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Accounts

The Chemistry of η^3-Vinylcarbene Complexes

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The chemistry of η^3-vinylcarbene transition-metal complexes is reviewed. The η^3-vinylcarbene complexes are prepared by 1) the alkylation of (η^3-acryloyl)tricarbonylferrate, 2) the treatment of cyclopropenes with [$Fe_2(CO)_9$], 3) the insertion of acetylenes into a carbene–metal double bond, 4) the reaction of acetylene with [$ReCl_3(Me_5C_5)]_2$, 5) the reaction of carbyne complexes with allyl bromides, and 6) the thermal decarbonylation of (η^1-vinylcarbene)pentacarbonylchromium. The structures of the complexes, which were determined by X-ray analyses, are represented by the hybrid of the resonance structures (**A**) and (**B**). The contribution of the two structures was very sensitive to the respective ML_n fragments. The vinylcarbene complex, [Fe(η^3-vinylcarbene)$(CO)_3$] (**1**), is a parent complex of a series of various complexes. The carbene carbons of the reported Fischer-type η^3-vinylcarbene complexes are electrophilic. Carbonylation of the η^3-vinylcarbene complexes gives η^4-vinylketene complexes. Treatment of the η^3-vinylcarbene(carbonyl)irons with an excess of tertiary phosphines or bidentate amines gives ferracyclopentenones. Reaction of **1** with isocyanides gives the first example of the η^4-vinylketenimine complex. Treatment of **1** with diazomethane gives (η^4-1,3-butadiene)tricarbonyliron. The complex **1** with a methoxycarbonyl group on the 3-position reacts with carbon monoxide to give a η^4-pyrone complex, which thermally rearranges to its isomer. The rearrangement was deduced to proceed via a η^4-methoxyfuran complex. The complex **1** reacts with hydride to give a η^3-allyl complex. Reaction of (η^3-2-trifluoromethylvinylcarbene)tricarbonyliron with K[BH(*s*-Bu)$_3$] or phenyllithium gives (η^4-difluorotrimethylenemethane)tricarbonyliron, leaving a fluoride ion. η^3-Vinylcarbene complexes react with acetylenes to give η^4-cyclopentadiene metal complexes. The reaction proceeds via a metallacyclohexadiene. The complex **1** reacts with an unsaturated metal complex M^2L_n to give a binuclear vinylcarbene complex or ($\eta^3:\eta^1$-allyl)(*Fe–M*^{2}). Reaction of **1** with $Ru(CO)_3(COD)$ provides a method for selective preparation of ($\eta^3:\eta^1$-allyl)(*Fe–Ru*), which reacts with acetylenes to give [Fe(η^4-ruthenacyclohexadiene)$(CO)_3$]. Formation of a η^3-vinylcarbene complex by the reaction of a carbene complex with acetylene, and subsequent carbonylation of this complex, is the essential pathway of the Dötz reaction.

Since the discovery of a carbene metal complex by E. O. Fischer in 1964,[1] the chemistry of carbon metal unsaturated bonds has been remarkably developed.[2—59] The first η^3-vinylcarbene (η^3-allylidene or π-vinylcarbene) complex was found in 1976;[7—10] its chemistry has received much attention during these two decades.[7—15,38—59] The complex has a three carbon-four electron η^3-vinylcarbene ligand, whose carbene carbon and the adjacent olefinic group are coordinated to a single metal. This coordination mode is a representative one among those of three-carbon ligands to a single metal center such as η^3-allyl,[60,61] η^3-propargyl,[62,63] or η^3-cyclopropenyl complexes[64,65] (Fig. 1). A theoretical study based on MO calculation pointed out that the η^3-vinylcarbene complexes can be viewed as a resonance hybrid with two limiting descriptions, (**A**) and (**B**) in Fig. 1.[24,25] Obviously, (**A**) and (**B**) are only mesomeric representations of the same species and their relative weighting will be delicately balanced as a function of the respective ML_n fragments (vide infra).

The chemistry of the η^3-vinylcarbene complex has been well developed, so it is now established to be a parent complex for a cascade of various complexes. From η^3-vinylcarbene complexes, a variety of mononuclear and binuclear complexes are derived (Scheme 1). For example, η^4-vinylketene,[11,13,20,44,45] η^4-vinylketenimine,[14] η^4-1,3-butadiene,[15,44] ferracyclopentenone,[11—13,16] η^3-allyl,[12,49] η^4-pyrone,[17,18] η^4-trimethylenemethane,[19] and η^4-cyclopentadiene[13,18] complexes etc. are derived. Further, homo-[20—22] and hetero-[23] binuclear vinylcarbene complexes can be derived.

Theoretical studies on η^3-vinylcarbene complexes[24—26] revealed that the η^3-vinylcarbene complexes are very important reaction intermediates in the Dötz reaction or polymerization of acetylene.[25] The Dötz reaction is the synthesis of various benzannulenes, cyclopentadienes, or cyclohexadienones by the reaction of chromium carbonyl carbene complexes with acetylenes.[27—42] The proposed mech-

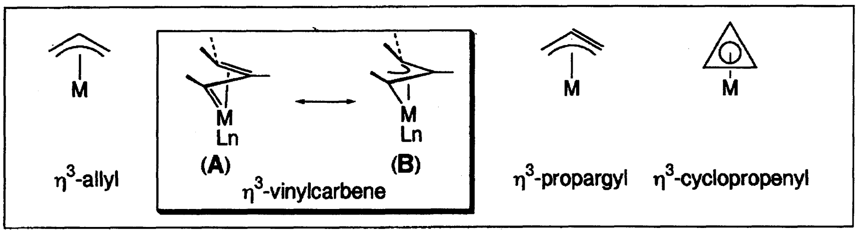
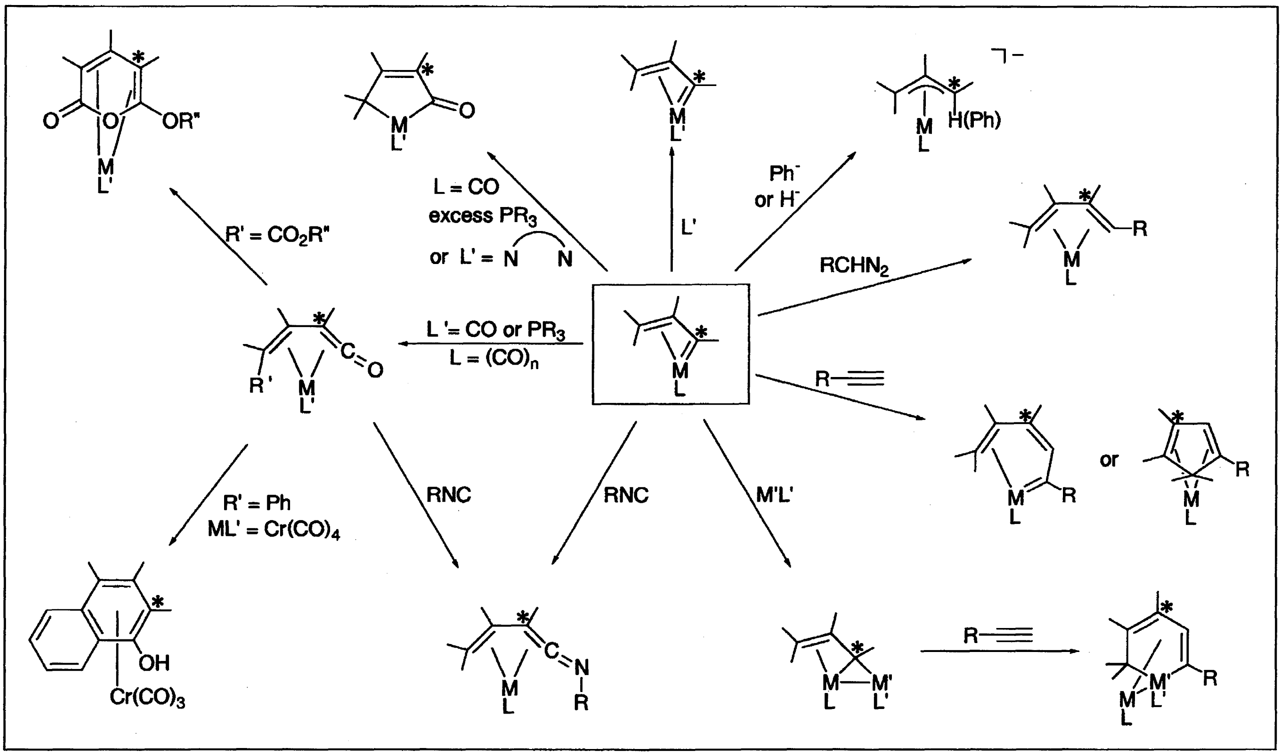
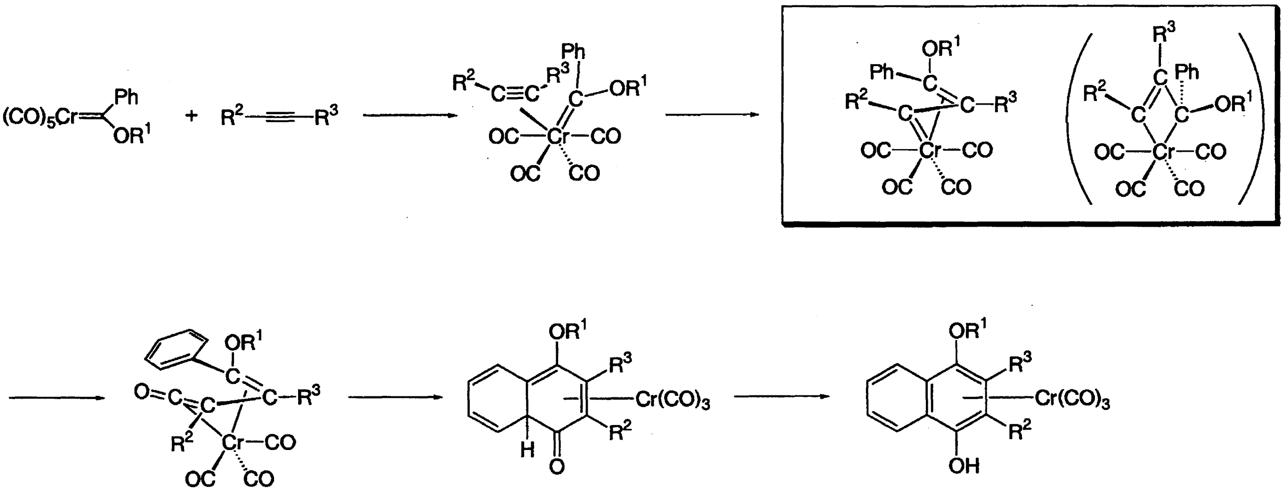


