ELSEVIER

Journal of Organometallic Chemistry 642 (2002) 80–90

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

[8 + 2] Cycloaddition of 8-oxoheptafulvene with cycloheptatrieneFe(CO)$_3$: synthesis of tricarbonyl[(2,3,4,5-η)-11-acetoxy-1*H*-cyclohept[*a*]azulene]iron

Noboru Morita *, Ryuji Yokoyama, Toyonobu Asao, Mituhiro Kurita, Shigeru Kikuchi, Shunji Ito *

Department of Chemistry, Graduate School of Science, Tohoku University, Aramaki Aza Aoba, Aoba-ku, Sendai 980-8578 Japan

Received 4 June 2001; received in revised form 22 August 2001; accepted 10 September 2001

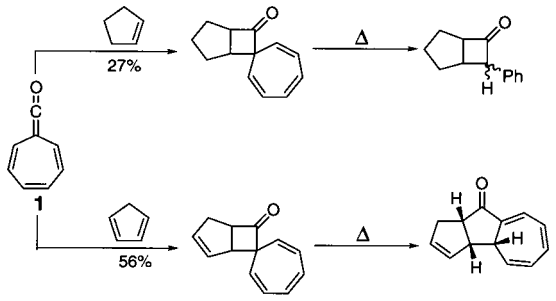
Abstract

8-Oxoheptafulvene reacted with cycloheptatrieneFe(CO)$_3$ by [8 + 2] cycloaddition to give tricyclo[8.5.0.0^{3,9}]pentadeca-3,5,7,11,13-pentaene-2-oneFe(CO)$_3$ (**3**), which easily reacted with another 8-oxoheptafulvene under the reaction conditions to give four products. One of them was a [2 + 4] cycloadduct (**5**) having an uncommon norcaradiene structure. Two products were [8 + 2] cycloadducts (**6** and **7**) having a γ-lactone structure. The remaining product was an acylated compound (**4**). On raising the reaction temperature, the yields of the acylated compound increased. The [1:1] cycloadduct **3** reacted also with acetyl chloride in the presence of triethylamine to give an acetate (**12**), which was oxidized with *o*-chloranil to give 11-acetoxy-1*H*-cyclohept[*a*]azuleneFe(CO)$_3$ (**15**).

Keywords: 8-Oxoheptafulvene; CycloheptatrieneFe(CO)$_3$; [8 + 2] Cycloaddition; Norcaradiene; 1*H*-Cyclohept[*a*]azuleneFe(CO)$_3$; Tricyclo[8.5.0.0^{3,9}]pentadeca-3,5,7,11,13-pentaene-2-one

1. Introduction

8-Oxoheptafulvene (**1**) has the structures of both ketene and heptafulvene. This compound exhibited reactivitiy toward olefins like ketene to give mainly [2 + 2] cycloadducts [1]. For example, the reaction of **1** with cyclopentene gives a 6-bicyclo[3.2.0]heptanone derivative, which contains a spiro cycloheptatriene skeleton. Thermal rearrangement of this adduct afforded 7-phenylbicyclo[3.2.0]heptan-6-one derivatives with a mixture of stereo isomers at C-7. Compound **1** also reacted with cyclopentadiene to give a cyclobutanone derivative [2]. However, this product isomerized on heating to give a formal [8 + 2] cycloadduct. The reaction of **1** with cyclohexa-1,3-diene also exhibited similar results [2]. In contrast to the above results, compound **1** did not react with cycloheptatriene (Scheme 1).



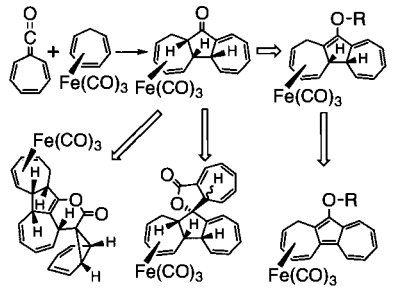
Scheme 1.

Falshow et al. reported that diphenylketene reacted with cycloheptatriene to give a [2 + 4] cycloadduct in 11% yield [3]. On the other hand, Goldschmidt reported that diphenylketene reacted with tricarbonyl(cycloheptatriene)iron (**2**) by a different mode to give a [2 + 2] cycloadduct in 25% yield, which easily isomerized to a [3 + 2] cycloadduct [4] (Scheme 2).

There are numerous inherent advantages in using olefins complexed to metal in organic synthesis. With respect to these advantages, we must emphasize the following points. Coordination of olefins to metal

* Corresponding author. Tel./fax: +81-22-2177714.
E-mail address: morita@funorg.chem.tohoku.ac.jp (N. Morita).

0022-328X/02/$ - see front matter
PII: S0022-328X(01)01240-2



Scheme 2.

sometimes activates cycloadditions and increases regio- and stereoselectivities of the reaction. Reagents attack mainly from the opposite face of the metal coordination side. These cycloadducts frequently undergo thermal isomerization to give interesting systems [5,6].

We have already reported the reaction of **1** with troponeFe$(CO)_3$, troponeCr$(CO)_3$, and related compounds to give the corresponding heptafulvalene complexes [7]. In continuing our studies on the reaction of **1** with cyclic olefins [1,2,7,8], we investigated the reaction of **1** with **2** and explored the utility of the reaction products. We present here, the [8 + 2] cycloaddition of **1** with **2** and further reactions. We also present the preparation of iron tricarbonyl complexes of a compound fused together with cycloheptatriene and azulene derivatives.

2. Results and discussion

2.1. Reaction of 8-oxoheptafulvene (1) with tricarbonyl(cycloheptatriene)iron (2)

8-Oxoheptafulvene (**1**) reacted with the excess of tricarbonyl(cycloheptatriene)iron (**2**) at room temperature for 6 h to give five products (Scheme 3). The products (**3**–**5**) were separated by column chromatography on silica gel. Although a mixture of products **6** and **7** could not be separated by column chromatography, we found that **6** and **7** were separable by gel permeation chromatography (GPC). As shown in Table 1, the yields of **3**–**7** depended on the solvents, reaction time and temperature. Cycloadduct **3** was the main product at room temperature. Raising the reaction temperature increased yield of **4** but decreased that of **3**. Compound **4** became the main product at reflux in benzene.

