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REACTION OF (1-3-η-VINYLCARBENE)IRON COMPLEXES WITH ENNEACARBONYLDIIRON; FORMATION OF A FERRACYCLOPENTADIENEIRON(Fe-Fe) COMPLEX AND A VINYLCARBENEDIIRON(Fe-Fe) COMPLEX

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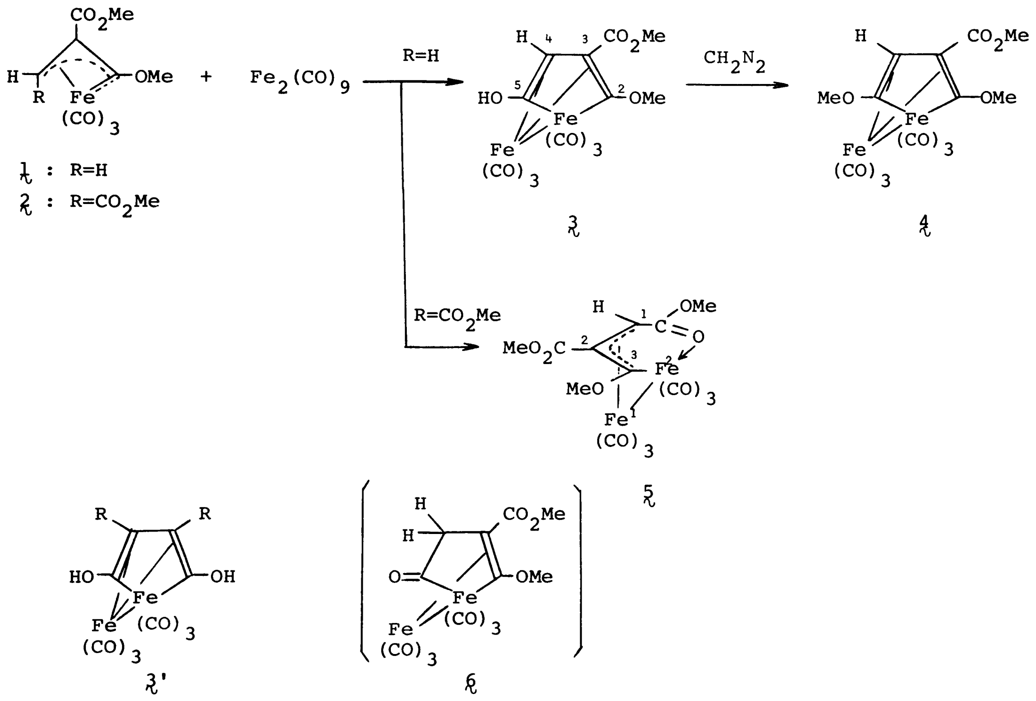
The (η^3-vinylcarbene)iron complex **1** reacts with $Fe_2(CO)_9$ to give a 'ferrole' derivative **3**. Methylation of **3** with diazomethane gives a methoxy derivative **4**. On the other hand, the 2-methoxycarbonylvinylcarbene complex **2** reacts with $Fe_2(CO)_9$ to give a vinylcarbene binuclear complex **5** containing the vinylcarbene moiety co-ordinated to two iron atoms. The structure of **5** has been determined by single-crystal X-ray diffraction study.

Much attention has been focused on the chemistry of transition-metal carbene complexes.1) Recently, the first (η^3-vinylcarbene)tricarbonyliron complexes, **1** and **2**, in which adjacent carbene and olefin are co-ordinated to one metal have been prepared2) and the highly distorted molecular structure of **2** was revealed by X-ray analysis.3) Complexes **1** and **2** are highly reactive to nucleophilic reagents such as carbon monoxide or tertiary phosphines, isonitriles and diazomethane affording η^4-vinylketene-,4) η^4-vinylketenimine-5) and η^4-butadiene-6) tricarbonyliron derivatives, respectively. The present paper deals with the reaction of the η^3-vinylcarbene complexes **1** and **2** with $Fe_2(CO)_9$.

Complex **1** readily reacted with $Fe_2(CO)_9$ in diethyl ether at 25 °C for 2 h under an argon atmosphere to give yellow crystals of (tricarbonyl)(2-5-η-1,1,1-tricarbonyl-5-hydroxy-2-methoxy-3-methoxycarbonylferracyclopenta-2,4-diene)iron(Fe-Fe) **3** in 51 % yield7) {**3**: IR(KBr disk, cm^{-1}) ν(OH) 3250, ν(C≡O) 2075, 2040, 1990, ester ν(C=O) 1705; ^{1}H nmr($CDCl_3$, δ ppm) 5.36(s, 1H olefinic H); ^{13}C nmr($CDCl_3$, δ ppm) 78.3[d, J(CH) 162 Hz, C^4], 85.3(s, C^3), 221.3 and 227.6(s, C^2 or C^5), See Scheme}. Treatment of **3** with diazomethane in diethyl ether under nitrogen at 25°C gave orange crystals of **4** derived by the methylation of the hydroxyl group in **3**



Scheme

in 63 % yield.

