ELSEVIER

Journal of Organometallic Chemistry 648 (2002) 164–175

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Reaction of (η^4-cycloheptatriene)Fe(CO)$_3$ with haloketenes: structure and reactivity of the cycloadducts

Shunji Ito [a,*], Ryuji Yokoyama [a], Toyonobu Asao [a], Masataka Watanabe [b], Nobuyuki Harada [b], Noboru Morita [a,*]

[a] *Department of Chemistry, Graduate School of Science, Tohoku University, Aramaki Aza Aoba, Aoba-ku, Sendai 980-8578, Japan*
[b] *Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Katahira 2-1-1, Aoba-ku, Sendai 980-8577, Japan*

Received 23 August 2001; received in revised form 8 November 2001; accepted 9 November 2001

Abstract

Reaction of (η^4-cycloheptatriene)Fe(CO)$_3$ (**1**) with dichloroketene (**2**) generated by treatment of trichloroacetyl chloride with activated zinc, gave a [2 + 2] cycloadduct **3** along with a small amount of σ,π-allyl complex **4** and ε-lactone-type 1:2 adduct **5**. However, **1** reacted with **2** generated by treatment of dichloroacetylchloride with triethylamine to give a 1:2 ester adduct **13** as a main product. Complex **1** also reacted with chloroketene, which was generated by treatment of dichloroacetyl chloride with activated zinc, to give a [2 + 2] cycloadduct **23** in a better yield in comparison with the case of **2**. The cycloadduct **3** was converted to several interesting compounds. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Cycloheptatriene; (η^4-Cycloheptatriene)Fe(CO)$_3$; Dichloroketene; [2 + 2] Cycloaddition; Chloroketene

1. Introduction

The cycloaddition of (η^4-cycloheptatriene)Fe(CO)$_3$ (**1**) [1] with various reagents has been extensively investigated [2]. Goldschmidt reported that **1** reacted with diphenylketene at room temperature to give a [2 + 2] cycloadduct in 25% yield. Furthermore, the [2 + 2] cycloadduct easily undergoes a dyotropic rearrangement to give a [3 + 2] cycloadduct (σ,π-allyliron tricarbonyl complex) [3]. In contrast to the reactivity of **1**, iron-free cycloheptatriene reacted with diphenylketene [4] or bis(trifluoromethyl)ketene [5] in different manners to give a [4 + 2] cycloadduct (at the C=C bond of ketene) or a 1:2 adduct by way of a [4 + 2] cycloadduct (at the C=O bond of ketene). The [2 + 2] cycloadducts of dichloroketene (**2**) to olefines have long attracted attention because they are useful intermediates for the synthesis of novel aromatic compounds, natural products and so on [6]. Therefore, we previously reported that cycloheptatriene reacted with **2** to give a [2 + 2] cycloadduct **18** along with a small amount of 1:2 cycloadduct **20** [7] in contrast to diphenylketene and bis(trifluoromethyl)ketene. The [2 + 2] cycloadduct **18** was found to be useful synthetic precursors for 2*H*-cyclohepta[*b*]furan-2-ones [8] and azulene derivatives [7]. In continuation of this research, we studied the reaction of **1** with **2** under several conditions and the reaction of **1** with chloroketene. We report here a [2 + 2] cycloaddition reaction of **1** with **2** or chloroketene, the structural features of unique 1:2 cycloadducts, and some interesting reactivities of the cycloadducts.

2. Results and discussion

2.1. Reaction of 1 with dichloroketene generated from trichloroacetyl chloride and zinc

At room temperature, **1** reacted with an excess of **2** generated by treatment of trichloroacetyl chloride with activated zinc in dry diethyl ether, to give **3** (55%), **4** (2%) and **5** (3%) as pale yellow crystals (Scheme 1). Column chromatography on neither silica gel nor alumina could be used for separation of the products because they decomposed in the column. They could be

---

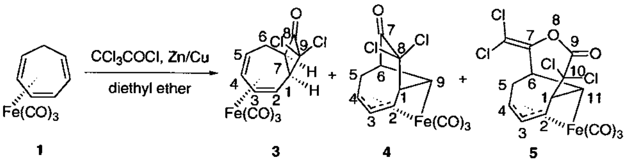
* Corresponding authors. Tel./fax: +81-22-217-7714.
E-mail address: morita@funorg.chem.tohoku.ac.jp (N. Morita).

PII: S0022-328X(01)01472-3

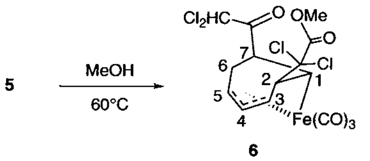
separated by gel permeation chromatography (GPC) using chloroform as an eluent. The structures of the products were determined as follows.

The mass spectra of products **3** and **4** gave the same molecular ion peaks at m/z 342, which exhibits the 1:1 cycloadducts of **2** to **1**. The mass spectrum of product **5** revealed a molecular ion peak at m/z 452, which corresponds to a 2:1 adduct of **2** to **1**.

The characteristic band of the carbonyl stretching absorption for the cyclobutanone moiety of **3** in the IR spectrum was observed at 1806 cm^{-1}. In addition, the typical absorption for the carbonyl ligand showed at 2056, 2051, and 1977 cm^{-1}. The ^{1}H-NMR spectrum of **3** reveals the diene proton signals coordinated to iron at δ 2.99 (H-2), 5.41 (H-3), 5.21 (H-4), and 3.03 (H-5) ppm. The ^{13}C-NMR spectrum reveals carbon signals of the carbonyl groups at δ 209.69 ($Fe(\underline{C}O)_3$) and 194.71 ppm (C-8). On the basis of these observations, the structure of **3** was determined as a [2 + 2] cycloadduct described in Scheme 1. The ^{1}H-NMR and ^{13}C-NMR data shown in Section 4 confirmed the structure of **3**. The decoupling and C, H COSY experiments verified their assignments.



Scheme 1.



Scheme 2.

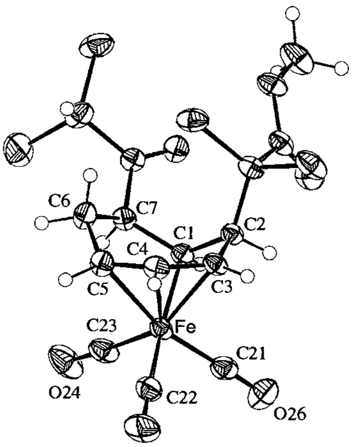


Fig. 1. ORTEP projection of **6** with the atom numbering scheme.

The characteristic carbonyl group absorption of the five-membered ring of **4** appeared at 1766 cm^{-1} in the IR spectrum, in addition to the typical ligand carbonyl absorptions at 2068 and 1992 cm^{-1}. In the ^{1}H-NMR spectrum of **4**, the signals for the characteristic σ,π-allylFe(CO)$_3$ structure [9] appeared at δ 4.57 (H-2), 4.39 (H-3), 4.61 (H-4), and 1.98 (H-9) ppm. On the basis of these observations, the structure of **4** was determined as a [3 + 2] cycloadduct described in Scheme 1.

The ^{1}H-NMR spectrum of **5** exhibited characteristic signals of the σ,π-allylFe(CO)$_3$ structure at δ 4.79 (H-2), 4.68 (H-3), 4.46 (H-4), and 2.02 ppm (H-11), which are similar to those of **4**. The structure for **5** was expected to be an ester or a lactone having a larger ring than the five-membered ring from the IR spectrum ($\nu_{c=o}$1744 cm^{-1}). In addition to these observations, considering the structure of known 1:2 ketene adducts, it was very difficult to estimate the structure of **5**. Suitable crystals of **5** for X-ray crystallographic analysis were not obtained. When **5** was recrystallized from methanol, we found that **5** was converted to the methyl ester **6** in quantitative yield (Scheme 2). Characteristic signals for the σ,π-allyl moiety of irontricarbonyl complexes in the ^{1}H-NMR spectrum of **6** still remained at δ 4.66 (H-3), 4.79 (H-4), 4.65 (H-5), and 2.17 (H-1) ppm and a methyl signal appeared at 3.92 ppm as a singlet. A strong carbonyl absorption band appeared at 1744 cm^{-1} in the IR spectrum. Compound **6** was considered to be a methyl ester bearing a σ,π-allyl structure similar to that of **4** and **5**. These spectroscopic data were not enough to determine the structure of **6** completely.

*2.2. X-ray crystallography of the methyl ester **6***

Since the methyl ester **6** gave suitable single crystals, the structure of **6** was established by X-ray crystallography. The molecular structure drawn by the ORTEP program and the numbering scheme for **6** are shown in Fig. 1. Selected bond lengths and bond angles are listed in Table 1. There were some reports on the X-ray structural analysis of σ,π-allyliron tricarbonyl complexes [2c,2j,9a,9b,9c] such as tricarbonyl[(2,3,4,9-η)-7,7,8,8-tetracyano-3-bicyclo[4.2.1]nonene-2,9-diyl]iron (**7**) [9a] and [(2,3,4,8-η)-bicyclo[3.2.2]nona-3,6-diene-2,8-diyl-9-one]tricarbonyliron (**8**) [9b,9c] and so on (Fig. 2). In comparison with these complexes, the following structural characteristics of **6** were observed. The configuration around the iron atom was approximately octahedral. The ligand carbonyl groups are approximately orthogonal to one another. One of the three ligand carbonyl groups attached to iron extended almost linearly from C(1) attached to iron. The other ligand carbonyl group and C(1) were at almost right angles to iron. The four complexed carbon atoms C(1), C(3), C(4), and C(5) comprised a moderately better plane. The angle at the center of the π-allyl system, C(3)–C(4)–C(5) (126.7°) was a little larger than the values of other similar σ,π-allyl complexes **7** (120.8°) [9a] and **8** (121.3°) [9b]. The angles around the ring were substantially larger than tetrahedral except C(1)–C(2)–C(3). Especially, the angle of C(2)–C(1)–C(7) (122.8°) was characteristically larger than the corresponding angles in **7** (114.9°) and **8** (107.6°). Since complex **6** is not a bridged molecule, there is less strain than in **7** and **8**. The bond lengths of the allylic moiety deviate a little from the double-bond C=C distance. On the basis of structure of **6**, the unique structure of **5** can be determined as shown in Scheme 1. Comparing the proton signals at carbons coordinating to iron in the obtained σ,π-allyl complexes **4**, **5**, and **6**, their signals were slightly shifted to higher field in the order of **6**, **5**, and **4** due to bridged strain.