Fig. 1. Typical coordination modes of η^3-three-carbon ligands to a single metal.



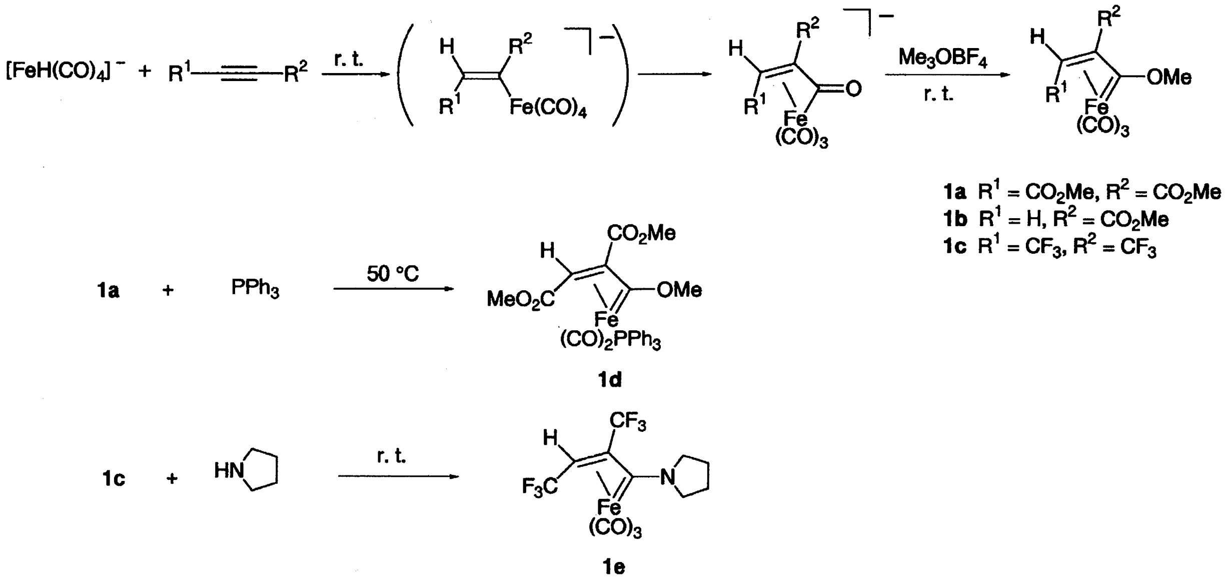
Scheme 1. Complexes derived from η^3-vinylcarbene complexes. The carbon with * is derived from the carbene carbon of the parent complex.



Scheme 2. Proposed mechanism for the Dötz reaction.

anism for the synthesis of naphthols by the Dötz reaction is shown in Scheme 2.[25] It is pointed out that the reactions of chromium carbene complexes with acetylene give η^3-vinylcarbene complexes rather than their tautomers, chromacylcobutene complexes.[25,26]

In this account, the development of the chemistry of η^3-



Scheme 3. Preparation of the first η^3-vinylcarbene complexes.

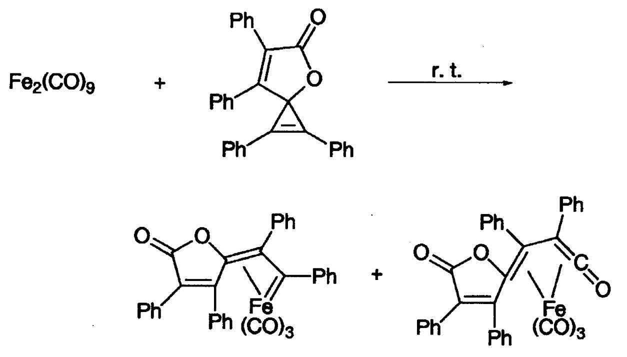
vinylcarbene complexes is summarized so as to disclose the characteristic feature of this complex. Chemistry of a η^1-vinylcarbene complex which is the tautomer of the η^3-vinylcarbene complex is also very important and attractive, however, it is out of the scope of this account. Only some recent leading papers are cited in the references.[66—92]

1. Preparation of η^3-Vinylcarbene Complexes

The first η^3-vinylcarbene complexes were prepared by the alkylation of (η^3-acryloyl)iron complexes which were derived by the addition of hydrido(tetracarbonyl)ferrate to acetylenes (Scheme 3).[7—13] The *trans*-addition of the hydridoferrate, $[FeH(CO)_4]^-$, to acetylenes such as dimethyl acetylenedicarboxylate followed by the alkenyl migration on the carbon monoxide and subsequent coordination of the olefinic group to the unsaturated iron gives 1e (η^3-acryloyl)ferrates.[9,10,13] The corresponding aminovinylcarbene complex **1e** was prepared by the reaction of **1c** with pyrrolidine.[13] A triphenylphosphine substituted complex **1d** was obtained by the treatment of **1a** with PPh_3.[18] The characteristic structures of the η^3-vinylcarbene complexes **1a** and **1e**, and the (η^3-acryloyl)ferrate[10,13] were revealed by X-ray analysis (vide infra).

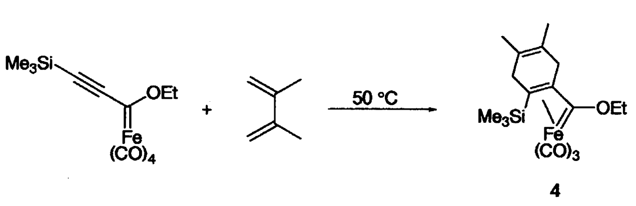
After the first η^3-vinylcarbene complex was found, several methods for the preparation of η^3-vinylcarbene complexes were reported as follows.

Reaction of a cyclopropene derivative with $[Fe_2(CO)_9]$ gives a mixture of a η^3-vinylcarbene complex (**2a**) and a η^4-vinylketene complex (**3a**). The result shows that the carbon–carbon bond of the cyclopropene derivatives is cleaved to give the vinylcarbene ligand.[43—45]



(1)

The Dields–Alder reaction of an alkynylcarbeneiron (Eq. 2)[46,47] and the Michael type addition of dimethylamine to the alkynylcarbene complex give η^3-vinylcarbene complexes, **4** and **5**, respectively.[48]



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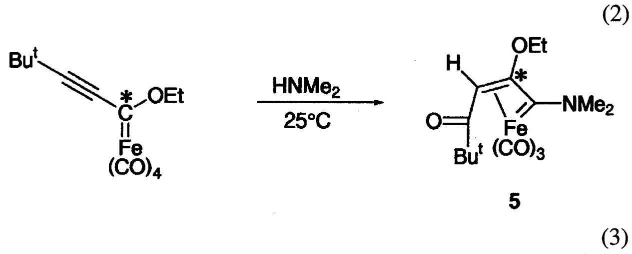
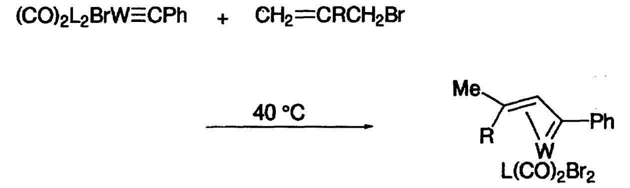


(3)

The latter reaction involves rearrangement via [Fe(η^4-furan)$(CO)_3$]. A related rearrangement via Fe(η^4-furan) complexes will be discussed later.