On the basis of mass spectra, product **3** ([M^+], 350) was the only one 1:1 adduct of **1** and **2**, and the other products **4**–**7** ([M^+], 468) were 2:1 adducts of **1** and **2**. These structures were established on the basis of their IR and NMR spectral data as follows.

2.2. Structure of a [1:1] cycloadduct (3)

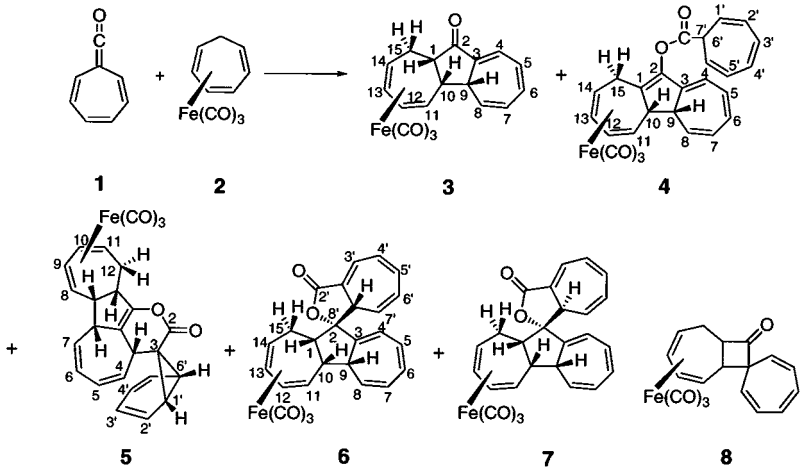
The cycloadduct **3** showed a carbonyl absorption at 1716 cm^{-1} in the IR spectrum, which suggested the presence of a conjugated carbonyl group of a five-membered ring. Compound **3** had nine olefinic protons, two methylene protons and three methine protons. Product **3** might be interpreted in terms of a [8 + 2] cycloaddition of **1** with **2**. The methylene carbon in the cycloadduct **3** appeared at 24.95 ppm, which is the highest field. The corresponding methylene protons appeared at 2.08 and 2.51 ppm, which were confirmed by C, H COSY. From these clues, the other ring protons and carbons of **3** were assigned by H, H COSY and by C, H COSY as shown in Section 4. Moreover, the configuration of the protons at the 1, 9, 10-positions in **3** was deduced to be *cis* on the basis of NOE experiments. Irradiation of H-9 gave NOE enhancements in the signals for H-1, H-8 and H-10. Irradiation of H-10 gave NOE enhancements in the signals for H-1, H-9 and H-11. It is well known that cycloheptatrieneFe$(CO)_3$ undergoes cycloaddition of olefins from the opposite face of coordinated iron [4–6]. Consequently, we considered that there was an iron in the same side toward these methine protons in the cycloadduct **3** as depicted in Scheme 3.

2.3. Structure of 4

A carbonyl absorption in the IR spectrum of **4** appeared at 1764 cm^{-1}. The corresponding carbonyl carbon in ^{13}C-NMR appeared at 169.78 ppm. These observations suggested that compound **4** was an ester. A signal at 27.93 ppm in the ^{13}C-NMR spectrum of the

Table 1
Correlation of reaction conditions of **1** with **2** and yield

Entry	Conditions			Yield (%)			
	Solvent	Time (h)	Temperature	**3**	**4**	**5**	**6** and **7**
1	Ether	3	Reflux	8	Trace	4	5
2	Benzene	6	r.t.	19.1	1.6	2.5	3.6
3	Benzene	12	r.t.	15	3	2	4
4	Benzene	11	60 °C	10	8	Trace	4
5	Benzene	6	Reflux	Trace	14	Trace	Trace



Scheme 3.

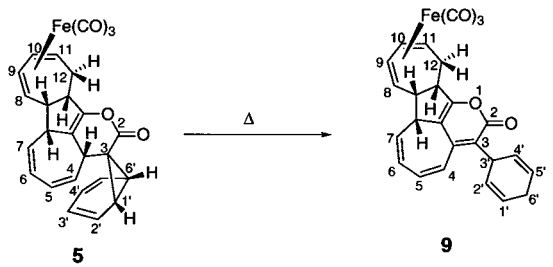
cycloadduct **4** was assigned as a methylene carbon by DEPT analysis. Proton signals at 2.81 and 2.62 ppm in ^{1}H-NMR were assigned as methylene protons by C, H COSY. From this clue, other ring protons and carbons of the enolate form of **3** were assigned by H, H COSY and C, H COSY. If the cycloadduct **4** was a [2:1] cycloadduct of **1** with **2**, 22 carbons might be observed besides the carbonyl carbons. But 19 carbon signals appeared in ^{13}C-NMR of **4**. Three carbon signals were missing. It was suggested that this molecule had a partially symmetric structure. The rest of the enolate ring protons of **4** appeared at 6.68, 6.31, 5.46, and 2.77 ppm (ratio of area, 2:2:2:1, respectively). The corresponding carbons were observed at 130.97, 126.06, 115.77, and 43.43 ppm on the basis of C, H COSY. These signals were assigned as typical monosubstituted cycloheptatrienyl ring protons and carbons. Therefore, the cycloadduct **4** is an ester of tropylcarboxylic acid as shown in Scheme 3. As the temperature was raised in the reaction of **1** with **2**, the yield of **4** increased. This observation meant that the enol form of **3** increased at higher temperature and reacted with another 8-oxoheptafulvene to give the acylated product **4**.