Table 1
Selected bond lengths (Å) and angles (°) with estimated S.D. in parentheses for **6**

Bond lengths			
Fe–C1	2.115(2)	C1–C2	1.540(3)
Fe–C3	2.154(2)	C2–C3	1.508(3)
Fe–C4	2.080(2)	C3–C4	1.400(3)
Fe–C5	2.125(2)	C4–C5	1.416(3)
Fe–C21	1.789(2)	C5–C6	1.513(3)
Fe–C22	1.814(2)	C6–C7	1.541(3)
Fe–C23	1.775(2)	C1–C7	1.525(3)
C21–O25	1.141(3)	C23–O24	1.143(3)
C22–O26	1.146(3)		
Bond angles			
C2–C1–C7	122.8(2)	C21–Fe–C23	100(1)
C1–C2–C3	104.0(2)	C22–Fe–C23	96.3(1)
C2–C3–C4	124.7(2)	C21–Fe–C22	91.1(1)
C3–C4–C5	126.7(2)	C1–Fe–C23	90.53(9)
C4–C5–C6	127.3(2)	C1–Fe–C22	173.12(9)
C5–C6–C7	112.0(2)	C1–Fe–C21	88.86(9)
C1–C7–C6	112.4(2)	C1–Fe–C3	68.43(7)
C4–Fe–C22	88.90(9)	C1–Fe–C4	86.09(8)
C4–Fe–C23	128.8(1)	C1–Fe–C5	80.04(8)

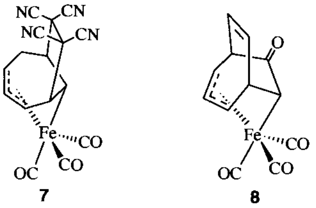
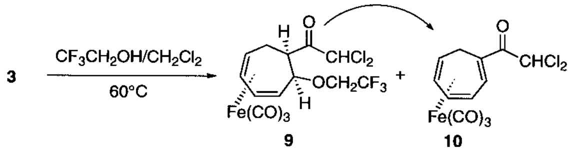
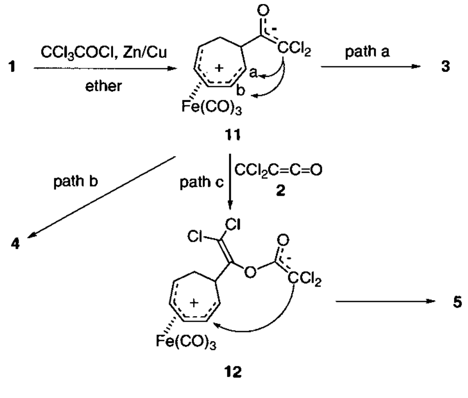


Fig. 2.



Scheme 3.



Scheme 4.

2.3. *Reaction mechanism of* **1** *with dichloroketene generated from trichloroacetyl chloride and zinc*

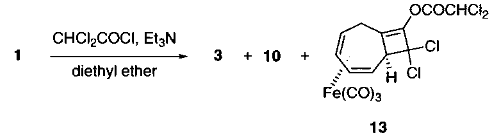
This type of the 1:2 adduct **5** was the first example in cycloaddition of ketenes to olefins. The adduct **3** did not react with trichloroacetyl chloride in the presence of zinc in contrast to the iron free [2 + 2] cycloadduct **18** [7]. When **1** reacted with excess of **2** at reflux temperature in dry diethyl ether for 14 h, the yields of **4** and **5** slightly increased to 8 and 6%, respectively. But the cycloadduct **3** was still the main product (30%).

Complex **3** did not undergo a dyotropic rearrangement [3a,10] to **4** in contrast to the case of **1** or tricarbonyl[(1,2,3,4-η)-3,7,7-trimethylcycloheptatriene]-iron and diphenylketene adducts [3]. A solution of **3** in trifluoroethanol was heated at 60 °C for 1 h, which was the same condition for the dyotropic rearrangement [3d] of 1:1 cycloadducts of diphenylketene and methylphenylketene to **1**, to give **9** and **10** in 31 and 21% yields, respectively. Although the isomerization of **3** to **10** via a η^5-cycloheptadienyl cationic iron complex was possible, another isomerization by way of **10** could be considered. Indeed, complex **9** was heated at 60 °C for 24 h in the same solvent to give **10** in 45% yield (Scheme 3). Complex **10** could also be prepared by Friedel–Crafts reaction of **1** with dichloroacetyl chloride in the presence of aluminum trichloride.

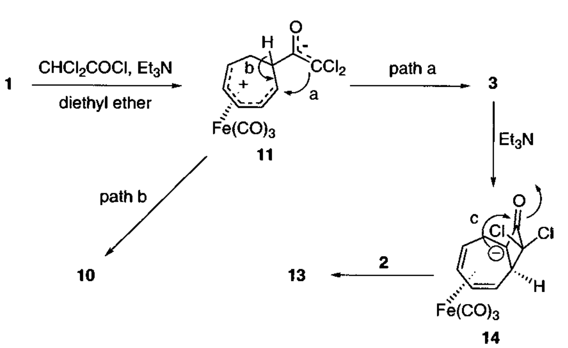
Since the dienium group by coordination to irontricarbonyl was known to be stabilized [2g,2i,2n] and σ,π-allyl complexes could not be obtained from **3**, and moreover, the new type of 1:2 adduct **5** was obtained in the reaction of **1** with **2**, the formation of **3**–**5** is assumed to be stepwise. Namely, the reaction of **1** with **2** generated a dipole intermediate **11** as shown in Scheme 4. The dipole intermediate **11** was converted to **3** and **4** by path a and path b, respectively. The intermediate **11** could be stable enough to undergo electrophilic attack of another **2** to give a new dipole intermediate **12**, followed by the ring closure to give the 1:2 adduct **5** (path c). The reaction was significantly dependent on the solvents. When this reaction was carried out in dry benzene or dry hexane, a solid product to which **1** was converted could be obtained instead of the cycloadducts **3**–**5**. However, the structure of this product was not clear yet. The solvent effects supported a nonconcerted stepwise mechanism.

*2.4. Reaction of **1** with dichloroketene came from dichloroacetyl chloride and triethylamine*

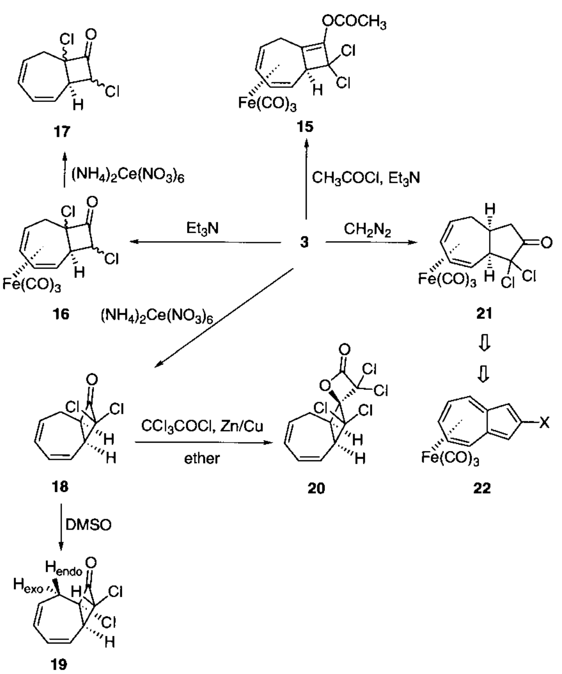
The reaction of **1** with an excess of **2**, which was generated by treatment of dichloroacetyl chloride with triethylamine, gave three products which were separated by GPC to afford **3** (8%), **10** (10%), and **13** (47%) (Scheme 5).



Scheme 5.



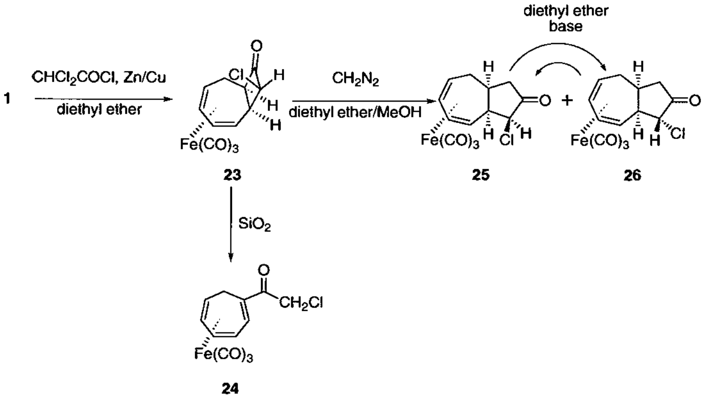
Scheme 6.



Scheme 7.

The molecular ion peak (*m*/*z* 342) of **13** reveals that it is a 1:2 adduct of **1** to **2**. There are characteristic carbonyl absorptions of the ester group at 1802 and 1725 cm^{-1} in the IR spectrum. In the ^{1}H-NMR spectrum, a methine proton (H-1) and a dichloromethyl proton ($OCOC\underline{H}Cl_2$) both appear as a singlet at δ 3.52 and 6.08 ppm, respectively. On the basis of these spectroscopic data, the structure of **13** was established as shown in Scheme 5. The reaction of a large excess of **1** with dichloroacetyl chloride in the presence of triethylamine gave **13** as a main product. A solution of triethylamine in THF was added dropwise to a solution of **3** and dichloroacetyl chloride in THF to give **13** without **10**. It has previously been reported that the iron-free [2 + 2] cycloadduct **18** reacted with dichloroketene generated from trichloroacetyl chloride and activated zinc, to give a different 1:2 adduct **20** as shown in Scheme 7 [7]. A plausible mechanism of the formation of **3**, **10** and **13** is depicted in Scheme 6. Under the condition in the presence of triethylamine, **1** reacted with **2** to give a dipole intermediate **11**. The intermediate **11** mainly closed the ring by path a to give the [2 + 2] cycloadduct **3**. At the same time, a small amount of **11** underwent deprotonation by triethylamine to give **10** by path b. The ring juncture proton adjacent to the carbonyl group of **3** was easily abstracted by triethylamine to give a carbanion **14** which tautomerized to give an enolate. The resulting enolate reacted with another dichloroketene to give **13**. Actually, the [2 + 2] cycloadduct **3** underwent acetylation with acetyl chloride in the presence of triethylamine to give an acetate **15** in 95% yield.