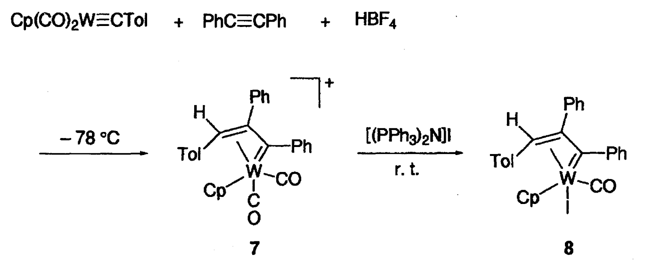
The reaction of tungsten carbyne complexes with allyl bromides gives a η^3-vinylcarbene complex (**6a**—**6c**).[51,52] The proposed reaction pathway for the formation of **6a**—**6c** is the coordination of the alkene portion of the allyl bromide and subsequent electrophilic attack of the bromomethyl group at the alkylidyne carbon followed by hydrogen migration.[52]



6a L = 4-picoline, R = H
6b L = 4-picoline, R = Me
6c L = 4-dimethylaminopyridine, R = H

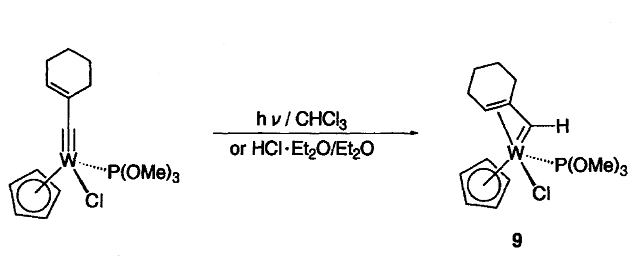
(4)

Reaction of a tungsten carbyne complex with acetylene in the presence of a protic acid gives a η^3-vinylcarbene complex (**7**).[49] The reaction proceeds via insertion of acetylene into a carbene carbon–metal bond, which was generated by the protonation of the carbyne complex.



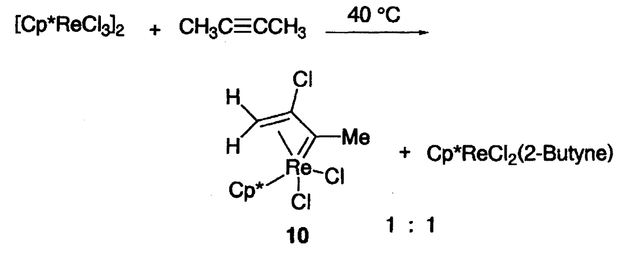
(5)

Photolysis of a η^1-vinylcarbyne complex in $CHCl_3$, or protonation of the vinylcarbyne complex provides a new route to the η^3-vinylcarbene complex.[50] In the former reaction, the formed 17-electron complex $[W(\eta^5\text{-}C_5H_5)(CO)\{P(OMe)_3\}M{\equiv}CR]\cdot$ abstracts a hydrogen atom from $CHCl_3$.



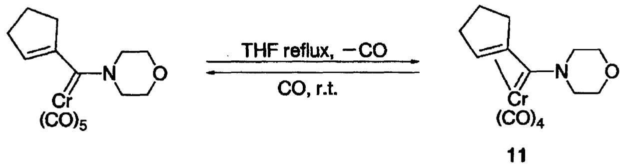
(6)

Reaction of $[Re(Me_5C_5)Cl_3]_2$ with 2-butyne gives an unusual η^3-vinylcarbene rhenium complex (**10**)[53,54] together with the equivalent amount of $[ReCl_2(Me_5C_5)(2\text{-butyne})]$. It appears that insertion of acetylene between the metal–chloride bond and the cleavage of one hydrogen of the methyl group, accompanied with disproportionation, occurred to give the (η^3-vinylcarbene)Re(V) (**10**).



(7)

Thermal decarbonylation of (η^1-vinylcarbene)pentacarbonylchromium gives a η^3-vinylcarbene complex **11**, which forms the η^1 complex reversibly by the treatment of CO at room temperature.[55,56]



(8)

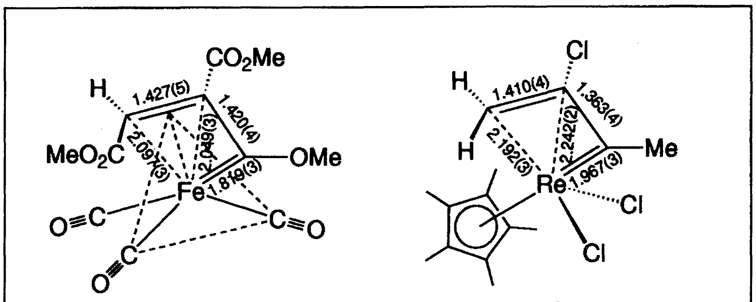
2. Structures of η^3-Vinylcarbene Complexes and the Coordination Mode of the η^3-Vinylcarbene Ligands

The representative structures of the η^3-vinylcarbene complexes **1a** and **10** determined by X-ray analyses are shown in Fig. 2.

The coordination profiles of various η^3-vinylcarbene complexes are summarized in Table 1. The C^1(carbene)–M bond lengths are between 1.809(8) and 1.876(7) Å for the Fe complexes: 1.967(3) and 1.999(7) Å for the W and Re complexes. The Fischer-type iron complexes **1a**, **1e**, **2a**, **4**, and **5**, show shorter bond lengths of carbene–metal bonds: 1.819(3), 1.876(7), 1.831(4), 1.809(8), and 1.865(2) Å, respectively, suggesting the enhanced back-donation from the metal to the carbene carbons. These are the shortest bond lengths for iron carbon double bonds.

P. Hofmann pointed out on the basis of an MO study that the η^3-vinylcarbene ligand in $[Cr(\eta^3\text{-vinylcarbene})(CO)_4]$ can operate as a 4 electron donor through its carbene lone pair and its double bond, *both being part of a distorted allyl system*, and the η^3-vinylcarbene complexes can be viewed as a resonance hybrid with two limiting descriptions (**A**) and (**B**), as in Fig. 1.[24,25] As he pointed out, the contributions of the structures (**A**) and (**B**) in Fig. 1 are different for these isolated complexes.

It seems that there are two types of η^3-vinylcarbene complexes. One type includes the complexes represented by the Fischer-type iron complexes described above, in which bond lengths of C^1–C^2, and C^2–C^3 are almost the same and they are between those of sp^2–sp^2 single bonds and carbon–carbon double bonds suggesting the delocalization of π-electrons over C^1–C^2–C^3 ligands and the larger contribution of the resonance structure of (**B**) in Fig. 1. These complexes are reasonably represented as "π-vinylcarbene" complexes. In complexes **8** and **10**, the bond lengths of C^2–C^3 are even longer than those of C^1–C^2 suggesting the larger contribution of (**B**) again. In these complexes, the bond lengths of

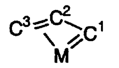


1a **10**

Fig. 2. Representative X-ray structures of η^3-vinylcarbene complexes.

Table 1. X-Ray Data of the η^3-Vinylcarbene Complexes Bond Lengths (Å) and Bond Angles (deg)

Complex	M–C^1	M–C^2	M–C^3	C^1–C^2	C^2–C^3	C^1–C^2–C^3	M–C^1–C^2	Ref.
1a	1.819(3)	2.049(3)	2.097(3)	1.420(4)	1.427(5)	109.4(3)	77.4(2)	8
1e	1.876(7)	1.990(9)	2.073(9)	1.43(1)	1.41(1)	113.0(9)	72.6(5)	13
2a	1.831(4)	2.120(5)	2.167(4)	1.410(6)	1.430(6)	113.0(4)	—	43
4	1.809(8)	2.118(7)	2.215(7)	1.42(1)	1.40(1)	113.6(6)	81.1(5)	46
5	1.865(2)	2.063(3)	2.131(3)	1.417(4)	1.412(5)	—	76.5(2)	48
6a	1.98(2)	2.38(2)	2.60(2)	1.44(2)	1.35(1)	122(2)	87.1(9)	52
8	1.999(7)	2.305(8)	2.293(8)	1.420(1)	1.443(11)	111.4(7)	82.9(4)	49
10	1.967(3)	2.242(3)	2.192(3)	1.363(4)	1.410(4)	117.3(3)	—	53
11	1.961(2)	2.238(2)	2.414(3)	1.441(3)	1.368(4)	121.7(2)	—	55

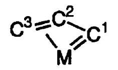


C2–M and C3–M are ordinary ones.