2.4. Structure of **5**

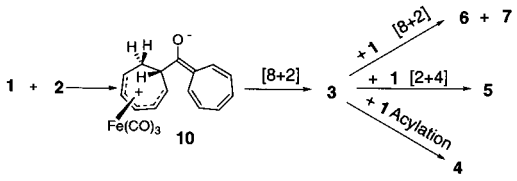
Since two characteristic carbonyl absorption bands in IR of compound **5** were observed at 1768 and 1742 cm^{-1}, compound **5** was estimated to be an ester or a lactone. The carbon signal at 25.98 ppm in ^{13}C-NMR of **5** was assigned as a methylene carbon (C-12) by DEPT. The proton signals at 2.14 and 2.10 ppm in ^{1}H-NMR of **5** were assigned as methylene protons at C-12 on the basis of C, H COSY. From these methylene protons, protons at H-3a, 4–11, 7a, 7b, and 12a were assigned on the basis of decoupling and H, H COSY experiments. The remaining proton signals were independent of the other protons mentioned above and related to each other as a 3.05–6.05–6.41–6.14–6.25–3.08–3.05 on the basis of the H, H COSY and C, H COSY. These signals at 3.05, 6.05, 6.41, 6.14, 6.25, and 3.08 were assigned to the protons of the norcaradiene moiety (H-1′, H-2′, H-3′, H-4′, H-5′, and H-6′, respectively). The three-membered ring carbons could not be found at 295 K, which is the usual temperature to take NMR spectra. When we recorded its ^{13}C-NMR at 309 K, their signals appeared at 23.62 and 52.17, and 59.33 ppm as broad signals probably due to the contribution of cycloheptatriene form. In order to establish the configuration of the norcaradiene moiety, NOE experiments were carried out. Irradiation of H-3a gave NOE enhancements in the signals for H-4, H-7a, H-2′, H-3′, H-4′, and H-5′. Irradiation of H-1′ gave NOE enhancements in the signals for H-2′ and H-6′. This observation suggested that this molecule had an endo-norcaradiene structure. Irradiation of H-7b gave NOE enhancements in the signals for H-7a, H-8, and H-12a. From these data, we established that this adduct was an endo-type norcaradiene derivative bearing spiro-δ-lactone as shown in Scheme 3. Although, there are numerous reports regarding the relation between the cycloheptatriene and norcaradiene forms [9] and especially, endo-type norcaradiene derivatives bearing a spiro-γ-lactone were known [2], this is the first example of a norcaradiene compound bearing a spiro-δ-lactone. This cycloadduct **5** came from cycloaddition of **1** with **3** by [2 + 4] mode. To the best of our knowledge, this [2 + 4] cycloaddition was the first example in the reaction of 8-oxoheptafulvene with enone. Furthermore, the cycloadduct **5** rearranged by thermal hydrogen 1,5-shift to **9** quantitatively (Scheme 4).

2.5. Structures of **6** and **7**

The carbonyl absorption bands in the IR spectra of adducts **6** and **7** can be seen at 1756 and 1758 cm^{-1},



Scheme 4.



Scheme 5.

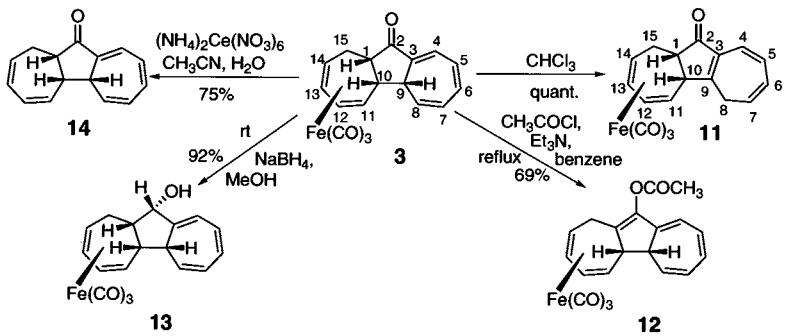
respectively, suggesting lactone structures. The signals in ^{1}H-NMR of **6** were divided into two groups. The proton group from H-1 to H-15 was assigned by a similar NMR technique described above as shown in Section 4. The other one was 7.18(H-3′)-6.74(H-4′)-6.82(H-5′)-6.20(H-6′)-5.37(H-7′)-2.82(H-7′a). These signals were assigned on the basis of H, H COSY as shown. There was still a possibility of four structures due to the difference in stereochemistry at C-2 (8′) and C-7′a on the basis of H, H COSY and C, H COSY of cycloadduct **6**. Irradiation of H-1 gave NOE enhancements in the signals for H-7′a and H-10, and H-15. Irradiation of H-10 and 11 gave NOE enhancements in the signals for H-1, H-9, H-7′a, and H-12. Irradiation of H-4 gave NOE enhancements in the signals for H-5 and H-7′. Consequently, there were protons H-1, H-9, H-10 and H-7′a in the same side. According to these results, the structure of **6** was established as shown in Scheme 3. Similarly, the structure of **7** was established as a stereo isomer of **6** at H-7a as shown in Scheme 3.

2.6. Reaction profile of *1* with *2*

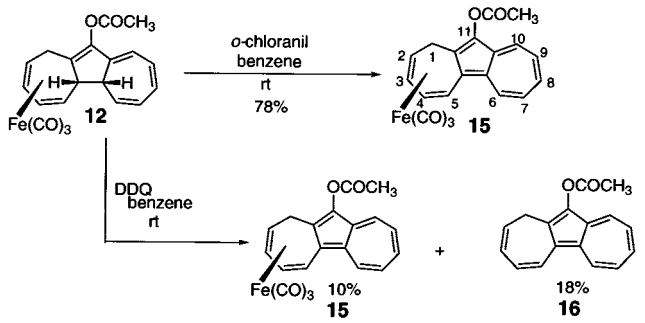
It is interesting that the [2 + 2]π cycloadduct **8** or its derivative could not be obtained by the reaction of **1** with **2**. Complex **2** was well known to receive electrophilic attack at the free double bond from the opposite face of iron to give an irontricarbonyl complex of substituted cycloheptadienium [6,10]. Consequently, on inspection of the reaction products and previous results, we considered that, first of all, cycloheptatrieneFe(CO)$_3$ attacked **1** as a nucleophile to give a zwitterion **10**, followed by ring closure to give the [8 + 2] cycloadduct **3**. Accordingly, **1** played the role of an 8π electronic ingredient in this cycloaddition. There was a probability that [2:1] adducts (**4**, **5**, **6**, and **7**) came from the reaction of **1** with **3** or **8**. Therefore, the reaction of **1** with **3** was carried out at room temperature for 5 h to give [2:1] adducts **4**, **5**, **6**, and **7** in 4, 15, 4, and 4% yields, respectively. These experiments suggested **1** initially reacted with **2** in [8 + 2] mode. Compound **1** further reacted with **3** to give several types of products (acylation, [2 + 4], and [8 + 2] cycloaddition). The reaction profile of **1** with **2** is shown in Scheme 5 on the basis of their structures. It is interesting that [8 + 2] adduct **3** exhibited several reactivities toward 8-oxoheptafulvene.