When the [2 + 2] cycloadduct **3** was treated with triethylamine in dry diethyl ether, the chlorine atom at C-9 migrated to C-7 to give an isomer **16**. We could not determine the configuration at C-7 and C-9 in **16** by comparing coupling constants and NOE experiments. Compound **16** was treated with cerium(IV) ammonium nitrate to give an iron-free compound **17**. On the other hand, treatment of **3** with cerium(IV) ammonium nitrate gave the corresponding free ligand **18** in 54% yield [7]. Compound **18** was also converted in DMSO at 65 °C to another isomer **19**, in which the chlorine atom also migrated from C-9 to C-7. Since irradiation of H-9 in **19** gave NOE enhancement in the signal for H-6_{endo}, the stereochemistry at C-7 and C-9 in **19** was established as shown in Scheme 7. Three possibilities regarding the structure of **17** still remained. Therefore, we endeavored to make a single crystal for X-ray crystallographic analysis but have not yet succeeded. At least, these chlorine rearrangements in **3** and **18** proceeded regio- and stereospecifically. Compound **3** reacted with diazomethane to give tricarbonyl[(2,3,4,5-η)-10,10-



Scheme 8.

dichloro-2,4-bicyclo[5.3.0]-deca-2,4-dien-9-one]iron (**21**) in 75% yield which would open up a convenient route to azulenoid compounds as shown in Scheme 7. The development of synthetic methods of unknown azulenoid irontricarbonyl mononuclear complexes such as **22** from **3** is currently underway and will be reported in due course.

2.5. Reaction of **1** with chloroketene

In order to investigate further the scope and limitations of the [2 + 2] cycloaddition between **1** and haloketenes, we turned our attention to the reaction of **1** with chloroketene. As a result, complex **1** did not react with chloroacetyl chloride in the presence of triethylamine, but it reacted with dichloroacetyl chloride in the presence of activated zinc to give a [2 + 2] *endo*-chloro cycloadduct **23** in 78% yield, stereospecifically. The cycloadduct **23** converted to **24** in the presence of silica gel by ring cleavage. The cycloadduct **23** also reacted with diazomethane to give a mixture of two stereoisomers, tricarbonyl[(2,3,4,5-η)-10-*endo*-chlorobicyclo[5.3.0]deca-2,4-dien-9-one]iron (**25**) and 10-*exo*-chloro derivative **26** in 19 and 30% yields, respectively. The ethereal solution of diazomethane was usually dried over potassium hydroxide pellets before using it [11]. When isomers **25** and **26** were dissolved in diethyl ether, the isomerization did not occur. However, we found that the isomerization between **25** and **26** occurred in the diethyl ether which was treated with potassium hydroxide pellets. Thus, the isomerization easily proceeded by a base. This isomerization reached equilibrium in a ratio of **25**:**26** = 1.0:1.8 (Scheme 8).

3. Conclusion

The expected [2 + 2] cycloadduct **3** was obtained by the reaction of **1** with trichloroacetyl chloride in the presence of activated zinc. A small amount of [3 + 2] cycloadduct **4** and unique 1:2 adduct **5** was also obtained. Complex **1** reacted with dichloroacetyl chloride in the presence of triethylamine to give the enol ester 1:2 adduct **13** as a main product. The [2 + 2] cycloadduct **3** easily converted to enol form in the presence of triethylamine and reacted further with another dichloroketene to give **13**. The [2 + 2] cycloadduct of **1** with chloroketene was also obtained in good yield by the reaction of **1** with dichloroacetyl chloride in the presence of activated zinc. The [2 + 2] cycloadducts **3** and **18** underwent chlorine atom migration in a different way. Furthermore, the [2 + 2] cycloadducts **3** and **23** underwent known ring cleavage and ring enlargement reaction at the four-membered ring without a dyotropic rearrangement.

4. Experimental

4.1. General

Melting points were determined on a Yanagimoto micro melting point apparatus MP-S3 and are uncorrected. Mass spectra were obtained with a JEOL HX-110 or a Hitachi M-2500 instrument usually at 70 eV. IR and UV spectra were measured on a Shimadzu FTIR-8100M and a Hitachi U-3410 spectrophotometer, respectively. ^{1}H-NMR spectra (^{13}C-NMR spectra) were recorded on a JEOL GSX 400 at 400 MHz (100 MHz), a Bruker AM 600, or a JEOL Lambda 600 spectrometer at 600 MHz (150 MHz). Column chromatography was performed on silica gel (Kieselgel 60). GPC was performed on a TSKgel G2000H$_6$. Elemental analyses were performed at the Instrumental Analysis Center of Chemistry, Graduate School of Science, Tohoku University.

*4.2. Reaction of (η^4-cycloheptatriene)$Fe(CO)_3$ (**1**) with dichloroketene (**2**) generated from trichloroacetyl chloride and zinc*

A solution of trichloroacetyl chloride (237 mg, 1.02 mmol) in dry Et_2O (10 ml) was added dropwise at room temperature (r.t.) to a mixture of activated zinc powder (682 mg, 10.4 matom) and (η^4-cycloheptatriene)-$Fe(CO)_3$ (**1**) (237 mg, 1.02 mmol) in dry Et_2O (20 ml) over a period of 2 h. After stirring the mixture for another 2 h, residual zinc powder was removed by filtration. The filtrate was washed with water and 5% aqueous $NaHCO_3$, dried over $MgSO_4$, and concentrated under reduced pressure. The products were separated by GPC with $CHCl_3$ to give tricarbonyl[(2,3,4,5-η)-9,9-dichlorobicyclo[5.2.0]nona-2,4-dien-8-one]iron (**3**) (188 mg, 55%), tricarbonyl[(2,3,4,9-η)-8,8-dichloro-3-bicyclo[4.2.1]nonene-2,9-diyl-7-one]iron (**4**) (4.7 mg, 2%), and tricarbonyl[(2,3,4,11-η)-10,10-dichloro-7-dichloromethylene-8-oxa-3-bicyclo[4.4.1]undecene-2,11-diyl-9-one]iron (**5**) (15 mg, 3%).

3: Yellow crystals; m.p. 78.5–79.0 °C; MS (70 eV) m/z (rel. intensity) 346 ($M^+ + 4$, 1), 344 ($M^+ + 2$, 7), 342 (M^+, 11), 314 ($M^+ - CO$, 37), 286 ($M^+ - 2CO$, 31), 223 (5), 194 (12), 158 (15), 148 (9), 131 (62), 104 (100), 91 (20), 78 (29), 70 (10), and 56 (20); UV–Vis (MeOH) λ_{max}, nm ($\log \varepsilon$) 242 sh (4.04) and 290 sh (3.47); IR (KBr disk) ν_{max} 2986 (w), 2946 (w), 2897 (w), 2845 (w), 2056 (s), 2051 (s), 1977 (s), 1806 (s), 1449 (w), 1435 (w), 1408 (w), 1366 (m), 1350 (w), 1314 (m), 1111 (w), 1021 (w), 945 (m), 926 (w), 904 (m), 789 (w), 768 (m), 747 (m), 642 (m), 631 (m), 615 (s), 607 (s), 561 (s), 515 (m), 482 (m), and 453 (w) cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) $\delta = 5.41$ (dd, $J = 7.5$, 5.3 Hz, H-3), 5.21 (dd, $J = 8.0$, 5.3 Hz, H-4), 3.89 (dd, $J = 10.7$, 8.5 Hz, H-7), 3.35 (dd, $J = 10.7$, 4.4 Hz, H-1), 3.03 (m, H-5), 2.99 (dd, $J = 7.5$, 4.4 Hz, H-2), 2.49 (dd, $J = 17.8$, 5.0 Hz, H-6), and 2.19 (ddd, $J = 17.8$, 8.5, 2.7 Hz, H-6); ^{13}C-NMR (150 MHz, $CDCl_3$) $\delta = 209.69$ ($Fe(\underline{C}O)_3$), 194.71 (C-8), 90.78 (C-4), 87.92 (C-9), 87.59 (C-3), 57.01 (C-5), 53.71 (C-2), 51.10 (C-7), 47.18 (C-1), and 22.33 (C-6). Anal. Found: C, 42.06; H, 2.63. Calc. for $C_{12}H_8Cl_2FeO_4$: C, 42.08; H, 2.35%.

4: Yellow crystals; m.p. 105.0 °C (decomp.); MS (70 eV) m/z (rel. intensity) 346 ($M^+ + 4$, 3), 344 ($M^+ + 2$, 19), 342 (M^+, 29), 314 ($M^+ - CO$, 24), 286 ($M^+ - 2CO$, 38), 258 ($M^+ - 3CO$, 19), 222 (10), 194 (18), 186 (5), 167 (6), 158 (19), 148 (7), 131 (78), 115 (9), 104 (100), 91 (27), 78 (48), 70 (11), 63 (7), and 56 (31); UV–Vis (MeOH) λ_{max}, nm ($\log \varepsilon$) 269 (4.78); IR (KBr disk) ν_{max} 2068 (s), 1992 (s), 1766 (m), 1456 (w), 1336 (w), 1122 (w), 928 (w), 882 (w), 858 (w), 830 (w), 808 (w), 762 (w), 698 (w), 666 (w), 612 (m), 600 (m), 588 (m), 564 (m), 520 (w), 504 (w), and 484 (w) cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) $\delta = 4.61$ (ddd, $J = 9.5$, 3.5, 1.4 Hz, H-4), 4.57 (ddd, $J = 7.7$, 6.2, 1.8 Hz, H-2), 4.39 (ddd, $J = 9.5$, 7.7, 0.7 Hz, H-3), 3.67 (dd, $J = 7.0$, 6.2 Hz, H-1), 2.85 (ddd, $J = 16.5$, 10.8, 3.5 Hz, H-5), 2.76 (ddd, $J = 16.5$, 1.4, 0.7 Hz, H-5), 2.73 (dd, $J =$ 10.8, 8.8 Hz, H-6), and 1.98 (ddd, $J = 8.8$, 7.0, 1.8 Hz, H-9); ^{13}C-NMR (150 MHz, $CDCl_3$) $\delta = 212.89$ ($Fe(\underline{C}O)_3$), 210.88 ($Fe(CO)_3$), 205.08 (C-7), 201.79 ($Fe(CO)_3$), 98.79 (C-3), 86.25 (C-8), 77.11 (C-4), 62.96 (C-2), 58.12 (C-1), 43.50 (C-6), 40.13 (C-5), and 18.76 (C-9). Found: C, 41.79; H, 2.30; Cl, 20.70%. Anal. Calc. for $C_{12}H_8Cl_2FeO_4$: C, 42.08; H, 2.35; Cl, 20.70.