The second type can be seen in the complexes, **6a** and **11**; here the bond lengths of C^1–C^2 are 1.44(2) and 1.441(3) Å, respectively, and they are close to those of single bonds between sp^2–sp^2 carbons. Further, bond lengths of C^2–C^3 double bonds are 1.35(1) and 1.368(4) Å; these values are very short for coordinated olefins. Especially in **6a**, the bond angle of C^1–C^2–C^3 is large, 122(2)° the bond length of M–C^3 is unusually long, 2.60(2) Å. In these complexes the delocalization of the π-electrons over the three carbons is unlikely and the contribution of only the resonance structure (**A**) is suggested.

Table 2. ^{13}C NMR Spectral Data of the η^3-Vinylcarbene Complexes

Complex	δ/ppm C^1	C^2	C^3	Ref.
1a	270.9	51.4	41.8	8
1d	272.6	54.6	39.5	12
1e	222.0	49.4	37.6	13
2a	253.1	95.9	83.4	43
5	226.0	49.4	107.0	48
6a	240.4	122.9	91.3	52
8	269.8	70.7	91.1	49
9	277.8	75.4	93.7	50
10	265.2	—	—	53
11	255.5	86.9	85.7	55



3. Spectra of η^3-Vinylcarbene Complexes

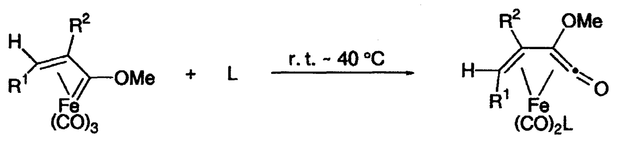
The most characteristic spectral feature of the η^3-vinylcarbene complexes is their ^{13}C NMR spectra. They show the ^{13}C NMR signals for the carbene carbons at $\delta = 226$—278. The representative data together with those of the olefinic carbons are summarized in Table 2. The signals for the carbenes are found in relatively higher fields than usual η^1-carbene complexes. For example, [Cr=C(OMe)(CR=CHR)-(CO)$_5$] shows the signal for carbene carbon at lower field than $\delta = 300$.[69,72)] The shifts of the signals of **1a**—**11** shown in Table 2 to the relatively higher field may be due to the shielding of the carbene carbon by enhanced back donation or by the delocalization of the π-electrons over the vinylcarbene ligand. The signals for the olefinic carbons show the chemical shifts for usually coordinated olefinic carbons.

4. Reactions of η^3-Vinylcarbene Complexes

As described in the introduction, a η^3-vinylcarbene complex shows versatile reactivity and now it is established to be a parent of a variety of complexes. The outline is summarized in Scheme 1. The carbene carbon of a Fischer-type η^1-carbene complex is well known to be electrophilic and reacts with nucleophiles. Fischer-type η^3-vinylcarbene complexes also react with a variety of nucleophiles to give a cascade of unique complexes. Some typical reactions are as follows.

4-1. Carbonylation of the η^3-Vinylcarbene Ligand. Fischer-type η^3-vinylcarbene complexes react with carbon monoxide to give η^4-vinylketene complexes. Insertion of carbon monoxide into the carbene carbon–metal double bond easily occurs. The first evidence of the formation of a η^4-vinylketene complex from a η^3-vinylcarbene complex is as follows. Complex **1b** reacts with carbon monoxide to give **12b** under mild reaction conditions in high yields.[11—13] Weiss's η^3-vinylcarbene complex **2a** also reacts with carbon monoxide to give η^4-vinylketene complex **3a**.

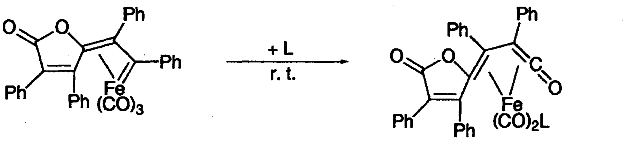
Reactions of the [M(η^3-vinylcarbene)(carbonyl)] complexes with Lewis bases such as phosphines or NaS_2CNEt_2 also induce the carbonylation of the η^3-vinylcarbene ligands, giving η^4-vinylketene complexes again.[51]



1a-c

12a R^1 = COOMe, R^2 = COOMe, L = PPh_2Me
12b R^1 = H, R^2 = COOMe, L = CO
12b' R^1 = H, R^2 = COOMe, L = PPh_3
12c R^1 = CF_3, R^2 = CF_3, L = PPh_3

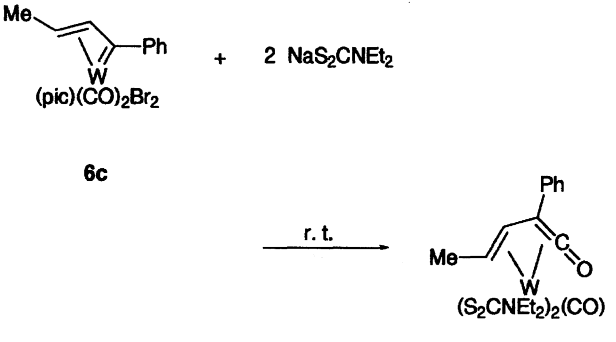
(9)



2a

3a L = CO
3b L = PPh_3
3c L = PPh_2Me
3d L = PPh_2H
3e L = $PPhMe_2$
3f L = PMe_3
3g L = $P(OPh)_3$
3h L = $P(OMe)_3$

(10)



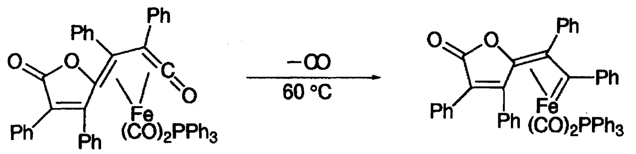
6c

13

(11)

The carbonylation of the η^3-vinylcarbene ligands to form the η^4-vinylketene complexes is the key reaction in the Dötz reaction (vide infra).[25]

The insertion of carbon monoxide into the carbene carbon–metal bond is reversible. Vinylketene complexes often give η^3-vinylcarbene complexes via decarbonylation reaction.[45]

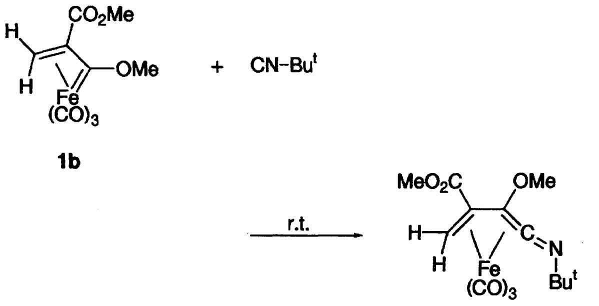


3b

2b

(12)

The reaction of complex **1b** with isocyanide gives the first example of a η^4-vinylketenimine complex (**14**), the structure of which is determined by X-ray analysis.[14] In this reaction, no carbon monoxide is inserted and only the isocyanide is inserted. Treatment of **14** with CH_3OSO_2F induces methylation on the nitrogen atom to give a η^4-vinylketeniminium complex.[14]



1b

14

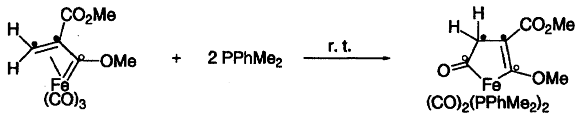
(13)

S. E. Thomas reported that the reaction of tricarbonyl(η^4-benzylideneacetone)iron(0) with methyllithium under 1 atm of carbon monoxide followed by quenching with tertiary butyl bromide gives tricarbonyl(η^4-vinylketene)iron(0) (**16**) (Scheme 4).[58] The reaction is reasonably explained by the formation of tricarbonyl(η^3-vinylcarbene)iron(0) (**20**) via the metathesis-type reaction between the iron–carbon and carbon–oxygen double bonds of the intermediate **19** (Scheme 5). Further, the tricarbonyl(η^4-vinylketene)iron(0) (**16**) reacts with isocyanides to give the η^4-vinylketenimine complex **17** showing that the reverse reaction of the η^4-vinylketene complex to the vinylcarbene complex occurs.

Carbonylation of η^3-vinylcarbene complex **1a**, which has an *anti*-methoxycarbonyl group, gives a η^4-pyrone complex.[17]

The mechanism of this reaction is tentatively explained by the annulation via the intramolecular nucleophilic attack of the methoxy group on the ketene group of the formed η^4-vinylketene intermediate **21** (Scheme 6).

