at δ 221.4 was assigned to C^3 (see footnotes in Table III) since this signal appears at too low of a field for a carbonyl carbon.[17] The signal shifted to higher field by about 50 ppm compared with that of the carbene carbon in **1b**, which would be due to the bond formation between C^3 and Fe^2. The spectrum also exhibited the signals for two ester carbonyl carbons at δ 168.8 and 186.3, the latter signal showing the coordination of the carbonyl group to the iron atom.[18] The variable-temperature ^{13}C NMR spectrum of **5** showed a temperature dependence in the terminal carbonyl region, results of which are shown in Figure 1. Seven resonances appeared in the δ 200–220 region at −68 °C, which can be assigned to six terminal carbonyls and a carbene carbon. Three signals at δ 206.9 (signal f in Figure 1), 207.3 (signal e), and 219.5 (signal b) at −68 °C showed a marked temperature dependence and the peaks coalesced at 46 °C (δ

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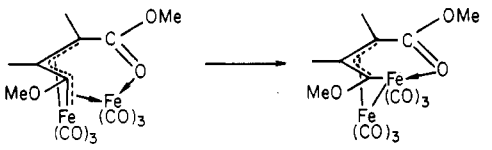
211.3). The other peaks, although two of them (signals c and d) overlapped with increasing the temperature, essentially did not show a significant temperature dependence. These observations show that one of the $Fe(CO)_3$ groups is fluxional near room temperature and the other is not. Probably the $Fe^1(CO)_3$ group coordinated by a π-allyl group would be fluxional.[19]

Comparing the structure of **5** with that of **1b**, the formation of **5** could be explained by the "coordination" of complex **1b** to the $Fe(CO)_3$ moiety as a bidentate ligand through the carbene–iron double bond and the ester group to form an (η^3:η^1-allyl)diiron(*Fe–Fe*) system (eq 4). Al-



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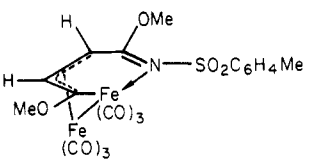
though several (η^3:η^1-allyl)dimetal(*M–M*) complexes such as **11–15** similar to **5** have been reported,[20-27] **5** is is the first



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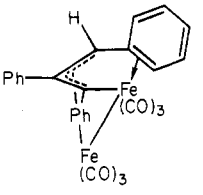

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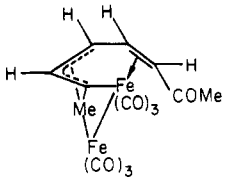

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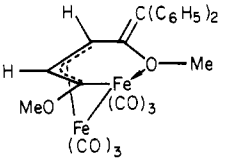

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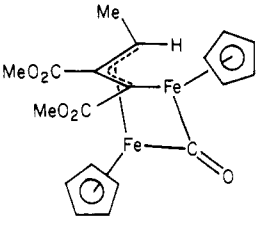

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example derived from a mononuclear carbene complex, and it should be noted that these complexes can be regarded as those which stabilize a vinylcarbene ligand on two metal atoms.

As described above, the reactions of $Fe_2(CO)_9$ with **1a** and **1b** gave **3** and **5**, respectively. This difference is due to whether the η^3-vinylcarbene ligand has a methoxycarbonyl group at the "anti" position or not. An η^3-