5: Yellow crystals; m.p. 126.0–126.5 °C; MS (70 eV) m/z (rel. intensity) 458 ($M^+ + 6$, 10), 456 ($M^+ + 4$, 34), 454 ($M^+ + 2$, 70), 452 (M^+, 52), 424 ($M^+ - CO$, 5), 396 ($M^+ - 2CO$, 15), 368 ($M^+ - 3CO$, 5), 333 (5), 306 (6), 242 (28), 216 (36), 207 (72), 179 (75), 151 (37), 128 (26), 115 (100), 105 (62), 91 (55), 77 (52), 65 (17), and 56 (33); UV–Vis (MeOH) λ_{max}, nm ($\log \varepsilon$) 250 sh (4.02) and 325 (3.13); IR (KBr disk) ν_{max} 2060 (s), 2002 (s), 1983 (s), 1744 (s), 1439 (m), 1348 (m), 1302 (m), 1262 (s), 1182 (w), 1063 (m), 994 (m), 976 (w), 918 (w), 897 (w), 878 (w), 866 (w), 779 (m), 758 (w), 745 (w), 716 (m), 687 (w), 656 (m), 646 (m), 627 (m), 610 (s), 590 (m), 578 (m), 559 (m), 525 (m), 502 (w), and 478 (w) cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) $\delta = 4.79$ (t, $J = 7.3$ Hz, H-2), 4.68 (t, $J = 7.3$ Hz, H-3), 4.46 (t, $J = 7.3$ Hz, H-4), 3.67 (dt, $J = 12.0$, 6.3 Hz, H-6), 3.54 (dd, $J = 7.3$, 6.3 Hz, H-1), 2.73 (ddd, $J = 16.1$, 12.0, 7.3 Hz, H-5), 2.21 (dd, $J = 16.1$, 6.1 Hz, H-5), and 2.02 (t, $J = 6.3$ Hz, H-11); ^{13}C-NMR (100 MHz, $CDCl_3$) $\delta = 212.44$ ($Fe(\underline{C}O)_3$), 210.47 ($Fe(\underline{C}O)_3$), 201.75 ($Fe(\underline{C}O)_3$), 159.99 (C-9), 145.44 ($C{=}\underline{C}Cl_2$), 112.78 (C-7), 100.54 (C-3), 86.45 (C-10), 72.78 (C-4), 64.85 (C-2), 56.53 (C-1), 46.45 (C-6), 31.05 (C-5), and 24.39 (C-11). Anal. Found: C, 37.05, H, 1.93. Calc. for $C_{14}H_8Cl_4FeO_5$: C, 37.18; H, 1.78%.

*4.3. Methanolysis of **5***

A solution of **5** (8.0 mg, 0.018 mmol) in MeOH (20 ml) was stirred at 60 °C for 2 h. After the solvent was removed under reduced pressure, tricarbonyl[(3,4,5,1-η)-7-(dichloromethylcarbonyl)-2-methoxycarbonyldichloromethyl-4-cycloheptene-1,3-diyl]iron (**6**) was obtained quantitatively.

6: Colorless crystals; m.p. 111.0–111.5 °C (decomp.); MS (70 eV) m/z (rel. intensity) 425 ($M^+ - CO_2Me$, 0.5), 402 (7), 358 (22), 343 (75), 330 (8), 315 (13), 289 (23), 275 (5), 261 (24), 239 (26), 207 (25), 197 (18), 179 (26), 163 (41), 145 (37), 131 (41), 115 (100), 103 (65), 91 (91), 77 (55), and 59 (37); UV–Vis (MeOH) λ_{max}, nm ($\log \varepsilon$) 250 sh (4.18) and 312 sh (3.47); IR (KBr disk) ν_{max} 2058 (s), 2002 (s), 1985 (s), 1744 (s), 1449 (w), 1439 (w), 1271 (m), 1262 (m), 1063 (w), 994 (w), 880 (w), 866 (w), 779 (w), 758 (w), 745 (w), 716 (m), 687 (w), 656 (w), 646 (w), 630 (m), 609 (m), 590 (m), 578 (m), 559 (w), 525 (w), 502 (w), and 478(w) cm^{-1}; ^{1}H-NMR (600

MHz, $CDCl_3$) $\delta = 6.12$ (s, $C\underline{H}Cl_2$), 4.79 (t, $J = 8.0$ Hz, H-4), 4.66 (t, $J = 8.0$ Hz, H-3), 4.65 (dd, $J = 8.8$, 8.0 Hz, H-5), 4.01 (dd, $J = 8.0$, 6.2 Hz, H-2), 3.92 (s, $OC\underline{H}_3$), 3.55 (td, $J = 9.2$, 4.0 Hz, H-7), 2.85 (dd, $J = 14.3$, 9.2 Hz, H-6), 2.73 (ddd, $J = 14.3$, 9.2, 8.8 Hz, H-6), and 2.17 (dd, $J = 6.2$, 4.0 Hz, H-1); ^{13}C-NMR (150 MHz, $CDCl_3$) $\delta = 195.11$ ($\underline{C}OCHCl_2$), 165.35 ($CCl_2\underline{C}O_2CH_3$), 100.97 (C-4), 85.11 ($\underline{C}Cl_2CO_2CH_3$), 72.99 (C-3), 69.05 ($CO\underline{C}HCl_2$), 62.19 (C-1), 57.09 (C-2), 57.03 (C-7), 54.42 ($CO_2\underline{C}H_3$), 29.10 (C-6), and 25.44 (C-1). Anal. Found: C, 37.13, H, 2.48. Calc. for $C_{15}H_{12}Cl_4FeO_6$: C, 37.08; H, 2.49%.

4.4. Crystal structure determination of **6**

Single crystals of **6** were grown from MeOH. Crystal data and details of the structure determination are provided in Table 2.

4.5. Ring cleavage of **3** with trifluoroethanol

A solution of **3** (347 mg, 1.01 mmol) in trifluoroethanol (30 ml) and CH_2Cl_2 (2 ml) was stirred at 60 °C for 1 h. After the solvent was removed under reduced pressure, the reaction mixture was separated by medium-pressure liquid chromatography on silica gel with EtOAc–hexane (5:95) to give tricarbonyl[(1,2,3,4-η)-6-dichloromethylcarbonyl-5-(2,2,2-trifluoro)ethoxycyclohepta-1,3-diene]iron (**9**) (133 mg, 31%) and tricarbonyl[(1,2,3,4-η)-6-dichloromethylcarbonylcycloheptatriene]iron (**10**) (74 mg, 21%).

9: Yellow crystals; m.p. 61.0–62.0 °C; MS (70 eV) m/z (rel. intensity) 442 (M^+, 0.7), 414 ($M^+ - CO$, 14), 358 ($M^+ - 3CO$, 11), 278 (8), 247 (6), 232 (42), 204 (46), 168 (18), 147 (17), 133 (35), 115 (26), 105 (100), 91 (76), 77 (16), 65 (10), and 56 (13); UV–Vis (MeOH) λ_{max}, nm (log ε) 219 sh (4.35) and 329 sh (3.30); IR (neat) ν_{max} 2053 (s), 1991 (s), 1966 (s), 1728 (m), 1460 (w), 1447 (w), 1406 (w), 1356 (w), 1343 (w), 1316 (m), 1281 (m), 1215 (m), 1183 (m), 1171 (m), 1144 (s), 1136 (s), 1121 (m), 1103 (m), 1055 (w), 984 (m), 889 (w), 831 (w), 795 (m), 769 (w), 696 (m), 679 (w), 658 (w), 637 (w), 618 (s), 585 (m), 567 (m), 556 (m), 534 (w), 515 (m), 486 (w), 465 (w), and 405 (w) cm^{-1}; ^1H-NMR (400 MHz, $CDCl_3$) $\delta = 5.88$ (s, $COC\underline{H}Cl_2$), 5.55 (dd, $J = 6.8$, 4.8 Hz, H-3), 5.44 (dd, $J = 7.6$, 4.8 Hz, H-2), 3.96 (dd, $J = 12.4$, 3.6 Hz, H-6), 3.83 (q, $J = 8.8$ Hz, $OC\underline{H}_2CF_3$), 3.65 (dd, $J = 12.4$, 3.2 Hz, H-5), 2.95 (d, $J = 6.8$ Hz, H-4), 2.78 (d, $J = 7.6$ Hz, H-1), 1.80 (ddd, $J = 12.4$, 3.6, 3.2 Hz, H-7), and 1.34 (q, $J = 12.4$ Hz, H-7); ^{13}C-NMR (100 MHz, $CDCl_3$) $\delta = 209.37$ ($Fe(\underline{C}O)_3$), 196.10 ($\underline{C}OCHCl_2$), 123.76 ($OCH_2\underline{C}F_3$), 89.37 (C-3), 88.79 (C-2), 79.89 (C-5), 68.82 ($CO\underline{C}HCl_2$), 65.82 ($O\underline{C}H_2CF_3$), 56.36 (C-1), 54.88 (C-4), 45.70 (C-6), and 31.73 (C-7). Anal. Found: C, 37.77; H, 2.51; Cl, 15.89. Calc. for $C_{14}H_{11}Cl_2F_3FeO_5$: C, 37.96; H, 2.50; Cl, 16.01%.