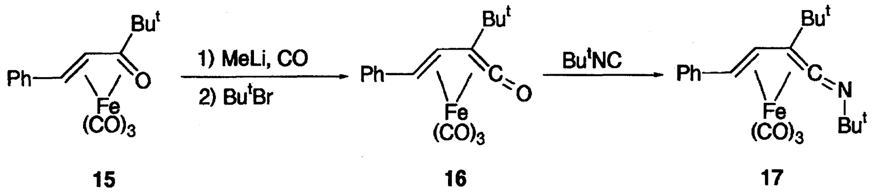
The treatment of the complex **1** with an excess amount of phosphines or the treatment of the η^4-vinylketene complexes with phosphine or carbon monoxide gives ferracyclopentenones **23**.[12,13] In these reactions, the products depend on the substituents on the olefinic group.



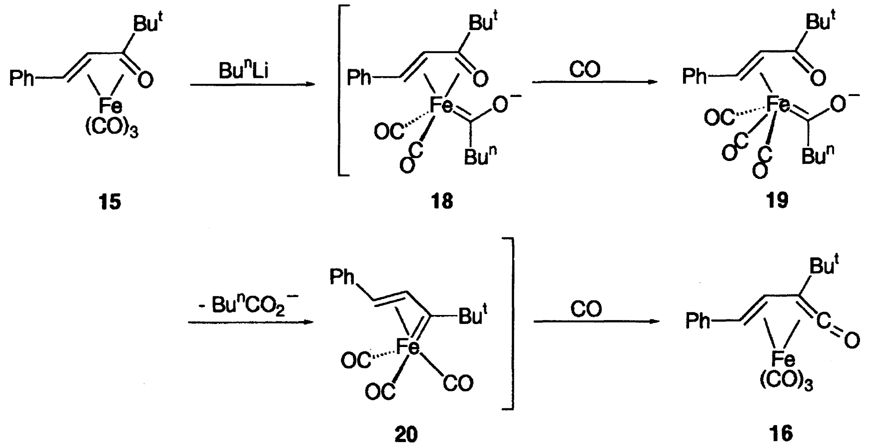
1b

23

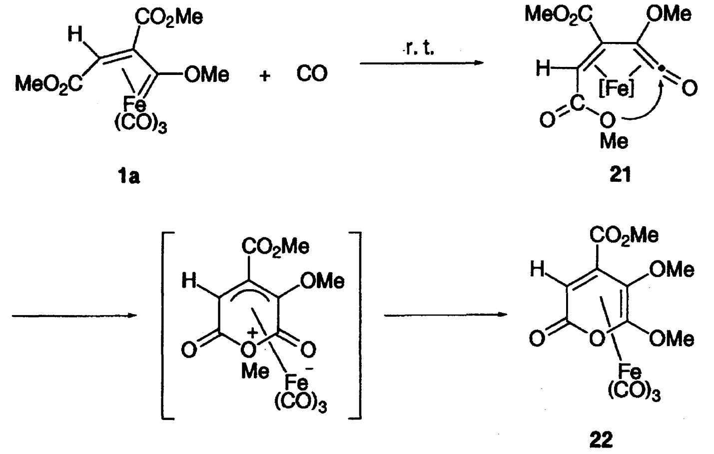
(14)



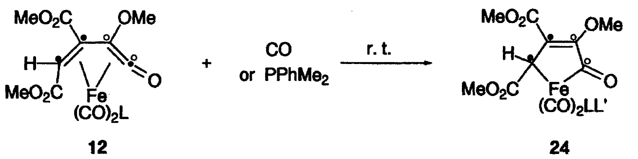
Scheme 4. η^4-Vinylketene or η^4-vinylketenimine complexes from [Fe(η^4-enone)(CO)$_3$].



Scheme 5. The proposed mechanism via (η^3-vinylcarbene)iron.

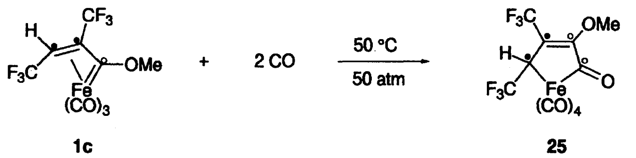


Scheme 6. A Plausible mechanism for the formation of the pyrone complex.



(15)

When the vinylcarbene ligand has an electron-withdrawing group such as methoxycarbonyl[12] or trifluoromethyl group[13] at the 3-position, e.g. as in the complexes **1a** or **1c**, 1-ferracyclopent-3-ene-2-one such as **24** or **25** are obtained.

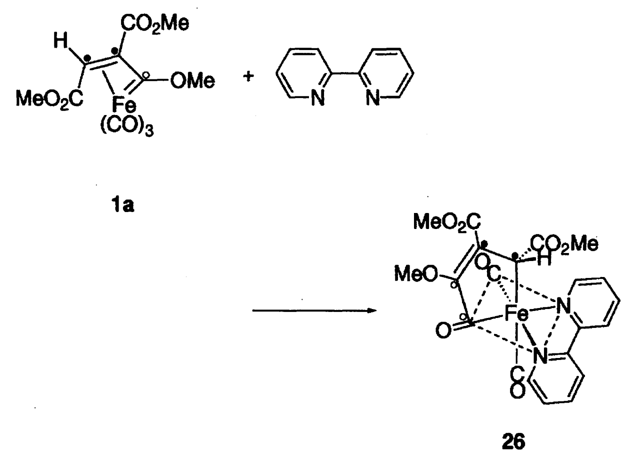


(16)

On the other hand, without such substituent, 1-ferracyclopent-4-ene-2-one derivatives such as **23** are obtained.[12]

The difference of the products is explained by the stability of the olefinic group coordinated to the metal center in the intermediate η^4-vinylketene complex. The electron-withdrawing group on the terminal carbon of the vinylketene ligand enhances the back-donation of the d-electrons from the metal to the *anti*-bonding orbital of the olefinic group to stabilize the coordination of the olefinic carbon.

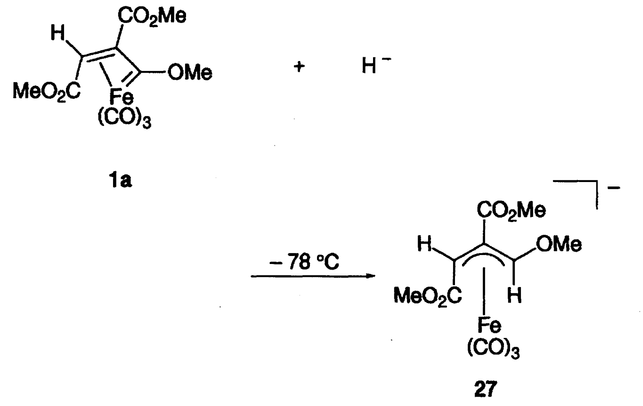
The reaction of the complex **1a** with 1,1′-dipyridyl gives a 1-ferracyclopent-3-en-2-one complex (**26**) whose structure was confirmed by X-ray analysis.[23] The insertion of carbon monoxide between the carbene carbon–iron bond occurs and the dipyridyl occupies the *mer* position of the methine carbon. The methoxycarbonyl group on the α-carbon is oriented to avoid the steric hindrance against the dipyridyl.



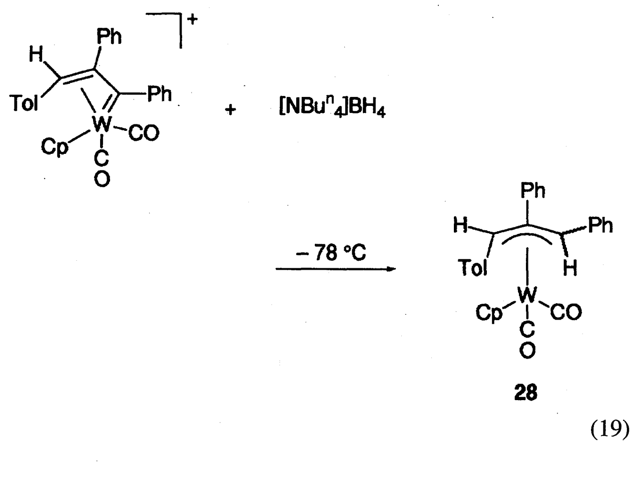
(17)

It would be worthwhile to examine the origin of the carbons in the skeletons of the complexes in Eqs. 14, 15, 16, and 17. The symbols (○) and (●) show that the carbon is derived from carbon monoxide and from acetylene, respectively. In complexes **24**, **25**, and **26**, one of the acetylenic carbons is doubly carbonylated, while in complex **23**, both acetylenic carbons are carbonylated.