2.7. Further reactivities of the [8 + 2] cycloadduct *3*

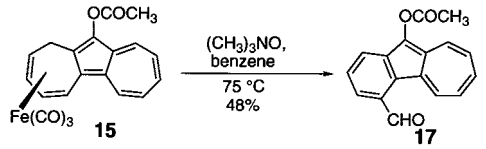
The reactivity of the [8 + 2] cycloadduct **3** was further exemplified by a rearrangement of the methine proton at C-9 in chloroform to give complex **11**. This rearrangement was very slow in benzene. Chloroform sometimes contains a trace amount of acid. We suspected that this was an acid-catalyzed isomerization. Complex **3** reacted with acetyl chloride in the presence of triethylamine in benzene to give an acetate **12** similar to cycloadduct **4**. Cycloadduct **3** was easily reduced with sodium boron hydride stereospecifically to give alcohol **13** in 92% yield. The cycloadduct **3** was decomplexed by ceric ammonium nitrate at room temperature to give **14** (75%). Under an analogous acylation condi-



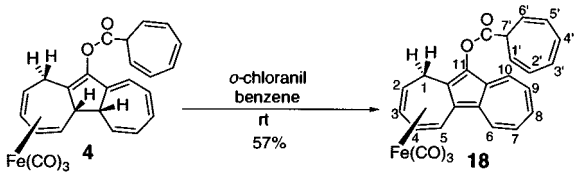
Scheme 6.



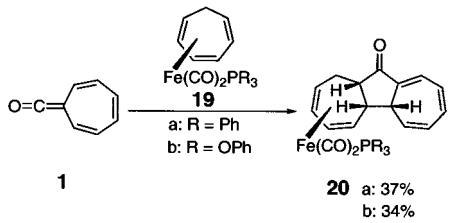
Scheme 7.



Scheme 8.



Scheme 9.



Scheme 10.

tion of **3**, we failed to obtain the corresponding acetates from the rearranged product **11** and iron-free compound **14** (Scheme 6).

2.8. Synthesis of tricarbonyl[(2,3,4,5-η)-1H-cyclohept-[a]azulene]iron and related compounds

There has been no report of a mononuclear azulenoid complex of iron tricarbonyl (Scheme 7). Dinuclear complexes in azulenoid organometallic complex are well known [11]. Due to development of a synthetic way for azulenoid complexes of iron tricarbonyl from **3**, we examined the oxidation condition of the acetate **12**. Compound **12** was treated with *o*-chloranil in benzene at room temperature to give tricarbonyl[(2,3,4,5-η)-11-acetoxy-1*H*-cyclohept[*a*]azulene]iron (**15**) in 78% yield. Oxidation of compound **12** with DDQ afforded compound **15** and iron-free compound **16**. Compound **15** was treated with trimethylamine *N*-oxide due to decomplexation to give further oxidized benzoazulene derivative **17** in 48% yield (Scheme 8). Complex **4** also oxidized with *o*-chloranil to give azulene **18** in 57% yield (Scheme 9).

Although the synthesis of 1*H*-cyclohept[*a*]azulene has been reported already [12], its irontricarbonyl complex is unknown. Complexes **15** and **18** were the first examples of mononuclear irontricarbonyl complexes in azulenoid compounds. By comparing the NMR and vis spectra of **15** and **16**, we observed characteristic changes by coordination to iron tricarbonyl. The chemical shift of the azulene ring protons changed to upper field (Δ 0.13–0.22 ppm) and the absorption maximum of the longest wavelength shifted to longer wavelength (Δ 22 nm) in the Vis spectra by coordination to irontricarbonyl.

We considered that the yield of [8 + 2] cycloadduct **3** was poor because electron density was not high. One of the three carbonyl ligands of complex **2** was exchanged with triphenylphosphine or triphenyl phosphite, which was expected to have a more electron-donating character to give **19a** [13] and **19b** [14], respectively. The compound **1** reacted with **19a** and **19b** to give [8 + 2] cycloadducts **20a** and **20b** in 37 and 34% yield, respectively (Scheme 10). We could not find a [2:1] cycloadduct due to the strong steric effect. According to these results, it is assumed that the cycloaddition of 8-oxoheptafulvene with cycloheptatriene iron complexes occurred in [8 + 2] fashion. [8 + 2] Cycloadducts were considered as potentially useful intermediates for preparing interesting condensed azulene derivatives. Improvement of this approach and its application to mononuclear iron complexes of azulenoid compounds are currently under way in our laboratory.

3. Conclusion

We have demonstrated that reaction of 8-oxoheptafulvene with cycloheptatrieneFe(CO)$_3$ underwent [8 + 2] cycloaddition to give **3**, which reacted with another 8-oxoheptafulvene by several types of reaction. Furthermore, we developed a synthetic way of tricarbonyliron complexes of 1*H*-cyclohept[*a*]azulene and related compounds from cycloadduct **3**. In the case of cycloheptatrieneFe(CO)$_2$PR$_3$, the yields of [8 + 2] cycloadduct increased.