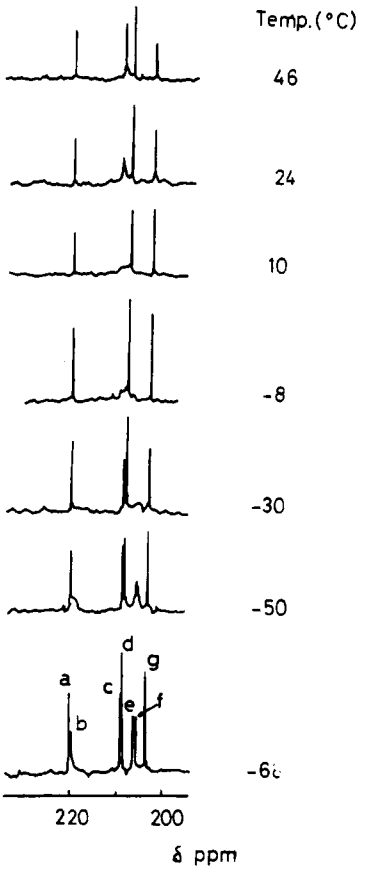

Figure 1. Variable-temperature ^{13}C NMR spectra of terminal carbonyl carbons and a carbene carbon of **5** in $CDCl_3$ solution.

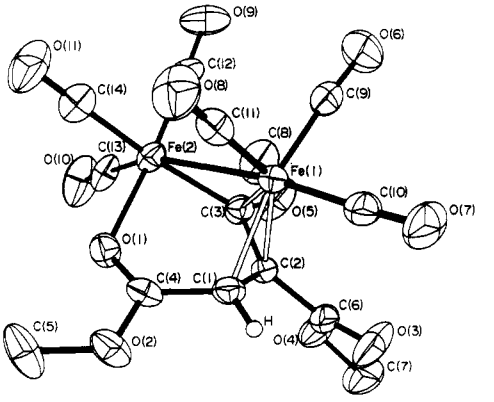

Figure 2. The molecular structure of complex **5**, hexacarbonyl-μ-[1-η^1-*anti*-2-(dimethoxycarbonyl)-3-*syn*-methoxy-η^3:η^1-allyl]-diiron(*Fe–Fe*) viewed perpendicular to the plane defined by the Fe(1), C(1), and C(4) atoms. Thermal ellipsoids enclose at 40% probability except that of H[C(1)], which is drawn by a sphere of an arbitrary radius.

vinylcarbene complex which can "coordinate" to a "$Fe(CO)_3$" moiety as a bidentate chelate ligand such as **1b** gives a binuclear vinylcarbene complex such as **5**, otherwise the insertion of carbon monoxide into the carbene carbon–iron bond is induced, affording **3**.

Recently, Weiss et al. reported the preparation of an (η^3:η^1-allyl)diiron complex (**12**) related to **5** in a yield of 6% together with a η^4-vinylketene complex (**17**) in the reaction of cyclopropene derivatives (**16**) with excess enneacarbonyldiiron, and the structure of **12** was determined.[21] Although Weiss did not mention the mechanism of the formation of **12**, the present results would explain the reaction mechanism as follows. First, a vinylcarbene species derived from the fission of the carbon–carbon bond

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(27) Johnson, B. F. G.; Kelland, J. M.; Lewis, J.; Mann, A. L.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1980**, 547.

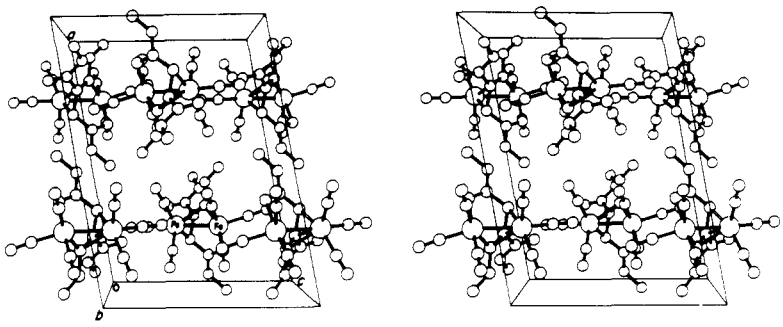
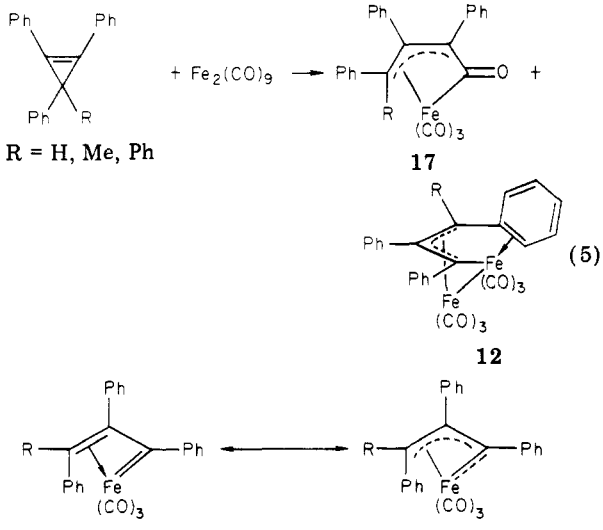