10: Yellow powder; m.p. 117.0 °C (decomp.); MS (70 eV) m/z (rel. intensity) 314 ($M^+ - CO$, 22), 286 ($M^+ - 2CO$, 42), 258 ($M^+ - 3CO$, 35), 223 (7), 194 (13), 182 (28), 158 (12), 131 (100), 115 (53), 104 (94), 91 (86), 84 (14), 77 (28), 65 (23), and 56 (32); UV–Vis (MeOH) λ_{max}, nm (log ε) 304 sh (3.83) and 346 sh (3.86); IR (KBr disk) λ_{max} 3029 (w), 2064 (s), 1993 (s), 1979 (s), 1655 (m), 1615 (m), 1588 (w), 1443 (w), 1414 (w), 1402 (w), 1223 (m), 1186 (m), 872 (w), 789 (w), 725 (w), 648 (w), 627 (w), 617 (m), 600 (m), 552 (m), and 465 (w) cm^{-1}; ^1H-NMR (600 MHz, $CDCl_3$) $\delta = 7.43$ (dd, $J = 8.6$, 1.8 Hz, H-5), 6.40 (s, $COC\underline{H}Cl_2$), 5.53 (td, $J = 5.3$, 1.8 Hz, H-3), 5.45 (dd, $J = 7.5$, 5.3 Hz, H-2), 3.58 (m, H-1), 3.12 (dd, $J = 8.6$, 5.3 Hz, H-4), 2.78 (dd, $J = 21.7$, 5.2 Hz, H-7), and 2.39 (d, $J = 21.7$ Hz, H-7); ^{13}C-NMR (150 MHz, $CDCl_3$) $\delta = 209.41$ ($Fe(\underline{C}O)_3$), 185.15 ($\underline{C}OCHCl_2$), 148.40 (C-5), 129.33 (C-6), 94.78 (C-3), 89.20 (C-2), 66.62 ($CO\underline{C}HCl_2$), 59.95 (C-1), 53.11 (C-4), and 29.07 (C-7). Anal. Found: C, 41.82; H, 2.41; Cl, 20.89. Calc. for $C_{12}H_8Cl_2FeO_4$: C, 42.03; H, 2.35; Cl, 20.68%.

4.6. Elimination of trifluoroethanol from **9**

A solution of **9** (52 mg, 0.12 mmol) in trifluoroethanol (10 ml) was stirred at 60 °C for 24 h. After the

Table 2
Crystal data for **6**

Empirical formula	$C_{15}H_{12}O_6Fe$
Formula weight	485.91
Crystal size (mm)	$0.35 \times 0.30 \times 0.25$
Unit cell dimensions	
a (Å)	15.353(1)
b (Å)	7.615(1)
c (Å)	16.136(1)
(°)	92.405(3)
V (Å^3)	1884.8(2)
Crystal system	Monoclinic
Space group	$P21/c$ (#14)
Z	4
Densities: D_{obs}; D_{calc} (g cm^{-3})	1.68; 1.71
$F(000)$	976
Linear absorption coefficient (cm^{-1})	13.07 (Mo–K$_\alpha$)
Diffractometer used	Mac Science MXC18
Radiation	Mo–K$_\alpha$ ($\lambda = 0.71073$)
Maximum sine $(\theta)/\lambda$	0.660
Total reflections measured	4434
Unique reflections	4171
Internal consistency: R_{int}	0.00
Function minimized was sum $[(W(F_o)^2-(F_c)^2)^2]$ where $w = 1.0/\text{sqrt}[(\Sigma(F_o))^2+(0.000x(F_o)^2$	
Reflections used	4102
Number of variables	277
Residuals: R; R_w	0.045; 0.056
Goodness-of-fit: S	1.92
Maximum shift/estimated S.D. in final cycle	0.14

solvent was removed under reduced pressure, the residue was purified by medium-pressure liquid chromatography on silica gel with EtOAc–hexane (5:95) to give **10** (18 mg, 45%).

*4.7. Preparation of **10** by Friedel–Crafts reaction*

A solution of **1** (243 mg, 1.05 mmol) in dry CH_2Cl_2 (10 ml) was added dropwise at 0 °C to a mixture of dichloroacetyl chloride (294 mg, 2.00 mmol) and aluminum trichloride (422 mg, 3.17 mmol) in dry CH_2Cl_2 (20 ml) over a period of 1 h. After stirring the mixture at r.t. for another 20 min, reaction mixture was poured into water, and neutralized with saturated aqueous $NaHCO_3$. Reaction product was extracted with Et_2O dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica with CH_2Cl_2 to give **10** (156 mg, 43%).

*4.8. Reaction of **1** with dichloroacetyl chloride in the presence of Et_3N*

A solution of dichloroacetylchloride (744 mg, 5.05 mmol) in dry Et_2O (20 ml) was added dropwise at r.t. to a solution of **1** (252 mg, 1.09 mmol) and Et_3N (524 mg, 5.18 mmol) in the same solvent (10 ml) over a period of 2 h. After stirring the mixture for another 2 h, precipitated triethylamine hydrochloride was removed by filtration. The filtrate was washed with saturated aqueous NaCl, dried over $MgSO_4$, and concentrated under reduced pressure. The reaction mixture was separated by GPC with $CHCl_3$ to give **3** (13 mg, 4%), **10** (47 mg, 13%) and tricarbonyl[(2,3,4,5-η)-9,9-dichloro-8-dichloromethylcarbonyloxybicyclo[5.2.0]nona-2,4,7-triene]iron (13) (225 mg, 46%).

13: Yellow plates; m.p. 101.0–101.5 °C; MS (70 eV) *m*/*z* (rel. intensity) 458 ($M^+ + 6$, 0.1), 456 ($M^+ + 4$, 0.3), 454 ($M^+ + 2$, 0.4), 452 (M^+, 0.3), 396 ($M^+ -$ 2CO, 20), 368 ($M^+ -$ 3CO, 50), 292 (6), 242 (40), 222 (10), 207 (22), 194 (8), 179 (14), 167 (37), 158 (28), 140 (8), 131 (84), 115 (96), 103 (100), 91 (38), 77 (75), 65 (18), and 56 (28); UV–Vis (MeOH) λ_{max}, nm (log ε) 226 sh (4.19) and 303 sh (3.17); IR (KBr disk) ν_{max} 3013 (m), 2984 (m), 2049 (s), 1802 (s), 1725 (m), 1455 (w), 1429 (m), 1404 (w), 1364 (m), 1308 (m), 1281 (s), 1240 (m), 1208 (m), 1190 (w), 1119 (s), 1046 (m), 947 (m), 932 (m), 916 (m), 903 (m), 864 (w), 855 (m), 826 (m), 779 (m), 752 (w), 737 (m), 668 (m), 640 (m), 612 (s), 567 (s), 548 (m), 517 (m), 488 (w), 471 (m), 446 (m), and 417 (w) cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) $\delta = 6.08$ (s, $\mathrm{OCOC\underline{H}Cl_2}$), 5.47 (dd, $J = 7.1$, 5.9 Hz, H-3), 5.33 (dd, $J = 7.3$, 5.9 Hz, H-4), 3.52 (d, $J = 2.0$ Hz, H-1), 3.21 (dd, $J = 7.1$, 2.0 Hz, H-2), 3.04 (dd, $J = 7.3$, 4.7 Hz, H-5), 2.92 (dd, $J = 17.6$, 4.7 Hz, H-6), and 2.59 (d, $J = 17.6$ Hz, H-6); ^{13}C-NMR (150 MHz, $CDCl_3$) $\delta =$ 209.53 ($\mathrm{Fe(\underline{C}O)_3}$), 160.36 ($\mathrm{O\underline{C}OCHCl_2}$), 134.08 (C-8), 127.31 (C-7), 90.26 (C-3), 88.70 (C-4), 84.55 (C-9), 63.21 ($\mathrm{OCO\underline{C}HCl_2}$), 57.61 (C-1), 56.16 (C-5), 55.73 (C-2), and 26.58 (C-6). Anal. Found: C; 36.80; H, 1.95; Cl, 31.17. Calc. for $C_{14}H_8Cl_2FeO_5$: C, 37.05; H, 1.78; Cl, 31.24%.

*4.9. Reaction of **3** with dichloroacetyl chloride in the presence of Et_3N*

A solution of Et_3N (177 mg, 1.75 mmol) in THF (20 ml) was added dropwise at r.t. to a solution of **3** (103 mg, 0.300 mmol) and dichloroacetyl chloride (350 mg, 2.37 mmol) in THF (20 ml) over a period of 0.5 h. After stirring for another 1.5 h, the precipitated triethylamine hydrochloride was removed by filtration, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on Florisil® with CH_2Cl_2 to give **13** (94 mg, 69%).

*4.10. Tricarbonyl[(2,3,4,5-η)-8-acetoxy-9,9-dichlorobicyclo[5.2.0]nona-2,4,7-triene]iron (**15**)*

A solution of Et_3N (604 mg, 5.97 mmol) in THF (30 ml) was added dropwise at r.t. to a solution of **3** (359 mg, 1.05 mmol) and acetyl chloride (628 mg, 8.00 mmol) in THF (30 ml) over a period of 1.5 h. After the precipitated triethylamine hydrochloride was removed by filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on Florisil® with CH_2Cl_2 to give tricarbonyl[(2,3,4,5-η)-8-acetoxy-9,9-dichlorobicyclo-[5.2.0]nona-2,4,7-triene]iron (**15**) (384 mg, 95%).