4. Experimental

4.1. General

Melting points (m.p.) were determined on a Yanagimoto micro melting point apparatus MP-S3 and are uncorrected. 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 Bruker AM-600 spectrometer at 600 MHz (150 MHz), a JEOL A500 at 500 MHz (125 MHz) and a JEOL GSX-400 at 400 MHz (100 MHz) in $CDCl_3$. Mass spectra were obtained with a JEOL HX-110 or a Hitachi M-2500 instrument usually at 70 eV. Column chromatography was performed on silica gel (Kieselgel 60). Gel permeation chromatography (GPC) was performed on a TSKgel G2000H$_6$. Elemental analyses were performed at the Instrumental Analysis Center of Chemistry, Faculty of Science, Tohoku University.

4.2. Reaction of 8-oxoheptafulvene (**1**) with tricarbonyl[(1,2,3,4-η)-1,3,5-cycloheptatriene]iron (**2**)

A solution of tropyl carboxylic acid chloride (2.34 g, 15.1 mmol) in dry benzene (100 ml) was added dropwise at room temperature (r.t.) to a solution of **2** (4.64 g, 20.0 mmol) and triethylamine (2.40 g, 23.7 mmol) in the same solvent (150 ml) over a period of 6 h under nitrogen atmosphere. After the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel with benzene to afford **3** (1.00 g, 18.9%), **4** (111 mg, 1.6%), **5** (178 mg, 2.5%), 1:1 mixture of **6** and **7** (261 mg, 3.7%). The mixture of **6** and **7** was separated by GPC with $CHCl_3$ as an eluent to afford lactone **6** (130 mg, 1.8%) and lactone **7** (130 mg, 1.8%).

4.2.1. Tricarbonyl[(11,12,13,14-η)-tricyclo[8.5.0.0^{3,9}]-pentadeca-3,5,7,11,13-pentaene-2-one]iron (**3**)

Yellow crystals; m.p. 134–136 °C; IR (KBr) ν_{max} 2048, 1982, 1958 and 1716 cm^{-1}; UV–vis (MeOH) λ_{max}, nm (log ε) 202 (4.51), 203 (4.53), 215 (4.50), 225 (4.52), 266 sh (3.77) and 341 sh (3.51); ^{1}H-NMR (600 MHz, $CDCl_3$) δ 6.78 (dd, $J = 6.6$, 2.0 Hz, H-4), 6.21 (dd, $J = 11.3$, 6.8 Hz, H-6), 6.10 (dd, $J = 11.3$, 6.7 Hz, H-5), 5.94 (ddd, $J = 11.1$, 6.8, 2.6 Hz, H-7), 5.42 (dd, $J = 11.1$, 2.4 Hz, H-8), 5.32 (dd, $J = 6.8$, 5.0 Hz, H-12), 5.26 (dd, $J = 6.8$, 5.0 Hz, H-13), 3.98 (dddd, $J = 6.1$, 2.6, 2.4, 2.0 Hz, H-9), 3.00 (td, $J = 6.1$, 2.2 Hz, H-10), 2.93 (ddd, $J = 6.8$, 5.2, 2.2 Hz, H-14), 2.78 (d, $J = 6.8$ Hz, H-11), 2.51 (dd, $J = 15.4$, 5.9 Hz, H-15), 2.12 (ddd, $J = 15.4$, 5.7, 2.3 Hz, H-15) and 2.08 (dd, $J = 5.7$, 2.2 Hz, H-1); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 210.86 (Fe(*C*O)$_3$), 203.95 (C-2), 135.41 (C-6), 134.02 (C-3), 129.75 (C-4), 129.65 (C-5), 127.93 (C-7), 91.04 (C-13), 88.33 (C-12), 58.36 (C-11), 55.91 (C-14), 49.67 (C-1), 46.81 (C-9), 41.29 (C-10) and 24.95 (C-15); HRMS (EI) calc. for $C_{18}H_{14}O_4Fe$ [M$^+$] 350.0242, Found: 350.0230; MS (70 eV) m/z 350 ([M$^+$], 7), 322 (68), 266 (100) and 238 (44); Anal. Calc. for $C_{18}H_{14}FeO_4$: C, 61.74; H, 4.03. Found: C, 61.98; H, 4.14%.

4.2.2. Tricarbonyl[(11,12,13,14-η)-tricyclo[8.5.0.0^{3,9}]-pentadeca-1,3,5,7,11,13-hexaen-2-yl]iron cyclohepta-1′,3′,5′-triene-7′-carboxylate (**4**)

Colorless crystals; m.p. 126.7–128.7 °C (dec.); IR (KBr) ν_{max} 3032, 2880, 2836, 2048, 1976 and 1764 cm^{-1}; UV–vis (MeOH) λ_{max}, nm (log ε) 233 (4.66) and 320 (3.90); ^{1}H-NMR (600 MHz, $CDCl_3$) δ 6.68 (t, $J = 2.9$ Hz, H-3′ and H-4′), 6.51 (dd, $J = 11.0$, 5.9 Hz, H-9), 6.38 (dd, $J = 11.0$, 5.8 Hz, H-6), 6.31 (dd, $J = 8.8$, 2.9 Hz, H-2′ and H-5′), 6.14 (ddd, $J = 9.7$, 5.8, 1.0 Hz, H-7), 5.76 (d, $J = 5.9$ Hz, H-4), 5.56 (dd, $J = 9.7$, 4.5 Hz, H-8), 5.50 (dd, $J = 7.2$, 4.5 Hz, H-12), 5.46 (dd, $J = 8.8$, 5.7 Hz, H-1′ and H-6′), 5.27 (dd, $J = 6.7$, 5.2 Hz, H-13), 3.81 (dd, $J = 8.5$, 1.0 Hz, H-10), 3.11 (dd, $J = 7.2$, 1.0 Hz, H-12), 3.01 (dd, $J = 6.7$, 5.5 Hz, H-14), 2.82 (dd, $J = 8.5$, 4.5 Hz, H-9), 2.81 (dd, $J = 18.0$, 5.5 Hz, H-15), 2.77 (t, $J = 5.7$ Hz, H-7′), and 2.62 (d, $J = 18.0$ Hz, H-15); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 210.82 (Fe(*C*O)$_3$), 169.78 (O*C*O), 142.61 (C-2), 135.82 (C-3), 135.01 (C-1), 130.97 (C-3′ and C-4′), 130.47 (C-5), 128.96 (C-6), 126.06 (C-2′ and C-5′), 125.47 (C-7), 118.70 (C-8), 115.77 (C-1′ and C-6′), 110.58 (C-4), 89.82 (C-13), 88.66 (C-12), 60.59 (C-11), 56.91 (C-14), 44.98 (C-10), 43.56 (C-9), 43.43 (C-7′) and 27.93 (C-15); HRMS (EI) calc. for $C_{26}H_{20}O_5Fe$ [M$^+$] 468.0660, Found: 468.0640; MS (70 eV) m/z 468 ([M$^+$], 7%), 412 (27), 384 (100) and 356 (22); Anal. Calc. for $C_{26}H_{20}FeO_5$: C, 66.69; H, 4.30. Found: C, 66.75; H, 4.40%.