4-2. Reaction of the η^3-Vinylcarbene Complex with Hydrides. Hydride attacks the electrophilic carbene carbon of η^3-vinylcarbene complexes to give η^3-allyl complexes.[12,49] This method provides a novel route to η^3-allyl complexes.



(18)



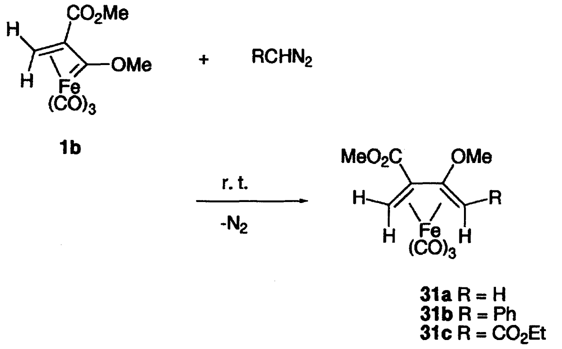
(19)

The reaction of the trifluoromethyl-substituted η^3-vinylcarbeneiron complex **1c** with a hydride, K[BH(*s*-Bu)$_3$], gives an unexpected product, trimethylenemethane complex **29** (Scheme 7),[19] the structure of which was confirmed by X-ray analysis.

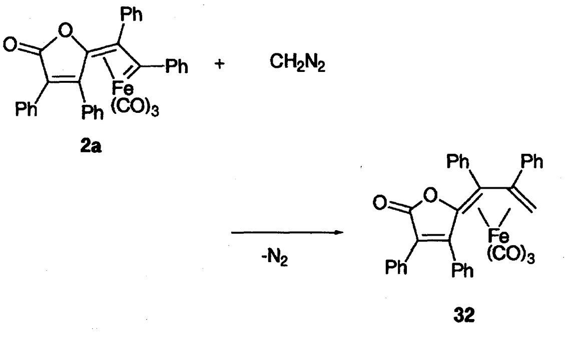
The mechanism of the formation of **29** is explained as follows. First, the corresponding η^3-allyl complex **30** is formed by the nucleophilic attack of the hydride on the carbene carbon, followed by the *syn–anti* isomerization and the leaving of the fluoride ion. Phenyllithium also attacks the carbene carbon to give the corresponding trimethylenemethane complex **29b**.[19]

The formed trimethylenemethane complex has a difluoromethylene group. Since (trimethylenemethane)irons are well known starting materials for organic syntheses such as annulation reactions,[93,94] **29** would be a useful complex for the synthesis of fluorinated organic compounds.

4-3. Reaction of the η^3-Vinylcarbene Complex with Diazo Compounds. The η^3-vinylcarbene complexes **1b**[15] and **2a**[45] react with diazo compounds to give η^4-1,3-butadiene complexes **31** and **32**. These reactions provide an alternative synthetic route to (η^4-1,3-diene)metal complexes.

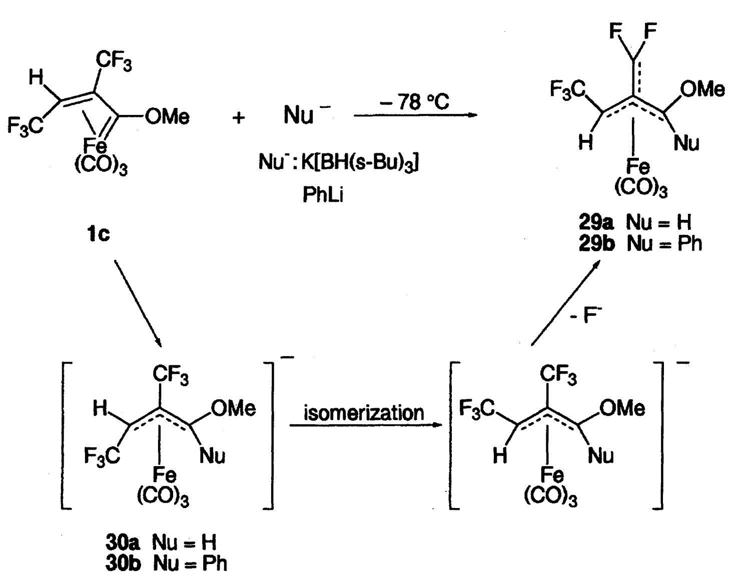


(20)

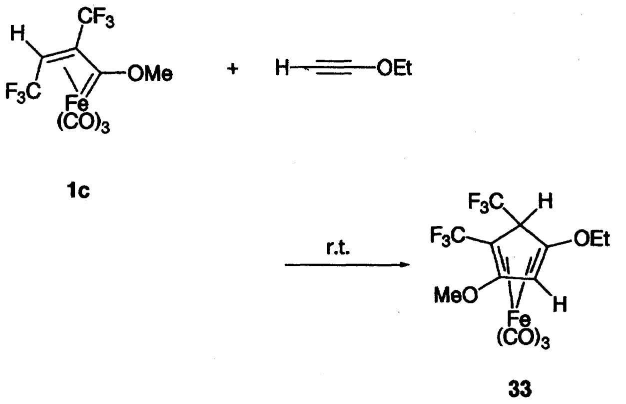


(21)

4-4. Reaction of the η^3-Vinylcarbene Complex with Acetylenes. The η^3-vinylcarbene complex **1c** reacts with ethoxyacetylene to give a η^4-cyclopentadiene complex **33**.[13]



Scheme 7. Mechanism for the formation of the (η^4-trimethylenemethane)iron complex.

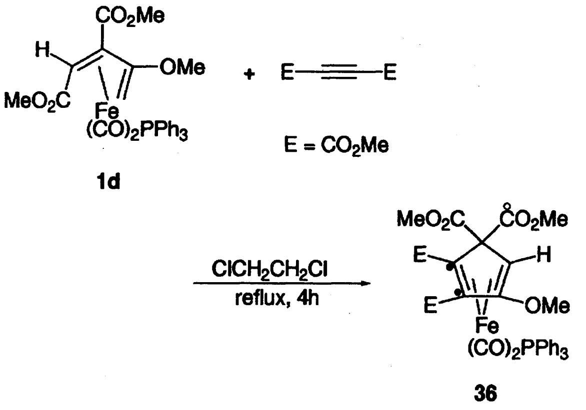


(22)

The reaction mechanism is postulated to be the formation of a ferracyclohexadiene complex, followed by reductive elimination.

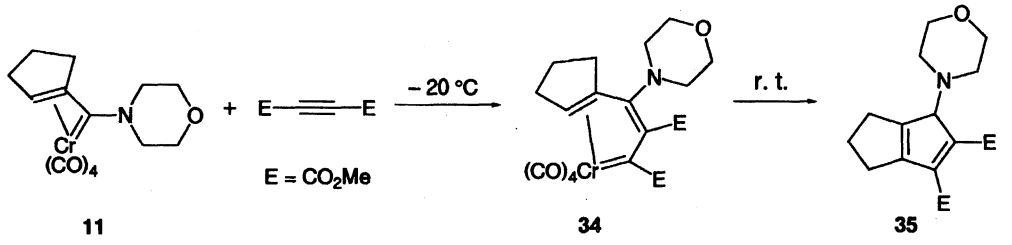
The complex **11** reacts with dimethyl acetylenedicarboxylate to give 5-6-η-1-η-metallahexatriene **34**, from which a cyclopentadiene derivative **35** is formed (Scheme 8).[50] A metallacyclohexadiene would be formed prior to the reductive elimination.

The triphenylphosphine-substituted vinylcarbene complex **1d** reacts with dimethyl acetylenedicarboxylate to give a η^4-cyclopentadiene complex **36**.[18] The product was unusual because it appears that 1,2-transfer of the methoxycarbonyl group occurred.