15: Yellow crystals; m.p. 109.5–110.0 °C; MS (70 eV) *m*/*z* (rel. intensity) 388 ($M^+ + 4$, 0.3), 386 ($M^+ + 2$, 1.1), 384 (M^+, 1.7), 356 ($M^+ -$ CO, 6), 328 ($M^+ -$ 2CO, 24), 300 ($M^+ -$ 3CO, 100), 265 (6), 258 (15), 222 (66), 194 (23), 186 (10), 167 (23), 158 (46), 150 (38), 131 (73), 115 (80), 103 (66), 91 (15), 77 (45), 65 (12), and 56 (23); UV–Vis (MeOH) λ_{max}, nm (log ε) 222 sh (4.42) and 320 sh (3.28); IR (KBr disk) ν_{max} 2051 (s), 1999 (s), 1973 (s), 1779 (m), 1709 (m), 1429 (w), 1364 (w), 1310 (m), 1238 (w), 1194 (m), 1183 (m), 1144 (m), 1053 (m), 1005 (w), 943 (w), 911 (w), 901 (w), 885 (w), 864 (w), 849 (w), 779 (m), 743 (w), 650 (w), 612 (m), 598 (m), 556 (m), 534 (w), 511 (w), 465 (w), and 446 (w) cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) $\delta = 5.45$ (dd, $J = 7.2$, 5.2 Hz, H-3), 5.30 (dd, $J = 7.0$, 5.2 Hz, H-4), 3.48 (d, $J = 2.0$ Hz, H-1), 3.22 (dd, $J = 7.2$, 2.0 Hz, H-2), 3.03 (m, H-5), 2.88 (dd, $J = 17.7$, 4.8 Hz, H-6), 2.54 (d, $J = 17.7$ Hz, H-6), and 2.22 (s, $\mathrm{OCO\underline{C}H_3}$); ^{13}C-NMR (150 MHz, $CDCl_3$) $\delta = 210.00$ ($\mathrm{Fe(\underline{C}O)_3}$), 166.22 ($\mathrm{O\underline{C}OCH_3}$), 135.17 (C-8), 124.83 (C-7), 90.24 (C-3), 88.64 (C-4), 85.34 (C-9), 57.46 (C-1), 56.84 (C-5), 56.54 (C-2), 26.80 (C-6), and 20.50 ($\mathrm{OCO\underline{C}H_3}$). Anal. Found: C, 43.40; H, 2.70; Cl, 18.37. Calc. for $C_{14}H_{10}Cl_2FeO_5$: C, 43.68; H, 2.62; Cl, 18.42%.

4.11. Rearrangement of **3** in the presence of Et_3N

Et_3N (121 mg, 1.20 mmol) was added at r.t. to a solution of **3** (353 mg, 1.03 mmol) in dry Et_2O (20 ml). After stirring the mixture for 1 h at r.t., the solvent was removed under reduced pressure. The residue was purified by a short column on Florisil® with CH_2Cl_2 to give tricarbonyl[(2,3,4,5-η)-7,9-dichlorobicyclo[5.2.0]-nona-2,4-dien-8-one]iron (16) (221 mg, 63%).

16: Yellow crystals; m.p. 102.0–102.5 °C; MS (70 eV) m/z (rel. intensity) 346 ($M^+ + 4$, 0.7), 344 ($M^+ + 2$, 2.5), 342 (M^+, 3.3), 314 ($M^+ - CO$, 28), 286 ($M^+ - 2CO$, 64), 258 ($M^+ - 3CO$, 6), 204 (6), 182 (30), 169 (9), 158 (19), 131 (69), 112 (8), 104 (100), 91 (53), 78 (38), 65 (15), and 56 (27); UV–Vis (MeOH) λ_{max}, nm (log ε) 221 sh (4.31) and 321 sh (3.21); IR (KBr disk) ν_{max} 2988 (w), 2923 (w), 2051 (s), 1973 (s), 1966 (s), 1790 (m), 1709 (m), 1578 (w), 1453 (w), 1429 (m), 1404 (w), 1364 (m), 1281 (s), 1237 (s), 1211 (m), 1190 (m), 1152 (m), 1130 (s), 1049 (m), 997 (w), 945 (m), 918 (m), 903 (m), 862 (m), 818 (m), 777 (m), 703 (m), 675 (m), 640 (m), and 610 (s) cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) $\delta = 5.74$ (d, $J = 8.5$ Hz, H-9), 5.43 (ddd, $J = 7.6, 5.2, 1.1$ Hz, H-3), 5.21 (ddd, $J = 9.2, 5.2, 1.1$ Hz, H-4), 3.31 (dd, $J = 8.5, 5.1$ Hz, H-1), 2.93 (dddd, $J = 9.2, 5.5, 2.5, 1.1$ Hz, H-5), 2.78 (dd, $J = 7.6, 5.1$ Hz, H-2), 2.76 (ddd, $J = 17.6, 5.5, 1.1$ Hz, H-6), and 2.48 (dd, $J = 17.6, 2.5$ Hz, H-6); ^{13}C-NMR (150 MHz, $CDCl_3$) $\delta = 193.58$ (C-9), 90.78 (C-5), 86.57 (C-4), 72.80 (C-8), 68.90 (C-1), 55.24 (C-6), 52.83 (C-3), 44.58 (C-2), and 32.72 (C-7). Anal. Found: C, 40.20; H, 2.30. Calc. for $C_{12}H_8Cl_2FeO_4 \cdot H_2O$: C, 39.93; H, 2.79%.

4.12. Decomplexation of **16** using cerium(IV) ammonium nitrate

To a solution of **16** (102 mg, 0.298 mmol) in MeCN (10 ml) was added ammonium cerium(IV) nitrate (241 mg, 0.440 mmol) at r.t. under nitrogen atmosphere. After stirring the mixture for 5 min at r.t., the reaction mixture was poured into water and extracted with CH_2Cl_2, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by a short column on Florisil® with CH_2Cl_2 to give 7,9-dichlorobicyclo[5.2.0]nona-2,4-dien-8-one (**17**) (37 mg, 61%).

17: Colorless oil; MS (70 eV) m/z (rel. intensity) 206 ($M^+ + 4$, 0.5), 204 ($M^+ + 2$, 2.6), 202 (M^+, 4.0), 167 (17), 139 (34), 126 (17), 103 (41), 91 (100), 77 (20), and 63 (6); UV–Vis (CH_3CN) λ_{max}, nm (log ε) 237 (3.72); IR (neat) ν_{max} 3036 (m), 2957 (w), 1802 (s), 1613 (w), 1428 (m), 1379 (w), 1333 (w), 1304 (w), 1254 (w), 1237 (m), 1210 (w), 1146 (m), 1086 (w), 1053 (m), 1009 (w), 972 (w), 938 (w), 912 (w), 893 (m), 851 (m), 777 (m), 729 (m), 708 (m), 666 (s), and 615 (m) cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) $\delta = 6.22$ (ddd, $J = 11.5, 4.7, 2.2$ Hz, H-3), 6.12 (dd, $J = 10.5, 4.7$ Hz, H-4), 6.09 (ddd, $J = 10.5, 6.9, 4.9$ Hz, H-5), 6.06 (dd, $J = 11.5, 4.4$ Hz, H-2), 5.29 (d, $J = 10.5$ Hz, H-9), 3.71 (ddd, $J = 10.5, 4.4, 2.2$ Hz, H-1), 2.88 (dd, $J = 13.7, 4.9$ Hz, H-6), and 2.57 (dd, $J = 13.7, 6.9$ Hz, H-6′); ^{13}C-NMR (100 MHz, $CDCl_3$) $\delta = 197.26$ (C-8), 130.13 (C-3 or C-4), 130.09 (C-4 or C-3), 128.82 (C-2 or C-5), 128.73 (C-5 or C-2), 86.78 (C-7), 65.07 (C-9), 48.90 (C-1), and 34.32 (C-6). HRMS calc. for $C_9H_8Cl_2O$: 201.9952, Found: 201.9943. Anal. Found: C, 50.79; H, 4.07. Calc. for $C_9H_8Cl_2O \cdot 1/2H_2O$: C, 50.97; H, 4.28%.

4.13. Decomplexation of **3** using cerium(IV) ammonium nitrate

To a solution of **3** (98 mg, 0.29 mmol) in MeCN (30 ml) was added cerium (IV) ammonium nitrate (195 mg, 0.356 mmol) at r.t. under nitrogen atmosphere. After stirring the mixture for 1.5 h, the reaction mixture was poured into water and extracted with Et_2O. The combined organic layers were washed with saturated aqueous NaCl, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by passing through a small amount of Florisil® with CH_2Cl_2 and further purified by GPC with $CHCl_3$ to give 9,9-dichlorobicyclo[5.2.0]nona-2,4-dien-8-one (**18**) (27 mg, 56%).

18: Pale yellow oil; MS (70 eV) m/z (rel. intensity) 206 ($M^+ + 4$, 0.9), 204 ($M^+ + 2$, 3.9), 202 (M^+, 4.8), 184 (14), 174 ($M^+ - CO$, 5), 167 (22), 159 (8), 149 (28), 139 (98), 131 (16), 125 (6), 113 (7), 109 (20), 103 (100), 91 (70), 73 (7), 65 (15), 55 (8), and 51 (32); UV–Vis (MeOH) λ_{max}, nm (log ε) 241 (3.66); IR (neat) ν_{max} 3031 (w), 2953 (w), 1809 (s), 1439 (w), 1287 (w), 1242 (w), 1208 (w), 1181 (w), 1157 (w), 1111 (m), 1086 (w), 1044 (w), 1017 (w), 986 (m), 970 (w), 897 (w), 843 (m), 828 (m), 808 (m), 756 (w), 714 (m), 696 (m), and 531 (m) cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) $\delta = 6.24$ (dd, $J = 11.8, 3.0$ Hz, H-2), 6.01 (m, H-4 and H-5), 5.94 (ddt, $J = 11.8, 5.5, 1.5$ Hz, H-3), 4.05 (ddd, $J = 12.4, 11.4, 4.0$ Hz, H-7), 3.74 (dtd, $J = 11.4, 3.0, 1.5$ Hz, H-1), 2.64 (dddd, $J = 13.9, 12.4, 5.9, 2.2$ Hz, H-6), 2.55 (ddd, $J = 13.9, 7.7, 4.0$ Hz, H-6); ^{13}C-NMR (150 MHz, $CDCl_3$) $\delta = 195.98$ (C-8), 131.47 (C-4 or C-5), 129.05 (C-2), 128.72 (C-3), 128.64 (C-5 or C-4), 91.18 (C-9), 66.00 (C-7), 51.22 (C-1), and 27.76 (C-6); HRMS calc. for $C_9H_8OCl_2$: 201.9952, Found: 201.9949. Anal. Found: C, 53.11; H, 4.21. Calc. for $C_9H_8Cl_2O$: C, 53.23; H, 3.97%.

4.14. Rearrangement of **18** to **19** in Me_2SO

A solution of **18** (753 mg, 3.71 mmol) in Me_2SO (20 ml) was stirred at 65 °C for 2 h. The reaction mixture was poured into water and extracted with Et_2O. The organic layer was dried over $MgSO_4$, and concentrated under reduced pressure. The reaction mixture was separated by medium-pressure liquid chromatography on silica gel with EtOAc–hexane (1:4) to give 7,9-dichlorobicyclo[5.2.0]nona-2,4-dien-8-one (**19**) (342 mg, 45%) and the recovered **18** (162 mg, 22%).