Figure 3. A stereoscopic drawing of the crystal structure of complex **5**, hexacarbonyl-μ-[1-η^1-*anti*-2-(dimethoxycarbonyl)-3-*syn*-methoxy-η^3:η^1-allyl]-diiron(*Fe–Fe*), viewed along the *b* axis.

Table V. Final Atomic Coordinates ($\times 10^4$; $\times 10^3$ for H) for Complex **5** ($(C_8H_{10}O_5)Fe_2(CO)_6$) with Esds in Parentheses

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Fe(1)	2451.3 (4)	3078.6 (5)	4049.6 (5)	C(7)	4276 (4)	−1149 (4)	5594 (5)
Fe(2)	2473.8 (4)	3918.5 (5)	6288.0 (5)	C(8)	4703 (3)	3101 (5)	6915 (5)
O(1)	1446 (2)	2751 (2)	6396 (2)	C(9)	3358 (3)	3979 (4)	3689 (4)
O(2)	426 (2)	1473 (3)	5376 (2)	C(10)	2371 (3)	2343 (4)	2578 (4)
O(3)	3071 (3)	−66 (3)	3857 (3)	C(11)	1537 (3)	4162 (4)	3670 (3)
O(4)	3825 (2)	−5 (2)	5779 (3)	C(12)	3248 (3)	5060 (4)	6078 (4)
O(5)	4121 (2)	2429 (3)	6085 (3)	C(13)	2834 (3)	3842 (4)	7931 (4)
O(6)	3942 (2)	4511 (3)	3414 (3)	C(14)	1606 (3)	5136 (4)	6194 (4)
O(7)	2335 (2)	1929 (3)	1632 (3)	H[C1]	157 (2)	104 (3)	416 (3)
O(8)	949 (2)	4810 (3)	3384 (3)	H[C5]	−67 (3)	147 (4)	590 (4)
O(9)	3743 (2)	5835 (3)	5953 (3)	H′[C5]	−29 (3)	266 (4)	606 (4)
O(10)	3082 (2)	3799 (4)	8957 (3)	H″[C5]	10 (3)	162 (4)	702 (3)
O(11)	1084 (2)	5890 (3)	6131 (3)	H[C7]	446 (3)	−109 (4)	487 (4)
C(1)	1811 (3)	1629 (3)	4714 (3)	H′[C7]	477 (3)	−122 (5)	625 (4)
C(2)	2780 (2)	1577 (3)	5151 (3)	H″[C7]	386 (3)	−172 (4)	553 (4)
C(3)	3209 (2)	2583 (3)	5809 (3)	H[C8]	453 (3)	327 (4)	756 (4)
C(4)	1231 (2)	2008 (3)	5554 (3)	H′[C8]	522 (3)	273 (4)	702 (4)
C(5)	−185 (3)	1840 (5)	6185 (4)	H″[C8]	473 (4)	379 (6)	655 (5)
C(6)	3250 (3)	423 (4)	4832 (3)				

of the cyclopropene derivatives is trapped by the "Fe(CO)$_3$" moiety to give an unstable intermediate, the η^3-vinylcarbene complex **18**. Then the insertion of carbon monoxide gives **17**,[8] and the "coordination" of **18** through the carbon–iron double bond and a phenyl group to another "Fe(CO)$_3$" may give **12** (eq 5).