The formation of **3** by the reaction of **1** with $Fe_2(CO)_9$ may be rationalized as follows. The attack of '$Fe(CO)_4$' moiety of $Fe_2(CO)_9$ on **1** would induce the insertion of a carbon monoxide into methylene carbon-iron bond of **1** to give an intermediate, 2-3-η-ferracyclopentenonetricarbonyliron(Fe-Fe) **6**.[4,8] The keto-enol isomerization then occurs to give the product **3**.

The ferrole complex **3**' similar to **3** was prepared by the reaction of acetylene with alkali solution of $Fe(CO)_5$,[9] but the mechanism of this double carbonylation of acetylene has not been revealed. The present result strongly suggests that this process proceeds via an η^3-vinylcarbene complex.

Complex **2** 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 {**5**: IR(KBr disk , cm^{-1}) ester ν(C=O) 1720, ν(C=O→Fe) 1600; ^1H nmr($CDCl_3$, δ ppm) 3.03(s, 1H olefinic H); ^{13}C nmr ($CDCl_3$, δ ppm) 38.4[d, J(CH) 162 Hz, C^1], 82.0(s, C^2), 221.4(s, C^3) }.

The structure of **5** was determined by X-ray analysis (Figure). Crystal Data.— $C_{14}H_{10}Fe_2O_{11}$, M=465.9, Monoclinic, space group $P2_1/n$; a=15.006(2), b=10.896(1), c= 11.078(2) Å, β=100.48(1)°, Z=4, Dm=1.72 g cm^{-3}, Dc=1.7376 g cm^{-3}: Least-squares calculations on 2850 non-zero independent reflections(Mo-Kα radiation) gave an R value of 4.6 %. The results demonstrate that **5** is an (η^3:η^1-allyl)diiron(Fe-Fe) complex in which Fe(1) is co-ordinated by a (1-3-η-allyl)[C(1), C(2) and C(3)]

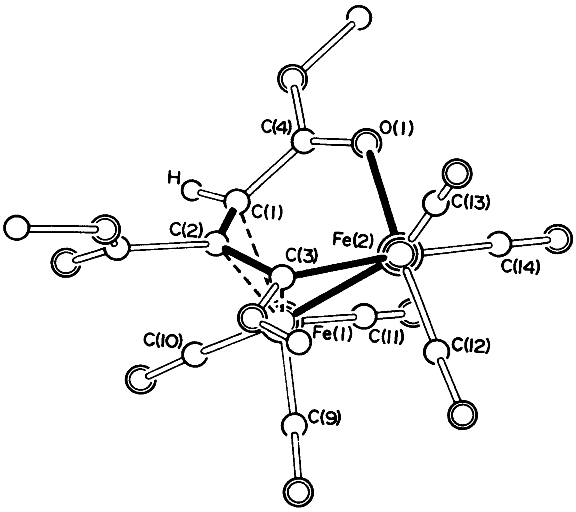


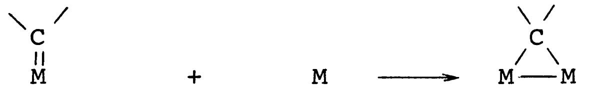
Figure. The molecular structure of vinylcarbenediiron complex **5**. The methyl hydrogen atoms are omitted. Important bond lengths (in Å) and angle (in °) are:

Fe(1)-Fe(2)	2.638(1)
Fe(1)-C(1)	2.054(4)
Fe(1)-C(2)	2.047(3)
Fe(1)-C(3)	2.140(3)
Fe(2)-C(3)	1.957(4)
Fe(2)-O(1)	2.019(3)
C(1)-C(2)	1.448(5)
C(2)-C(3)	1.405(5)
C(1)-C(2)-C(3)	118.7(3)

○ : C
◎ : O

system and Fe(2) is σ-bonded with C(3) and co-ordinated by the ester group. The co-ordinations about Fe(1) and Fe(2) were both highly distorted octahedron as has been reported in other (η^3:η^1-allyl)diiron complexes.$^{10)}$ Comparing the structures of **5** with **2**, the formation of **5** could be explained by the 'co-ordination' of the complex **2** to $Fe(CO)_3$ 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. Although several (η^3:η^1-allyl)dimetal(M-M) complexes similar to **5** have been reported,$^{10,11)}$ **5** is the first 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.

Although both η^1-carbene M (M=metal) **7** and μ-carbene M_2 species **8** have been reported to be one of the possible active species in Fischer-Tropsch reaction,$^{12)}$ the possibility that **8** is formed from **7** has not yet been pointed out. The present reaction could be considered to be the model reaction that **8** is formed from **7** suggesting the presence of such a process on the surface of heterogeneous catalysts (Eq.).



7 **8**

(Eq.)

As described above, the reaction of $Fe_2(CO)_9$ with **1** gives a 'ferrole' derivative **3** while that with **2** gives a binuclear vinylcarbene complex **5**. The difference of these reactions is due to whether the η^3-vinylcarbene ligand has a methoxycarbonyl group at the 'anti'-position or not. An η^3-vinylcarbene complex which can 'co-ordinate' to a 'Fe(CO)$_3$' moiety as a bidentate chelate ligand such as **2** gives **5**, otherwise the insertion of carbon monoxide into the carbene carbon-iron bond is induced affording **3**.

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