19: Colorless plates; m.p. 42.5–43.0 °C; MS (70 eV) *m*/*z* (rel. intensity) 206 ($M^+ + 4$, 0.4), 204 ($M^+ + 2$, 2), 202 (M^+, 3), 139 (39), 103 (36), and 91 (100); IR (KBr disk) ν_{max} 3042 (w), 3013 (w), 2938 (w), 1804 (s), 1613 (w), 1429 (w), 1422 (w), 1381 (w), 1335 (w), 1246 (w), 1221 (w), 1184 (m), 1150 (w), 1115 (w), 1051 (w), 992 (w), 963 (w), 841 (m), 808 (m), 766 (w), 727 (m), 700 (s), 662 (m), and 637 (m) cm^{-1}; UV–Vis (MeOH) λ_{max}, nm (log ε) 241 (3.78); ^{1}H-NMR (400 MHz, $CDCl_3$) $\delta =$ 6.34 (dd, $J = 11.2$, 6.3 Hz, H-2), 6.24 (dd, $J = 10.5$, 5.0 Hz, H-4), 6.16 (dd, $J = 11.2$, 5.0 Hz, H-3), 5.97 (dt, $J = 10.5$, 6.6 Hz, H-5), 4.79 (d, $J = 8.6$ Hz, H-9), 3.24 (dd, $J = 8.6$, 6.3 Hz, H-1), and 2.61 (d, $J = 6.6$ Hz, H-6$_{endo}$ and H-6$_{exo}$); ^{13}C-NMR (100 MHz, $CDCl_3$) $\delta =$ 197.14 (C-8), 131.46 (C-2), 130.46 (C-4), 129.21 (C-3), 128.46 (C-5), 84.70 (C-7), 64.55 (C-9), 53.28 (C-1), and 34.42 (C-6). Anal. Found: C, 53.20; H, 3.99; Cl, 34.73. Calc. for $C_9H_8Cl_2O$: C, 53.23; H, 3.97; Cl, 34.92%.

*4.15. Ring expansion of **3** with CH_2N_2*

A solution of diazomethane (8 mmol) in Et_2O (8 ml) was added to a solution of **3** (533 mg, 1.56 mmol) in MeOH (3 ml) and Et_2O (30 ml) at r.t. After the consumption of **3** was monitored by TLC, the solvent was removed under reduced pressure. The residue was purified by column chromatography on Florisil® with CH_2Cl_2 to give tricarbonyl[(2,3,4,5-η)-10,10-dichloro-2,4-bicyclo[5.3.0]deca-2,4-dien-9-one]iron (**21**) (419 mg, 75%).

21: Yellow crystals; m.p. 81.0–82.0 °C; MS (70 eV) *m*/*z* (rel. intensity) 360 ($M^+ + 4$, 0.1), 358 ($M^+ + 2$, 0.4), 356 (M^+, 0.6), 328 ($M^+ - CO$, 23), 272 ($M^+ - 3CO$, 38), 257 (5), 237 (7), 200 (6), 172 (9), 146 (7), 131 (5), 117 (26), 105 (100), 91 (12), 77 (10), and 56 (7); UV–Vis (MeOH) λ_{max}, nm (log ε) 220 sh (4.37) and 296 sh (3.46); IR (KBr disk) ν_{max} 2974 (w), 2924 (w), 2056 (s), 1992 (s), 1973 (s), 1969 (m), 1769 (m), 1445 (w), 1435 (w), 1410 (w), 1400 (w), 1374 (w), 1356 (w), 1339 (w), 1290 (w), 1269 (w), 1240 (w), 1290 (w), 1269 (w), 1240 (w), 1159 (w), 1130 (w), 1078 (w), 1032 (w), 903 (w), 881 (w), 830 (w), 806 (w), 769 (w), 722 (m), 609 (s), 563 (m), 488 (w), 470 (w), and 459 (w) cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) $\delta = 5.36$ (m, H-3 and H-4), 3.01 (dd, $J = 5.5$, 2.2 Hz, H-1), 2.95 (dd, $J = 4.6$, 2.2 Hz, H-2), 2.91 (m, H-5), 2.79 (m, H-7), 2.48 (dd, $J = 19.8$, 9.3 Hz, H-8), 2.38 (ddd, $J = 17.4$, 5.9, 2.4 Hz, H-6), 2.26 (dd, $J = 19.8$, 9.9 Hz, H-8), and 2.16 (dt, $J = 17.4$, 4.2 Hz, H-6); ^{13}C-NMR (150 MHz, $CDCl_3$) $\delta = 210.02$ ($Fe(\underline{C}O)_3$), 200.65 (C-9), 91.09 (C-7), 90.58 (C-10), 87.80 (C-4), 55.56 (C-5), 52.34 (C-1), 51.97 (C-2), 35.96 (C-8), 30.98 (C-7), and 29.00 (C-6); Anal. Found: C, 43.97; H, 2.92. Calc. for $C_{13}H_{10}Cl_2FeO_4$: C, 43.74; H, 2.82%.

*4.16. Reaction of **1** with chloroketene*

A solution of dichloroacetyl chloride (1.70 g, 11.5 mmol) in dry Et_2O (20 ml) was added dropwise at r.t. to a mixture of activated zinc powder (1.96 g, 30.0 matom) and **1** (864 mg, 3.72 mmol) in dry Et_2O (10 ml). After stirring the mixture for another 2 h, residual zinc powder was removed by filtration. The filtrate was washed with water and 5% aqueous $NaHCO_3$, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on Florisil® with CH_2Cl_2 to give tricarbonyl[(2,3,4,5-η)-9-*endo*-chlorobicyclo[5.2.0]nona-2,4-dien-8-one]iron (**23**) (910 mg, 78%).

23: Pale yellow crystals; m.p. 107.5–108.0 °C; MS (70 eV) *m*/*z* (rel. intensity) 310 ($M^+ + 2$, 5), 308 (M^+, 14), 280 ($M^+ - CO$, 67), 252 ($M^+ - 2CO$, 91), 224 ($M^+ - 3CO$, 20), 197 (8), 188 (63), 182 (8), 169 (100), 160 (90), 148 (29), 134 (79), 121 (13), 115 (13), 105 (32), 91 (64), 84 (18), 77 (26), 70 (23), 63 (5), and 56 (70); UV–Vis (MeOH) λ_{max}, nm (log ε) 225 sh (4.27) and 303 sh (3.32); IR (KBr disk) ν_{max} 3000 (w), 2965 (m), 2938 (w), 2907 (w), 2880 (w), 2048 (s), 1981 (s), 1792 (s), 1428 (m), 1406 (w), 1366 (m), 1329 (w), 1308 (w), 1250 (w), 1157 (w), 1113 (w), 1046 (w), 1017 (w), 889 (w), 878 (w), 843 (w), 818 (w), 787 (w), 714 (w), 619 (s), 610 (s), 563 (m), 511 (m), 465 (w), 457 (w), and 418 (w) cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) $\delta = 5.40$ (t, $J = 7.0$ Hz, H-3), 5.20 (t, $J = 7.0$ Hz, H-4), 4.99 (dd, $J = 5.5$, 4.7 Hz, H-9), 3.19 (m, H-1 and H-7), 3.01 (dd, $J = 7.0$, 4.7 Hz, H-5), 2.92 (d, $J = 7.0$ Hz, H-2), 2.45 (dd, $J = 17.6$, 4.7 Hz, H-6), and 2.49 (d, $J = 17.6$ Hz, H-6); ^{13}C-NMR (150 MHz, $CDCl_3$) $\delta = 199.87$ (C-8), 90.63 (C-4), 87.61 (C-3), 65.69 (C-9), 57.38 (C-5), 54.39 (C-2), 50.85 (C-1 or C-7), 32.86 (C-7 or C-1), and 22.56 (C-6). Anal. Found: C, 46.87; H, 2.91. Calc. for $C_{12}H_9ClFeO_4$: C, 46.72; H, 2.94%.

*4.17. Ring opening reaction of **23***

A solution of **23** (107 mg, 0.347 mmol) in a small amount of CH_2Cl_2 was placed on the top of silica gel column for 12 h at r.t. Elution with CH_2Cl_2 gave tricarbonyl[(1,2,3,4-η)-6-(chloromethyl)carbonylcycloheptatriene]iron (**24**) (94 mg, 88%).

24: Yellow crystals; m.p. 70.5–71.0 °C; MS (70 eV) *m*/*z* (rel. intensity) 280 ($M^+ - CO$, 25), 252 ($M^+ - 2CO$, 74), 224 ($M^+ - 3CO$, 53), 196 (15), 188 (61), 160 (21), 146 (8), 133 (39), 115 (25), 105 (20), 91 (100), 84 (11), 77 (8), 65 (17), and 56 (35); IR (KBr disk) ν_{max} 2932 (w), 2909 (w), 2053 (s), 1983 (s), 1960 (s), 1950 (s), 1750 (w), 1671 (m), 1628 (m), 1447 (w), 1414 (w), 1406 (w), 1393 (w), 1204 (m), 1175 (w), 860 (w), 627 (w), 608 (m), 554 (m), and 505 (w) cm^{-1}; UV–Vis (MeOH) λ_{max}, nm (log ε) 301 (3.83) and 375 (3.71); ^{1}H-NMR (600 MHz, CDCl$_3$) $\delta = 7.20$ (br s, H-5), 5.46 (m, H-2 and H-3), 4.27 (br s, COC$\underline{H}_2$Cl), 3.55 (br s, H-1), 2.94 (br s, H-4), 2.76 (br d, $J = 21.2$ Hz, H-7), and 2.29 (br d, $J = 21.2$ Hz, H-7); ^{13}C-NMR (150 MHz, CDCl$_3$) $\delta = 209.70$ (Fe($\underline{C}$O)$_3$), 190.36 ($\underline{C}$OCH$_2$Cl), 145.91 (C-5), 132.72 (C-6), 94.50 (C-2 or C-3), 89.10 (C-3 or C-2), 60.00 (C-1), 53.09 (C-4), 44.19 (CO$\underline{C}$H$_2$Cl), and 28.73 (C-7). Anal. Found: C, 46.79; H, 3.02. Calc. for $C_{12}H_9ClFeO_4$: C, 46.72; H, 2.94%.