16, R = H, Me, Ph

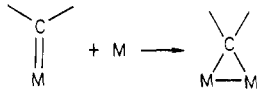
17

(5)

12

18

Although both (η^1-carbene)M (M = metal) (**19**) and μ-carbene-M$_2$ species (**20**) are regarded to be the possible active species in Fischer–Tropsch reaction,[28] the possibility that **20** is formed from **19** has not yet been pointed out. The present reaction could be considered to be the model reaction that **20** is formed from **19**, suggesting the presence of such a process on the surface of heterogeneous catalysts (eq 6).



(6)

19 20

X-ray Molecular Structure of 5. The molecular geometry and atom-numbering system are shown in Figure 2 and the crystal packing arrangement in Figure 3, while Tables V and VI summarise the results obtained. These results demonstrated that **5** is an (η^3:η^1-allyl)diiron(*Fe–Fe*) complex in which Fe(1) is coordinated by a 1–3-η-allyl [C(1), C(2), and C(3)] system and Fe(2) is σ bonded with C(3) and coordinated by the ester group. The coordinations about Fe(1) and Fe(2) were both a highly distorted octahedron as has been reported in other (η^3:η^1-allyl)diiron complexes.[20,23] Several (η^3:η^1-allyl)diiron(*Fe–Fe*) complexes such as **11**,[20] **12**,[21] **13**,[22] **14**,[23] and **15**,[24] as well as a dimolybdenum,[25] a dicobalt,[26] and a tetraosmium[27] complex have been reported. To compare the geometry of **5** with those of **11–15**, the bond distances and angles were summarized in Table VII. The Fe(1)–Fe(2) (2.638 Å), Fe(2)–C(3) (1.957 Å), C(2)–C(3) (1.405 Å), and C(1)–C(2) (1.448 Å) lengths in **5** are within the normal range in comparison with those of **11–15**. The Fe(1)–C(3) length of 2.140 Å belongs to the longer region (1.969–2.138 Å in **11–15**). On the other hand, the Fe(1)–C(2) bond (2.047 Å) is rather short as found in **15** (2.042 Å), and the Fe(1)–C(1) length of 2.054 Å is also shorter than those in **11–15** (2.081–2.116 Å). The longer Fe(1)–C(3) length may be due to the substituent effect of the methoxy group attached to C(3) which increases the electron density on C(3) to cause reduced back-donation of electrons from

(28) E.g., Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479.

Table VI. Bond Lengths (Å) and Angles (Deg)

(A) Bond Lengths in Complex 5 ($(C_8H_{10}O_5)Fe_2(CO)_6$)

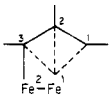
Fe(1)-Fe(2)	2.638 (1)	O(2)-C(5)	1.450 (6)	C(1)-C(4)	1.445 (5)
Fe(1)-C(1)	2.054 (4)	O(3)-C(6)	1.191 (5)	C(1)-H[C1]	0.91 (3)
Fe(1)-C(2)	2.047 (3)	O(4)-C(6)	1.316 (4)	C(2)-C(3)	1.405 (5)
Fe(1)-C(3)	2.140 (3)	O(4)-C(7)	1.451 (6)	C(2)-C(6)	1.515 (5)
Fe(1)-C(9)	1.780 (4)	O(5)-C(3)	1.357 (4)	C(5)-H1C5	0.842 (38)
Fe(1)-C(10)	1.801 (4)	O(5)-C(8)	1.361 (6)	C(5)-H2C5	0.913 (47)
Fe(1)-C(11)	1.801 (4)	O(6)-C(9)	1.137 (6)	C(5)-H3C5	0.973 (36)
Fe(2)-O(1)	2.019 (3)	O(7)-C(10)	1.133 (5)	C(7)-H1C7	0.893 (46)
Fe(2)-C(3)	1.957 (4)	O(8)-C(11)	1.129 (5)	C(7)-H2C7	0.941 (43)
Fe(2)-C(12)	1.747 (4)	O(9)-C(12)	1.149 (5)	C(7)-H3C7	0.881 (44)
Fe(2)-C(13)	1.804 (4)	O(10)-C(13)	1.131 (5)	C(8)-H1C8	0.826 (50)
Fe(2)-C(14)	1.849 (4)	O(11)-C(14)	1.129 (6)	C(8)-H2C8	0.857 (44)
O(1)-C(4)	1.233 (4)	C(1)-C(2)	1.448 (5)	C(8)-H3C8	0.856 (60)
O(2)-C(4)	1.323 (4)				