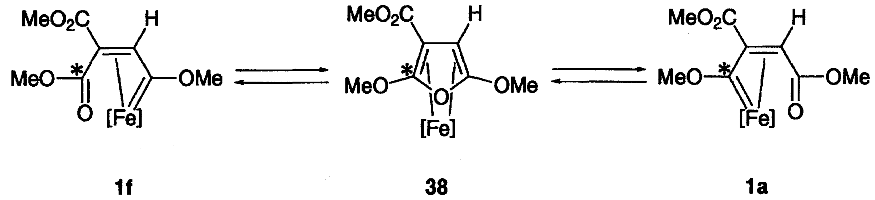


(23)

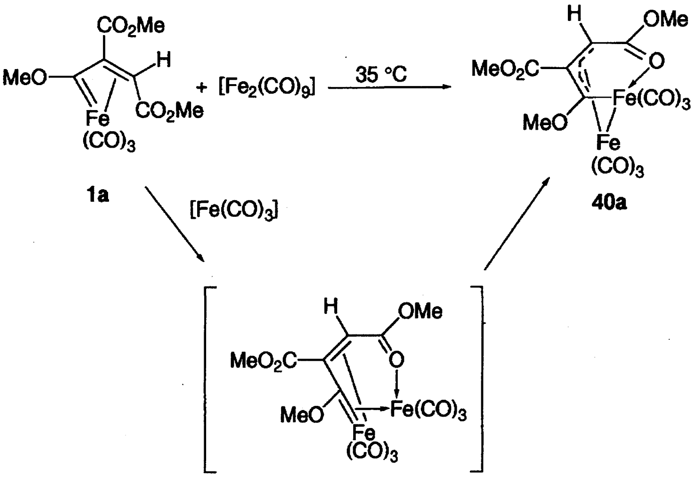
It was reported that the transfer of the methoxycarbonyl group also occurred in the alkylation of a η^3-acryloyl(tricarbonyl)ferrate **37** (Eq. 24).[17]



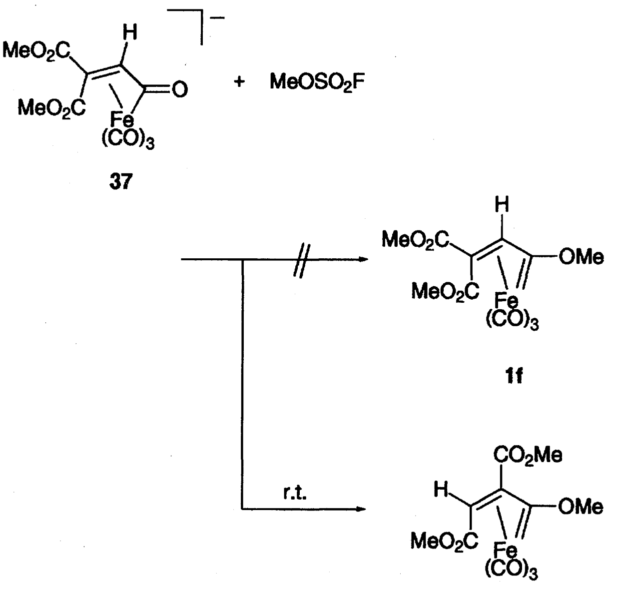
Scheme 8. The reaction of **11** with dimethyl acetylenedicarboxylate.



Scheme 9. Apparent 1,2-shift of the methoxycarbonyl group on the methoxy vinylcarbene complexes **1a** and **1f**. The asterisk * shows the carbene carbon in **1a**.



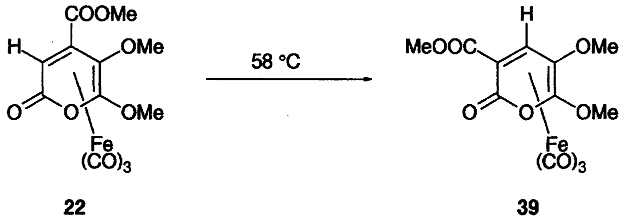
Scheme 10. Preparation of the μ-vinylcarbene(*Fe–Fe*) complex.



(24)

The reaction would proceed via a methoxyfuran complex **38** by the nucleophilic attack of the carbonyl oxygen of the methoxycarbonyl group to the carbene carbon (Scheme 9).[17]

In fact, methoxyfuran is the precursor of the vinylcarbene ligand (see below). The reaction is reversible. In Eqs. 23 and 24, the reverse reaction of that illustrated in Scheme 9 occurs to form the rearranged cyclopentadiene complex **36**.

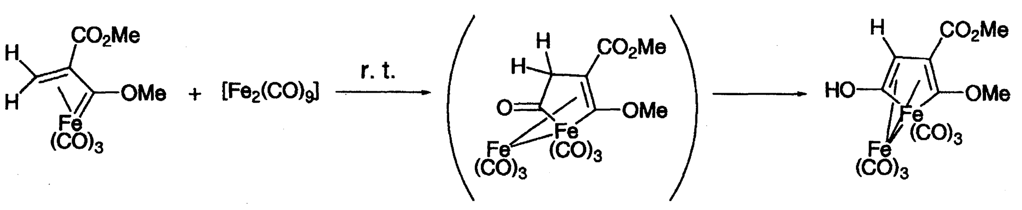


(25)

The 1,2-shift of the methoxycarbonyl group was also observed in the rearrangement of η^4-pyrone complex **22** to **39**.[17] The pyrone complex **22**, which was derived from **1a** by carbonylation and annulation, rearranges to **39** at 58 °C. This reaction is reasonably explained to proceed via the rearrangement from **1a** to **1f** (Scheme 9).

4.5. Dinuclear μ-Vinylcarbene Complexes from η^3-Vinylcarbene Complexes. The η^3-vinylcarbene complex **1** reacts with low valent metal complexes to give novel dinuclear μ-vinylcarbene complexes. The complex **1a** reacts with $[Fe_2(CO)_9]$ to give (μ-vinylcarbene)(*Fe–Fe*) or (η^3 : η^1-allyl)(*Fe–Fe*) **40a**.[20,21] The structure of **40a** was confirmed by X-ray analysis.[21] The reaction is regarded to be the coordination of **1a** to $Fe(CO)_3$ moiety through the carbene–iron double bond and the methoxycarbonyl group (Scheme 10).

The reaction of the η^3-vinylcarbene complex **1b**, which has no methoxycarbonyl group on the 3-position, with $[Fe_2(CO)_9]$ gives ferracyclopenta-2,4-diene(*Fe–Fe*) complex **42** (Scheme 11).[21] The mechanism of the formation of **42** is explained as follows. In the absence of an electron-withdrawing group on the 3-position in **1b**, carbonylation of

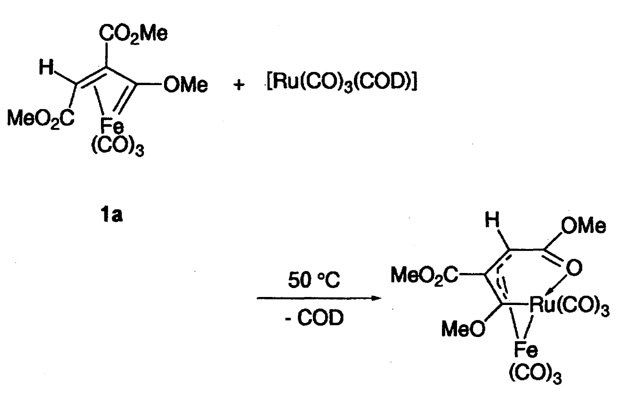


1b **41** **42**

Scheme 11. Formation of the ferrole derivative **42** from η^3-vinylcarbene complex **1b**.

the vinylcarbene occurs on the 3-position to give dinuclear ferracyclopentenone derivative **41**, followed by the 1,3-proton shift to gives **42**. These results show that the substituents on the 3-position of the vinylcarbene ligand controls the reaction again. The methoxycarbonyl group suppresses the carbonylation reaction to give **40**.

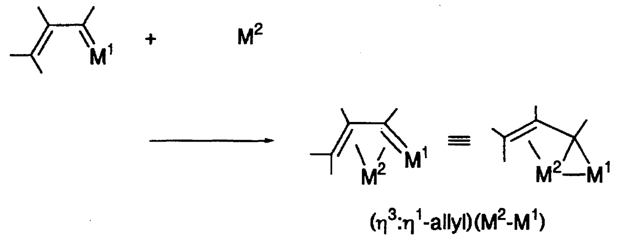
The complex **1a** reacts with [Ru(CO)$_3$(COD)] [COD: 1,5-cyclooctadiene] to give a heterobinuclear complex (μ-vinylcarbene)(*Fe–Ru*) or (η^3 : η^1-allyl)(*Fe–Ru*) **43**.[23]



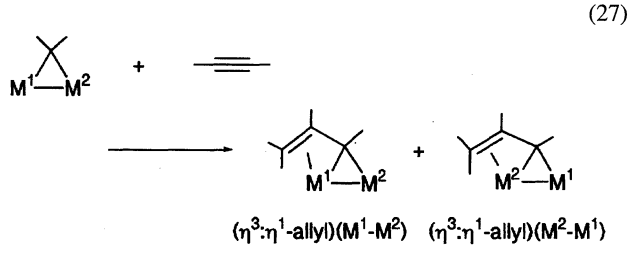
1a **43**

(26)

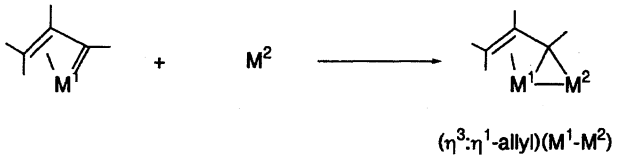
Two representative methods for the preparation of a hetero-binuclear μ-vinylcarbene complex have been reported. One is the reaction of (η^1-vinylcarbene)M^1 with unsaturated metal complex M^2 [95,96] (Eq. 27) and the other is the reaction of μ-methylene(M^1–M^2) with acetylene (Eq. 28).[97]