4.2.3. Tricarbonyl[(8,9,10,11-η)-3,3a,7a,7b,12,12a-hexahydro-2H-cyclohept[a]azuleno[c,d]pyren-2-one-3-spiro-7′-bicyclo[4.1.0]hepta-2′,4′-diene]iron (**5**)

Colorless crystals; m.p. 147.0–150.0 °C (dec.); IR (KBr) ν_{max} 2048, 1974, 1950, 1768 and 1742 cm^{-1}; UV–vis (MeOH) λ_{max}, nm (log ε) 227 sh (4.59), 257 sh (4.28) and 281 sh (4.12); ^{1}H-NMR (600 MHz, $CDCl_3$) δ 6.41 (dd, $J = 8.8$, 6.9 Hz, H-3′), 6.25 (dd, $J = 8.9$, 6.8 Hz, H-5′), 6.14 (dd, $J = 8.9$, 6.9 Hz, H-4′), 6.05 (dd, $J = 8.8$, 6.8 Hz, H-2′), 5.85 (ddd, $J = 11.8$, 6.6, 1.5 Hz, H-6), 5.75 (dd, $J = 11.8$, 4.7 Hz, H-7), 5.63 (ddd, $J = 11.1$, 6.6, 2.9 Hz, H-5), 5.56 (dd, $J = 11.1$, 2.8 Hz, H-4), 5.25 (ddd, $J = 7.8$, 4.9, 1.3 Hz, H-9), 5.20 (dd, $J = 7.7$, 4.9 Hz, H-10), 3.80 (t, $J = 6.8$ Hz, H-6′), 3.46 (m, H-7a), 3.05 (t, $J = 6.8$ Hz, H-1′), 3.00 (td, $J = 6.4$, 3.8 Hz, H-7b), 2.92 (dddd, $J = 7.7$, 5.9, 2.8, 1.3 Hz, H-11), 2.74 (dddd, $J = 5.0$, 3.9, 2.8, 1.1 Hz, H-12a), 2.65 (ddd, $J = 7.8$, 3.8, 1.1 Hz, H-8), 2.36 (dd, $J = 2.9$, 2.8 Hz, H-3a), 2.14 (ddd, $J = 16.7$, 5.9, 3.9 Hz, H-12) and 2.10

(dt, $J = 16.7$, 5.0 Hz, H-12); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 211.37 (Fe(CO)$_3$), 173.74 (C-2), 146.91 (C-12b), 135.11 (C-4), 132.76 (C-5), 128.15 (C-4′), 126.90 (C-6), 125.86 (C-3′), 125.42 (C-2′), 124.80 (C-5), 122.93 (C-5′), 115.75 (C-12c), 89.55 (C-10), 88.88 (C-9), 59.33 (C-6′), 57.18 (C-8), 57.09 (C-11), 52.17 (C-1′), 50.52 (C-7a), 45.44 (C-7b), 42.80 (C-12a), 31.17 (C-3a), 25.96 (C-12) and 23.62 (C-3); HRMS (EI) calc. for $C_{26}H_{20}FeO_5$ [M^+] 468.0660, Found 468.0600; MS (70 eV) m/z 468 ([M^+], 3), 440 (94), 384 (83) and 356 (100); Anal. Calc. for $C_{26}H_{20}O_5Fe \cdot 1/2H_2O$: C, 65.43; H, 4.44. Found: C, 65.49; H, 4.42%.

*4.2.4. (1SR,7′aSR)-Tricarbonyl[(11,12,13,14-η)-tricyclo[8.5.0.0^{3,9}]pentadeca-3,5,7,11,13-pentaene-2-spiro-8′-(7′a,8′-dihydro-2′H-cyclohepta[c]furan-2′-one)]-iron (**6**)*

Colorless crystals; m.p. 130.0–135.0 °C (dec.); IR (KBr) ν_{max} 2044, 1972 and 1756 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.18 (dd, $J = 6.0$, 2.2 Hz, H-3′), 6.82 (dd, $J = 11.1$, 6.1 Hz, H-5′), 6.74 (dd, $J = 11.1$, 6.0 Hz, H-4′), 6.61 (dd, $J = 11.0$, 5.9 Hz, H-5), 6.55 (dd, $J = 11.0$, 5.8 Hz, H-6), 6.20 (ddd, $J = 10.0$, 6.1, 2.2 Hz, H-6′), 6.12 (ddd, $J = 9.8$, 5.8, 2.2 Hz, H-7), 5.98 (dd, $J = 5.9$, 1.5 Hz, H-4), 5.63 (ddd, $J = 7.9$, 4.7, 2.0 Hz, H-12), 5.52 (dd, $J = 7.6$, 4.7 Hz, H-13), 5.43 (dd, $J = 9.8$, 4.2 Hz, H-8), 5.37 (dd, $J = 10.0$, 3.6 Hz, H-7′), 3.17 (ddd, $J = 8.3$, 7.6, 2.0 Hz, H-14), 3.00 (m, H-10 and H-11), 2.82 (dt, $J = 3.6$, 2.2 Hz, H-7′a), 2.29 (m, H-9), 2.05 (ddd, $J = 14.2$, 8.3, 5.7 Hz, H-15), 1.79 (dt, $J = 12.4$, 5.7 Hz, H-1), 1.31 (dd, $J = 14.2$, 12.4 Hz, H-15); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 211.18 (Fe(CO)$_3$), 167.97 (C-2′), 139.05 (C-2′a), 136.34 (C-5′), 130.53 (C-6), 130.09 (C-3′), 129.96 (C-5), 129.20 (C-4′), 125.93 (C-6′), 124.94 (C-7′), 124.49 (C-7), 123.18 (C-8), 122.38 (C-4), 121.04 (C-3), 92.17 (C-2), 91.83 (C-12), 88.77 (C-13), 60.75 (C-14), 60.13 (C-11), 59.12 (C-1), 49.25 (C-7′a), 42.29 (C-9), 40.83 (C-10) and 29.69 (C-15); HRMS calc. for $C_{26}H_{20}O_5Fe$ [M^+] 468.0660, Found: 468.0631; MS (70 eV) m/z 468 ([M^+], 4), 440 (28), 384 (100) and 340 (33); Anal. Calc. for $C_{26}H_{20}FeO_5$: C, 66.68; H, 4.31. Found: C, 66.27; H, 4.68%.