(B) Bond Angles in Complex 5 ($(C_8H_{10}O_5)Fe_2(CO)_6$)

Fe(2)-Fe(1)-C(1)	81.8 (1)	Fe(1)-Fe(2)-C(13)	152.0 (1)	Fe(1)-C(2)-C(3)	74.0 (2)
Fe(2)-Fe(1)-C(2)	75.9 (1)	Fe(1)-Fe(2)-C(14)	107.9 (1)	Fe(1)-C(2)-C(6)	126.6 (3)
Fe(2)-Fe(1)-C(3)	46.9 (1)	O(1)-Fe(2)-C(3)	91.2 (1)	C(1)-C(2)-C(3)	118.7 (3)
Fe(2)-Fe(1)-C(9)	98.0 (1)	O(1)-Fe(2)-C(12)	172.1 (1)	C(1)-C(2)-C(6)	115.9 (3)
Fe(2)-Fe(1)-C(10)	173.1 (1)	O(1)-Fe(2)-C(13)	90.2 (2)	C(3)-C(2)-C(6)	125.4 (3)
Fe(2)-Fe(1)-C(11)	82.6 (1)	O(1)-Fe(2)-C(14)	85.3 (2)	Fe(1)-C(3)-Fe(2)	80.0 (1)
C(1)-Fe(1)-C(2)	41.4 (1)	C(3)-Fe(2)-C(12)	94.1 (2)	Fe(1)-C(3)-O(5)	125.6 (3)
C(1)-Fe(1)-C(3)	71.6 (1)	C(3)-Fe(2)-C(13)	99.1 (2)	Fe(1)-C(3)-C(2)	66.9 (2)
C(1)-Fe(1)-C(9)	158.5 (2)	C(3)-Fe(2)-C(14)	160.8 (2)	Fe(2)-C(3)-O(5)	128.7 (3)
C(1)-Fe(1)-C(10)	91.3 (2)	C(12)-Fe(2)-C(13)	94.8 (2)	Fe(2)-C(3)-C(2)	119.6 (3)
C(1)-Fe(1)-C(11)	101.6 (2)	C(12)-Fe(2)-C(14)	87.8 (2)	O(5)-C(3)-C(2)	111.6 (3)
C(2)-Fe(1)-C(3)	39.1 (1)	C(13)-Fe(2)-C(14)	99.7 (2)	O(1)-C(4)-O(2)	120.6 (3)
C(2)-Fe(1)-C(9)	117.6 (2)	Fe(2)-O(1)-C(4)	117.9 (2)	O(1)-C(4)-C(1)	124.6 (3)
C(2)-Fe(1)-C(10)	98.8 (2)	C(4)-O(2)-C(5)	116.6 (3)	O(2)-C(4)-C(1)	114.7 (3)
C(2)-Fe(1)-C(11)	138.9 (2)	C(6)-O(4)-C(7)	116.5 (3)	O(3)-C(6)-O(4)	124.9 (4)
C(3)-Fe(1)-C(9)	92.4 (2)	C(3)-O(5)-C(8)	125.7 (4)	O(3)-C(6)-C(2)	123.1 (3)
C(3)-Fe(1)-C(10)	130.5 (2)	Fe(1)-C(1)-C(2)	69.1 (2)	O(4)-C(6)-C(2)	111.9 (3)
C(3)-Fe(1)-C(11)	129.4 (2)	Fe(1)-C(1)-C(4)	112.8 (2)	Fe(1)-C(9)-O(6)	176.5 (4)
C(9)-Fe(1)-C(10)	88.3 (2)	Fe(1)-C(1)-H[C1]	117 (2)	Fe(1)-C(10)-O(7)	176.8 (4)
C(9)-Fe(1)-C(11)	99.6 (2)	C(2)-C(1)-C(4)	118.8 (3)	Fe(1)-C(11)-O(8)	176.8 (3)
C(10)-Fe(1)-C(11)	99.1 (2)	C(2)-C(1)-H[C1]	116 (2)	Fe(2)-C(12)-O(9)	178.1 (4)
Fe(1)-Fe(2)-O(1)	87.6 (1)	C(4)-C(1)-H[C1]	115 (2)	Fe(2)-C(14)-O(10)	178.2 (4)
Fe(1)-Fe(2)-C(3)	53.0 (1)	Fe(1)-C(2)-C(1)	69.6 (2)	Fe(2)-C(14)-O(11)	179.0 (4)
Fe(1)-Fe(2)-C(12)	91.0 (1)				