(27)



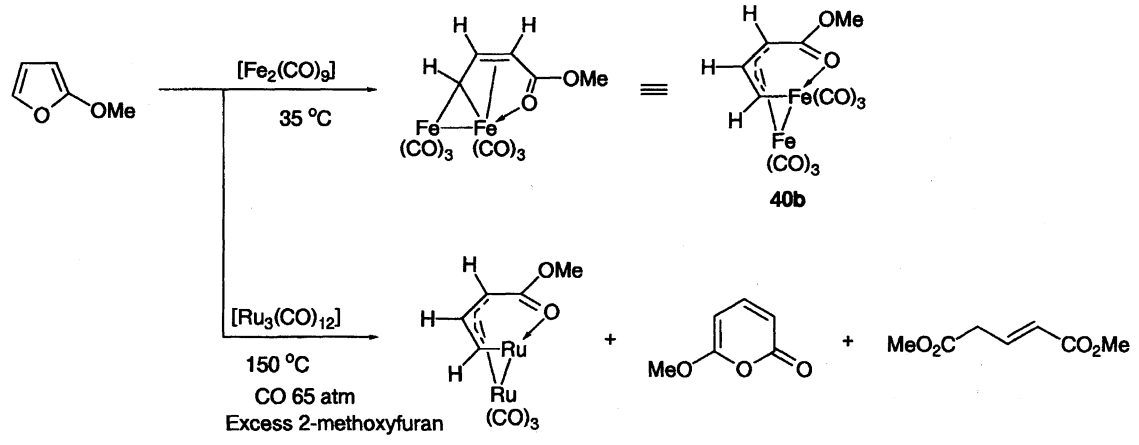
(28)



(29)

By these methods, however, (η^3 : η^1-allyl)(M^1–M^2) could not be synthesized selectively. The reaction of the η^3-vinylcarbene complex **1** with unsaturated complex M^2, provides a tool for the selective preparation of (η^3 : η^1-allyl)(M^1–M^2) (Eq. 29).[23]

Complex **43** reacts with acetylene to give a (η^4-ruthenacyclohexadiene)iron(*Ru–Fe*) complex **45**[55] (Eq. 30). The acetylene inserts between the ruthenium–carbon bond. This



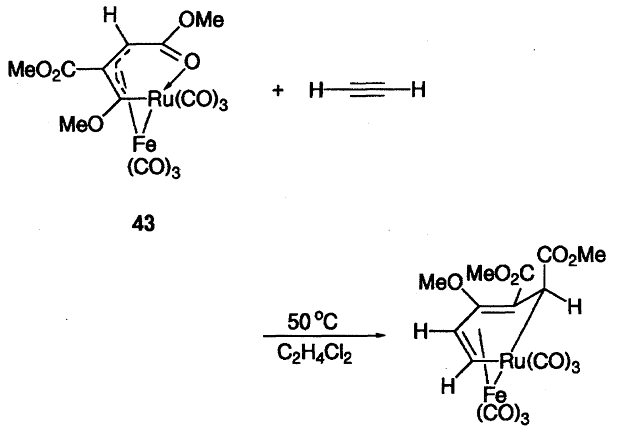
40b

44

Scheme 12. Reactions of 2-methoxyfuran with [Fe$_2$(CO)$_9$] or [Ru$_3$(CO)$_{12}$].

complex **45** would be a precursor of a (η^6-ruthenabenzene)-iron complex.

The reaction of 2-methoxyfuran with $[Fe_2(CO)_9]$ provides a route to a binuclear μ-vinylcarbene complex **40b** (Scheme 12).



43

45

(30)

The reaction of 2-methoxyfuran with $[Ru_3(CO)_{12}]$ gives the corresponding binuclear complex **44** together with 6-methoxy-2-pyrone and dimethyl glutaconate. These facts show that 2-methoxyfuran is a precursor of a vinylcarbene ligand and also support the reaction mechanism represented by Scheme 9.

5. The Role of the η^3-Vinylcarbene Complex in the Dötz Reaction

As described in the introduction briefly, the η^3-vinylcarbene complex is a key intermediate in the Dötz reaction.[24—26,38—42] The Dötz reaction is a stoichiometric reaction of (α,β-unsaturated-carbene)chromium with acetylenes to give a variety of annelated compounds, such as phenols, naphthols, indenes, cyclopentadienes, cyclohexenones, and cycloheptenones. This reaction is a valuable tool for the synthesis of natural products.[28] The key reaction is the insertion of acetylene into the metal–carbene double bond and the carbonylation of the intermediate to form the (η^4-vinylketene)chromium complex.

Reaction of a carbene complex with acetylene is a fundamental reaction. It had been postulated that the reaction proceeds via a metallacyclobutene, or a η^1-vinylcarbene complex.[28] Recently, P. Hofmann pointed out on the basis of MO calculations that the reaction of a chromium carbene complex with acetylene gives a η^3-vinylcarbene complex directly. They claimed the route to metallacyclobutene is unfavorable for Group 6 metals. The most stable route is the direct formation of a η^3-vinylcarbene complex. This result is now widely accepted by organic chemists, and the mechanism of the Dötz reaction is now explained via η^3-vinylcarbene complexes. The carbonylation of the η^3-vinylcarbene complex giving η^4-vinylketene complex can be fully understood by the carbonylation of iron complexes.[12]

The stability of the isolated η^3-vinylcarbene Fe, W, and Re complexes was also examined by MO calculation. Results showed the reasonable stability of these η^3-vinylcarbene complexes. Further, it was found that the structure should be represented by the resonance hybrid of the structures (**A**) and (**B**) in Fig. 1.

Quite recently, Hess, Dötz and their co-worker performed the density functional study on the benzannulation and cyclopentannulation in a chromium complex.[26] They found that the rate determining step of these annulation reactions is the dissociation of the cis carbon monoxide of the carbene carbon. They also found that the coupling of the coordinated carbene and alkyne on Cr gives the η^3-vinylcarbene complex.

6. Conclusion

The review of the chemistry of the thirteen kinds of isolated η^3-vinylcarbene transition-metal complexes exhibited the characteristic profiles of the complexes.

The methods for the preparation of the η^3-vinylcarbene complexes are still limited. The complexes are prepared by 1) the alkylation of (η^3-acryloyl)tricarbonylferrate, 2) the treatment of cyclopropenes with $[Fe_2(CO)_9]$, 3) the insertion of acetylenes into a carbene–metal double bond, 4) the reaction of carbyne complexes with allyl bromides, 5) the reaction of acetylene with $[ReCl_3(Me_5C_5)]_2$, and 6) the thermal decarbonylation reaction of (η^1-vinylcarbene)pentacarbonylchromium.

The structures of the η^3-vinylcarbene complexes, which have been determined by X-ray analyses, are represented by the hybrid of the resonance structures (**A**) and (**B**). The contribution of the two structures was very sensitive to the respective ML_n fragments.

The η^3-vinylcarbene complexes showed versatile reactivity. The carbene carbons of the Fischer-type η^3-vinylcarbene complexes are electrophilic. $[Fe(\eta^3\text{-vinylcarbene})(CO)_3]$ (**1**) is a parent complex of a series of various complexes such as η^4-vinylketene, η^4-vinylketenimine, ferracyclopentenones, η^4-1,3-butadiene, η^4-pyrone, η^3-allyl, η^4-difluorotrimethylenemethane, η^4-cyclopentadiene single metal complexes, and dinuclear complexes, ($\eta^3:\eta^1$-allyl)(M^1–M^2), ferroles, and $[Fe(\eta^4\text{-metallacyclohexadiene})(CO)_3]$.

Formation of a η^3-vinylcarbene complex by the reaction of a carbene complex with acetylene and its subsequent carbonylation is the essential pathway of the Dötz reaction.

It should be noted that the metals in the isolated η^3-vinylcarbene complexes are still limited to Fe, Cr, W, and Re. Application for other metals will promise novel progress of this field; remarkable development of the annulation reactions is expected. Application of the η^3-vinylcarbene complexes for the synthesis of metallacycles will be expanded in the near future.

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T. Kondo, and K. Fujita, and Mrs. T. Sasaki, K. Watanabe, K. Kafuku, K. Ito, and T. Suzuki for collaboration in the studies on the η^3-vinylcarbene complexes.

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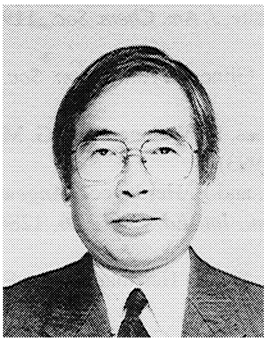

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