4.18. Ring expansion of **23** with CH_2N_2

To a solution of **23** (316 mg, 1.02 mmol) in dry MeOH (50 ml) was added a solution of diazomethane (4 mmol) in Et$_2$O (4 ml) six times every 30 min. After the solvent was removed by reduced pressure, the residue was passed through a short column of Florisil® with CH$_2$Cl$_2$. The products were separated by medium-pressure liquid chromatography on silica gel with EtOAc–hexane (2:3) to give tricarbonyl[(2,3,4,5-η)-10-*endo*-chlorobicyclo[5.3.0]deca-2,4-dien-9-one]iron (**25**) (61 mg, 19%) and tricarbonyl[(2,3,4,5-η)-10-*exo*-chlorobicyclo[5.3.0]deca-2,4-dien-9-one]iron (**26**) (101 mg, 30%).

25: Pale yellow crystals; m.p. 145.5–146.0 °C (decomp.); MS (70 eV) *m*/*z* (rel. intensity) 324 (M$^+$ + 2, 0.4), 322 (M$^+$, 1.1), 294 (M$^+$ − CO, 44), 266 (M$^+$ − 2CO, 18), 238 (M$^+$ − 3CO, 100), 223 (28), 202 (36), 195 (5), 184 (17), 174 (34), 148 (16), 130 (14), 121 (7), 115 (12), 105 (10), 91 (32), 84 (11), 77 (12), 65 (8), and 56 (32); UV–Vis (MeOH) λ_{max}, nm (log ε) 222 sh (4.26) and 298 sh (3.32); IR (KBr disk) ν_{max} 2996 (w), 2932 (w), 2909 (m), 2047 (s), 1985 (s), 1950 (s), 1750 (s), 1447 (w), 1437 (w), 1414 (w), 1377 (s), 1360 (w), 1348 (w), 1302 (w), 1285 (w), 1196 (w), 1144 (w), 1117 (w), 1105 (w), 1059 (w), 1019 (w), 962 (w), 947 (w), 878 (w), 864 (w), 831 (w), 752 (w), 712 (w), 610 (s), 563 (m), 520 (w), 469 (w), and 438 (w) cm^{-1}; ^{1}H-NMR (600 MHz, CDCl$_3$) $\delta = 5.35$ (m, H-3 and H-4), 4.41 (d, $J = 6.9$ Hz, H-10), 2.96 (t, $J = 6.9$ Hz, H-1), 2.93 (d, $J = 7.5$ Hz, H-2), 2.86 (t, $J = 6.5$ Hz, H-5), 2.42 (m, H-7 and H-8$_{exo}$), and 2.23 (m, H-6$_{endo}$, H-6$_{exo}$, and H-8$_{endo}$); ^{13}C-NMR (150 MHz, CDCl$_3$) $\delta = 210.40$ (Fe($\underline{C}$O)$_3$), 207.88 (C-9), 90.30 (C-3 or C-4), 88.36 (C-4 or C-3), 69.66 (C-10), 55.15 (C-5), 52.19 (C-2), 42.46 (C-1), 37.62 (C-8), 31.94 (C-7), and 28.90 (C-6). Anal. Found: C, 47.53; H, 3.45. Calc. for $C_{13}H_{11}ClFeO_4 \cdot 1/2H_2O$: C, 47.10; H, 3.65%.

26: Yellow crystals; m.p. 122.0–123.0 °C; MS (70 eV) *m*/*z* (rel. intensity) 324 (M$^+$ + 2, 0.3), 322 (M$^+$, 0.9), 294 (M$^+$ − CO, 41), 266 (M$^+$ − 2CO, 16), 238 (M$^+$ − 3CO, 100), 230 (25), 202 (41), 184 (16), 174 (33), 160 (13), 148 (19), 130 (14), 121 (9), 115 (13), 105 (13), 91 (33), 84 (12), 77 (13), 65 (8), and 56 (36); UV–Vis (MeOH) λ_{max}, nm (log ε) 224 sh (4.27) and 296 sh (3.43); IR (KBr disk) ν_{max} 2928 (w), 2054 (s), 1983 (s), 1960 (s), 1759 (s), 1435 (w), 1416 (m), 1219 (w), 1152 (w), 1061 (w), 837 (w), 712 (w), 610 (s), 561 (m), 538 (m), 515 (w), 488 (w), 467 (w), 459 (w), and 415 (w) cm^{-1}; ^{1}H-NMR (600 MHz, CDCl$_3$) $\delta = 5.40$ (dd, $J = 7.6$, 4.8 Hz, H-4), 5.35 (ddd, $J = 7.5$, 4.8, 1.2 Hz, H-3), 3.73 (d, $J = 3.4$ Hz, H-10), 2.96 (dddd, $J = 7.6$, 5.0, 3.6, 1.2 Hz, H-5), 2.72 (td, $J = 3.5$, 3.4 Hz, H-1), 2.67 (dd, $J = 7.5$, 3.5 Hz, H-2), 2.65 (ddddd, $J = 9.2$, 8.3, 5.9, 5.0, 3.5 Hz, H-7), 2.38 (dd, $J = 19.6$, 9.2 Hz, H-8$_{exo}$), 2.28 (ddd, $J = 17.0$, 5.9, 3.6 Hz, H-6$_{exo}$), 2.19 (dd, $J = 19.6$, 8.3 Hz, H-8$_{endo}$), and 1.96 (dt, $J = 17.0$, 5.0 Hz, H-6$_{endo}$); ^{13}C-NMR (150 MHz, CDCl$_3$) $\delta = 210.31$ (Fe($\underline{C}$O)$_3$), 209.68 (C-9), 90.77 (C-4), 87.98 (C-3), 64.37 (C-10), 56.48 (C-5), 56.27 (C-2), 46.77 (C-1), 39.30 (C-8), 32.98 (C-7), and 28.31 (C-6). Anal. Found: C, 48.00; H, 3.37. Calc. for $C_{13}H_{11}ClFeO_4$: C, 48.41; H, 3.44%.

5. Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 172540 for compound **6**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This research was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan.

References

[1] R. Burton, L. Pratt, G. Wilkinson, J. Chem. Soc. (1961) 594.

[2] (a) H.J. Dauben Jr., D.J. Bertelli, J. Am. Chem. Soc. 83 (1961) 497 and 5049;
(b) M.A. Hashmi, J.D. Munro, P.L. Pauson, J.M. Williamson, J. Chem. Soc. (A) (1967) 240;
(c) M. Green, S. Tolson, J. Weaver, D.C. Wood, P. Woodward, Chem. Commun. (1971) 222;
(d) B.F.G. Johnson, J. Lewis, P. McArdle, G.L.P. Randall, J. Chem. Soc. Dalton (1972) 456;
(e) M. Green, S. Heathcock, D.C. Wood, J. Chem. Soc. Dalton (1973) 1564;
(f) Z. Goldschmidt, Y. Bakal, Tetrahedron Lett. (1977) 955;
(g) G.A. Taylor, J. Chem. Soc. Perkin I (1979) 1716;
(h) D.L. Reger, A. Gabrielli, J. Organomet. Chem. 187 (1980) 243;
(i) E.A.K. von Gustorf, F.-W. Grevels, I. Fischler, The Organic Chemistry of Iron, Academic Press, New York, 1978 and 1981, vols. 1 and 2;

(j) T. Ishizu, K. Harano, M. Yasuda, K. Kanematsu, Tetrahedron Lett. 22 (1981) 1601;
(k) A.J. Deeming, in: G. Wilkinson (Ed.), Comprehensive Organometallic Chemistry, vol. 4, Pergamon Press, Oxford, 1982, pp. 377–512;
(l) Z. Goldschmidt, S. Antebi, I. Goldberg, J. Organomet. Chem. 260 (1984) 105;
(m) Z. Goldschmidt, S. Antebi, H.E. Gottlieb, D. Cohen, U. Shmveli, Z. Stein, J. Organomet. Chem. 282 (1985) 369;
(n) Z. Goldschmidt, E. Genizi, Synthesis (1985) 949;
(o) Z. Goldschmidt, H.E. Gottlieb, E. Genizi, D. Cohen, I. Goldberg, J. Organomet. Chem. 301 (1986) 337;
(p) R.C. Kerber, in: G. Wilkinson (Ed.), Comprehensive Organometallic Chemistry II, vol. 7, Pergamon Press, Oxford, 1995, pp. 101–229 and references cited therein.
[3] (a) Z. Goldschmidt, S. Antebi, Tetrahedron Lett. (1978) 271;
(b) Z. Goldschmidt, S. Antebi, J. Organomet. Chem. 259 (1983) 119;
(c) Z. Goldschmidt, S. Antebi, D. Cohen, I. Goldberg, J. Organomet. Chem. 273 (1984) 347;
(d) Z. Goldschmidt, H.E. Gottlieb, J. Organomet. Chem. 329 (1987) 391.
[4] C. Falshaw, A. Lakoues, G. Taylor, J. Chem. Res. (S) (1985) 106.
[5] D.C. England, C.G. Krespan, J. Org. Chem. 35 (1970) 3300.
[6] J. Hyatt, P.W. Raynolds, Org. React. 45 (1994) 159. (L.A. Paquette, " Ketene Cycloadditions").
[7] R. Yokoyama, S. Ito, T. Asao, M. Watanabe, N. Harada, C. Kabuto, N. Morita, J. Chem. Soc. Perkin Trans. 1 (2001) 2257.
[8] N. Morita, M. Kudo, R. Yokoyama, S. Ito, Heterocycles 54 (2001) 679.
[9] (a) J. Weaver, P. Woodward, J. Chem. Soc. (A) (1971) 3521;
(b) A.H.-J. Wang, I.C. Paul, J. Organomet. Chem. 69 (1974) 301;
(c) F.A. Cotton, J.M. Troup, J. Organomet. Chem. 76 (1974) 81.
[10] M.T. Reetz, Angew. Chem. Int. Ed. Engl. 11 (1972) 129 and 130.
[11] F. Arndt, in: A.H. Blatt (Ed.), Organic Syntheses, Coll. Vol. 2, Wiley, New York, 1945, p. 165.