Table VII. Representative Bond Lengths and Angles of Complex 5 and 11-15[a,b]

complex	Fe^1-Fe^2	Fe^2-C_3	C_2-C_3	C_1-C_2	Fe^1-C_3	Fe^1-C_2	Fe^1-C_1	$\angle C_1C_2C_3$	ref
5	2.638	1.957	1.405	1.448	2.140	2.047	2.054	118.7	this work
11	2.636	1.909	1.469	1.447	2.138	2.077	2.116	116	18
12	2.602	1.997	1.414	1.442	2.080	2.079	2.084	112.9	19
13	2.642	2.002	1.404	1.413	2.088	2.078	2.081	115.4	20
14	2.62	1.94	1.38	1.44	2.09	2.07	2.09	118	21
15	2.540	1.968	1.457	1.433	1.969	2.042	2.111	119.3	22

[a] 

[b] Lengths in angstroms and angles in degrees.

Fe(1) to C(3). The shorter Fe(1)–C(2) and Fe(1)–C(1) lengths could be explained by the enhanced back-donation due to the electron withdrawing methoxycarbonyl groups at C(2) and C(1).

Considering the substituent effects, Table VII shows that complex **5** is regarded to be an analogue of **11–15**. Alternatively, all these complexes consist of a substituted vinylcarbene ligand and the binuclear iron carbonyl. Generally, (η^3:η^1-allyl)dimetal(*M–M*) would be the most stable form of a vinylcarbene–dinuclear metal system.

Experimental Section

All of experimentals were performed in an atmosphere of argon. Infrared spectra were recorded on a JASCO A-302 grating spectrometer, ^1H NMR spectra on a JEOL JNM-FX-100 spectrometer, and ^{13}C NMR spectra on a JEOL JNM-FX-100 spectrometer at 25.05 MHz. Molecular weights were determined by cryoscopy in benzene. Solvents were dried by published techniques and were distilled in an atmosphere of argon before use. Tricarbonyl(1-3-η-vinylcarbene)iron complexes (**1a,b**),[6] enneacarbonyldiiron,[29] diazomethane[30] were prepared by the methods described in the literature.

Reaction of 1a with $Fe_2(CO)_9$. To a solution of **1a** (0.80 g, 3 mmol) in diethyl ether (40 cm^3) was added $Fe_2(CO)_9$ (1.09 g, 3 mmol), and the solution was stirred for 2 h at 25 °C. The solution was filtered, and the filtrate was distilled off in vacuo. The residual solid was dissolved in the mixture of methylene dichloride–chloroform (1:1). The solution was concentrated to ca. 5 cm^3 and cooled on dry ice for 12 h to give yellow crystals of **3** (0.67 g, 51%).