*4.2.5. (1SR, 7′aRS)-Tricarbonyl[(11,12,13,14-η)-tricyclo[8.5.0.0^{3,9}]pentadeca-3,5,7,11,13-pentaene-2-spiro-8′-(7′a,8′-dihydro-2′H-cyclohepta[c]furan-2′-one)]-iron (**7**)*

Colorless crystals; m.p. 176.0–178.0 °C (dec.); IR (KBr) ν_{max} 2044, 1978, 1952 and 1758 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.20 (d, $J = 5.8$ Hz, H-3′), 6.87 (dd, $J = 11.0$, 6.1 Hz, H-5′), 6.79 (dd, $J = 11.0$, 5.8 Hz, H-4′), 6.48 (m, H-5 and H-6), 6.35 (ddd, $J = 9.8$, 6.1, 2.0 Hz, H-6′), 6.09 (ddd, $J = 9.7$, 3.8, 1.8 Hz, H-7), 5.97 (dd, $J = 3.0$, 1.8 Hz, H-4), 5.65 (m, H-7′ and H-12), 5.56 (dd, $J = 7.7$, 4.7 Hz, H-14), 5.42 (dd, $J = 9.7$, 4.4 Hz, H-8), 3.25 (ddt, $J = 8.8$, 7.7, 1.8 Hz, H-14), 3.06 (m, H-10 and H-11), 2.82 (dt, $J = 4.2$, 2.0 Hz, H-7′a), 2.53 (dt, $J = 12.3$, 5.5 Hz, H-1), 2.19 (m, H-9), 2.04 (ddd, $J = 14.2$, 8.8, 5.5 Hz, H-15) and 1.38 (dd, $J = 14.2$, 12.3 Hz, H-15); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 211.36 (Fe(CO)$_3$), 167.65 (C-2′), 145.27 (C-2′a), 135.97 (C-5′), 130.47 (C-6), 130.16 (C-5), 129.55 (C-4′), 129.13 (C-3′), 126.74 (C-6′), 124.34 (C-7), 123.08 (C-8), 120.64 (C-3), 120.41 (C-7′), 117.53 (C-4), 92.00 (C-12), 90.33 (C-2), 88.85 (C-13), 61.77 (C-14), 60.33 (C-11), 49.77 (C-1), 49.24 (C-7′a), 41.71 (C-9), 40.81 (C-10) and 23.16 (C-15); HRMS (EI) calc. for $C_{26}H_{20}O_5Fe$ [M^+] 468.0660, Found: 468.0626; MS (70 eV) m/z 468 ([M^+], 2), 440 (47), 384 (100) and 340 (42); Anal. Calc. for $C_{26}H_{20}FeO_5$: C, 66.68; H, 4.31. Found: C, 66.29; H, 4.68%.

*4.3. Thermal rearrangement of **5** to tricarbonyl-[(8,9,10,11-η)-3-(cyclohexa-1,4-dien-3-yl)-2H-(7a,7b,12,12a-tetrahydro-cyclohept[a]azuleno[c,d])-pyren-2-one]iron (**9**)*

A solution of adduct **5** (102 mg, 0.218 mmol) in benzene (30 ml) was heated at 80 °C under nitrogen atmosphere for 24 h. After the solvent was removed, the residue was purified by column chromatography on silica gel with CH_2Cl_2 to afford **9** (97.2 mg, 95%). Yellow crystals; m.p. 135.0–136.0 °C (dec.); IR (KBr) ν_{max} 2045, 1973 and 1698 cm^{-1}; UV–vis (CH_3CN) λ_{max}, nm (log ε) 344 (4.10) and 400 sh (3.66); ^{1}H-NMR (600 MHz, $CDCl_3$) δ 6.83 (d, $J = 12.1$ Hz, H-4), 6.11 (m, H-5), 5.94 (m, H-6), 5.93 (m, H-7), 5.82 (m, H-1′), 5.76 (m, H-5′), 5.66 (m, H-4′), 5.61 (m, H-2′), 5.29 (ddd, $J = 7.7$, 5.0, 1.2 Hz, H-9), 5.20 (dd, $J = 7.7$, 5.0 Hz, H-10), 4.69 (m, H-3′), 3.88 (dd, $J = 5.9$, 2.9 Hz, H-7a), 3.03 (td, $J = 5.9$, 2.9 Hz, H-7b), 2.96 (m, H-11), 2.81 (ddd, $J = 9.0$, 5.9, 2.7 Hz, H-12a), 2.75 (m, H-6′ and H-6′), 2.69 (ddd, $J = 7.7$, 2.9, 1.2 Hz, H-8), 2.50 (dd, $J = 17.4$, 9.0 Hz, H-12) and 2.22 (ddd, $J = 17.4$, 6.0, 2.7 Hz, H-12); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 161.96 (C-2), 147.38 (C-12b), 134.65 (C-7), 133.33 (C-5), 127.99 (C-4′), 127.08 (C-2′), 125.88 (C-4), 125.50 (C-6), 123.83 (C-1′), 123.27 (C-5′), 120.99 (C-12c), 116.11 (C-3a), 89.54 (C-10), 88.96 (C-9), 65.85 (C-3), 56.38 (C-11), 54.84 (C-8), 48.08 (C-7a), 44.77 (C-7b), 42.35 (C-12a), 34.61 (C-3′), 25.65 (C-6′) and 24.56 (C-12); MS (70 eV) m/z 468 ([M^+], 0.49), 440 (29), 384 (100), 327 (31), 278 (47), 250 (25), 191 (12), 178 (19), and 78 (20); Anal. Calc. for $C_{26}H_{20}FeO_5 \cdot 2H_2O$: C, 61.92; H, 4.80. Found: C, 62.00; H, 4.35%.