Methylation of (3) with Diazomethane. Into the solution of **3** (0.22 g, 0.5 mmol) in dry diethyl ether was bubbled excess

(29) King, R. B. "Organometallic Syntheses"; Academic Press: New York, 1965; Vol. 1, p 92.

(30) Boer, T. J.; Backer, H. J. "Organic Syntheses"; Wiley: New York, 1963; Coll. Vol. 4, p 250.

(31) Cromer, D. T.; Waber, J. T. "International Table for X-ray Crystallography"; Kynoch Press: Birminham, England, 1974; Vol. IV, Values for iron are taken from p 78 and those for hydrogen, carbon, and oxygen taken from pp 72–73. Anomalous dispersion corrections for Fe, C, and O are taken from p 149.

diazomethane gas in a nitrogen stream at room temperature. After the evaporation of the solvent, the residual solid was dissolved in the mixture of diethyl ether–*n*-hexane (3:2). The solution was concentrated to ca. 2 cm^3 and cooled on dry ice to afford orange crystals of **4** (0.15 g, 64%).

Reaction of 1b with $Fe_2(CO)_9$. To a solution of **1b** (0.98 g, 3 mmol) in diethyl ether (20 cm^3) was added $Fe_2(CO)_9$ (1.09 g, 3 mmol), and the solution was stirred for 1.5 h at 35 °C. After the evaporation of the solvent, the residual solid was extracted through a glass filter with 30-cm^3 portions of *n*-hexane. The concentration of the filtrate afforded red crystals of **5** (1.09 g, 78%).

Crystal Structure Determination of 5. Recrystallization under nitrogen from a 1:5 chloroform–petroleum ether solution gave reddish brown single crystals. Specimens used for X-ray diffraction studies were sealed into thin-walled glass capillaries under an argon atmosphere. The crystal system and the space group were obtained from preliminary oscillation and Weissenberg photographs about the *c* axis with Cu Kα radiation. Accurate cell parameters were determined by a least-squares treatment of the 2θ angles of the 47 reflections in the range of 20–35° measured on a computer-controlled four-circle diffractometer with Mo Kα radiation (λ = 0.710 69 Å).

Crystal Data: $C_{14}H_{10}Fe_2O_{11}$, M_r = 465.9, monoclinic, space group $P2_1/n$; a = 15.006 (2) Å, b = 10.896 (1) Å, c = 11.078 (2) Å, β = 100.48 (1)°, V = 1 781.1 (5) Å^3; D_{measd} = 1.72 g cm^{-3} (by flotation method with sodium iodide aqueous solution), Z = 4, D_{calcd} = 1.7376 (5) g cm^{-3}; $F(000)$ = 936, μ = 17.30 cm^{-1}. A specimen of dimensions ca. 0.28 × 0.28 × 0.25 mm was used for X-ray data collection on the diffractometer. Integrated intensities were collected at 21 °C up to 55 °C in 2θ by the θ–2θ continuous scan mode at a θ scan rate of 2° min^{-1} with graphite-monochromated Mo Kα radiation. Stationary background counts of 10-s duration were made on either side of the scan. Intensities of five standard reflections were monitored before every 50 reflections to check the deteriorations of the specimen. No significant variation was observed for these monitoring intensities during the data collection. The intensities were corrected for the Lorentz and polarization effects but not for absorption and extinction. Of the 4080 independent reflections measured, 2850 with $|F_o| > 3\sigma(|F_o|)$ were accepted as "observed" and used in the subsequent calculations.

Solution and Refinement of the Structure. The structure was solved by the heavy-atom method. Two Fe atoms were located from a Patterson map and the other nonhydrogen atoms located from subsequent Fourier syntheses. The structure was refined by the diagonal least-squares calculations with isotropic thermal factors for all the atoms. At this stage the residual index, $R = \sum|\Delta F|/\sum|F_o|$, where $\Delta F = |F_o| - |F_c|$, was 0.10. The hydrogen atoms were located from a difference Fourier map. The structure was then refined by the block-diagonal least squares with anisotropic thermal factors for the nonhydrogen atoms and isotropic ones for the hydrogen atoms. In the refinement the function minimized was $\sum w(\Delta F)^2$, where the weight $1/w$ was $\sigma^2(|F_o|) + a|F_o|^2$ for the block-diagonal least-squares. The constant a was chosen to give approximately equal distribution of the mean $w(\Delta F)^2$ for several subgroups of increasing $|F_o|$ and was 0.0001 in the final cycles of the refinement. The final residual indices were R = 0.046 and $R_w = [\sum w(\Delta F)^2/\sum|F_o|^2]^{1/2}$ = 0.037. In the final cycle of least-squares refinement no individual parameter except in the hydrogen atoms shifted by more than one-half of its estimated standard deviation. In the final difference map there were no peaks greater than 0.35 e Å^{-3}. Atomic scatterring factors were taken from ref 31, including corrections for the effects of anomalous dispersion. All computations were performed on a FACOM 230/38 computer and a MELCOM 70/30 computer at Kwansei Gakuin University.

Acknowledgment. We thank Professor Y. Takegami for helpful discussions.

Registry No. 1a, 6111-92-0; **1b**, 60941-31-3; **3**, 80485-09-2; **4**, 80485-10-5; **5**, 80485-11-6; $Fe_2(CO)_9$, 15321-51-4.

Supplementary Material Available: Tables of fractional coordinates and temperature factors and structure factors for complex **5** (13 pages). Ordering information is given on any current masthead page.

Synthesis and Structure of Dicyclopentenouranocene, $U[C_8H_6(CH_2)_3]_2$

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Received July 31, 1981

The title compound **1** was synthesized by the reaction of dipotassium bicyclo[6.3.0]undeca-2,4,6-triene-1,8-diide, **3**, and UCl_4, and its crystal and molecular structure was determined by single-crystal X-ray diffraction. The compound crystallizes in the orthorhombic space group *Pbca* with eight molecules in the unit cell with dimensions a = 17.393 (8) Å, b = 22.468 (12) Å, and c = 8.931 (4) Å. The uranium atom is located centrally between the two eight-membered rings with bond distances U–C = 2.64 ± 0.03 Å and C–C = 1.40 ± 0.02 Å. The effects of annulation on the physical properties of uranocene are discussed.

Introduction and Results

As part of a continuing study of annulated derivatives[1,2] of uranocene[3] we report the synthesis and X-ray structure determination of bis[π-(cyclopenteno[8]annulene)]uranium(IV) (dicyclopentenouranocene), **1**.[4] This compound has significance for two reasons. First, it was expected to involve a conformation sufficiently well-defined to assist NMR interpretation. Second, it would be the first X-ray

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(2) Luke, W. D.; Berryhill, S. R.; Streitwieser, A., Jr. *Inorg. Chem.* **1981**, *20*, 3086.
(3) Streitwieser, A., Jr.; Muller-Westerhoff, U.; Sonnichsen, G.; Mares, F.; Morrell, D. G.; Hodgson, K. O.; Harmon, C. A. *J. Am. Chem. Soc.* **1973**, *95*, 8644.
(4) Controversy exists in naming sandwich organometallic actinide compounds of cyclooctatetraene. Other possible names are bis(η^8-bicyclo[6.3.0]undeca-2,4,6-triene-1,8-diide)uranium(IV) and bis(η^8-cyclopentenocyclooctatetraene)uranium(0). The former does not properly describe delocalization of charge in the ligand while the latter fails to convey the proper formal oxidation state of the metal or the delocalized nature of the cyclooctatetraene ligand. Thus, we have chosen to name these compounds organometallic derivatives of [8]annulene or as substituted uranocenes in analogy with ferrocene nomenclature.
(5) Karraker, D.; Stone, J.; Jones, E., Jr.; Edelstein, N. *J. Am. Chem. Soc.* **1970**, *92*, 4841.

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