*4.4. Rearrangement of compound **3** in $CHCl_3$ to tricarbonyl[(1,2,3,4-η)-tricyclo[8.5.0.0^{3,9}]pentadeca-3(9),4,6,11,13-pentaene-2-one]iron compound (**11**)*

A solution of compound **3** (21.0 mg, 0.0600 mmol) in $CHCl_3$ (20 ml) was stirred at r.t. for 12 h under

nitrogen atmosphere. After the solvent was removed, rearrangement product (**11**) was obtained quantitatively. Pale yellow crystals; m.p. 133.0–134.8 °C; IR (KBr) ν_{max} 2041, 1975 and 1707 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 6.73 (d, $J = 11.0$ Hz, H-4), 6.57 (dd, $J = 11.0$, 5.8 Hz, H-5), 6.18 (dd, $J = 9.7$, 5.8 Hz, H-6), 5.46 (dt, $J = 9.7$, 6.3 Hz, H-7), 5.06 (dd, $J = 7.8$, 5.1 Hz, H-13), 4.88 (ddd, $J = 7.4$, 5.1, 0.5 Hz, H-12), 3.17 (ddd, $J = 7.8$, 5.9, 1.9 Hz, H-14), 3.09 (dd, $J = 7.4$, 3.0 Hz, H-11), 3.05 (dd, $J = 6.8$, 3.0 Hz, H-10), 2.97 (dd, $J =$ 13.7, 6.3 Hz, H-8), 2.86 (dd, $J = 13.7$, 6.3 Hz, H-8), 2.80 (dd, $J = 17.6$, 5.9 Hz, H-15), 2.46 (dd, $J = 7.7$, 6.8 Hz, H-1) and 2.19 (ddd, $J = 17.6$, 7.7, 1.9 Hz, H-15); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 201.57 (Fe(*C*O)$_3$), 204.41 (C-2), 169.93 (C-9), 132.51 (C-3), 131.23 (C-5), 128.67 (C-6), 122.62 (C-4), 121.18 (C-7), 92.34 (C-13), 85.02 (C-12), 59.07 (C-14), 58.73 (C-11), 47.24 (C-1), 43.25 (C-10), 30.20 (C-8) and 24.58 (C-15); MS (70 eV) m/z 350 ([M^+], 0.6%) and 266 (100); Anal. Calc. for $C_{18}H_{14}FeO_4$: C, 61.74; H, 4.03. Found: C, 61.44; H, 4.27%.

*4.5. Acetylation of compound **3**: synthesis of tricarbonyl[(11,12,13,14-η)-2-acetoxytricyclo[8,5,0,0^{3,9}]-pentadeca-1,3,5,7,11,13-hexane]iron (**12**)*

A solution of acetyl chloride (653 mg, 8.32 mmol) in dry benzene (150 ml) was added dropwise at reflux temperature to a solution of compound **3** (350 mg, 1.00 mmol) and triethylamine (1.00 g, 9.88 mmol) in the same solvent (30 ml) over a period of 12 h. After white crystals of triethylammonium chloride was removed by filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2 as an eluent to afford **12** (271 mg, 69%). Colorless crystals; m.p. 160.5–161.5 °C; IR (KBr) ν_{max} 2040, 1972, 1956, 1925 and 1759 cm^{-1}; UV–vis (CH_3CN) λ_{max}, nm (log ε) 233 (4.15) and 320 (3.39); ^{1}H-NMR (600 MHz, $CDCl_3$) δ 6.51 (dd, $J = 11.0$, 6.0 Hz, H-5), 6.38 (dd, $J = 11.0$, 5.8 Hz, H-6), 6.13 (ddd, $J = 9.8$, 5.8, 1.9 Hz, H-7), 5.74 (d, $J = 6.0$ Hz, H-4), 5.55 (dd, $J = 9.8$, 4.6 Hz, H-8), 5.49 (dd, $J = 7.3$, 5.0 Hz, H-12), 5.26 (dd, $J = 7.6$, 5.0 Hz, H-13), 3.79 (d, $J = 8.6$ Hz, H-10), 3.11 (dd, $J = 7.3$, 1.6 Hz, H-11), 3.02 (t, $J = 7.6$ Hz, H-14), 2.86 (m, H-9 and H-15), 2.59 (d, $J = 18.1$ Hz, H-15) and 2.20 (s, Me); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 210.8 (Fe(*C*O)$_3$), 167.61 (O*C*O), 142.76 (C-2), 136.00 (C-3), 134.9 (C-1), 130.50 (C-5), 128.88 (C-6), 125.46 (C-7), 118.77 (C-8), 110.54 (C-4), 89.78 (C-13), 88.65 (C-12), 60.67 (C-11), 57.03 (C-14), 44.96 (C-10), 43.52 (C-9), 27.91 (C-5) and 20.42 (Me); MS (70 eV) m/z 392 ([M^+], 2%), 336 (37), 308 (100) and 191 (29); Anal. Calc. for $C_{20}H_{16}FeO_5$: C, 61.25; H, 4.11. Found: C, 61.09; H, 4.17%.

*4.6. Reduction of **3** with $NaBH_4$ to tricarbonyl[(11,12,13,14-η)-tricyclo[8.5.0.0^{3,9}]-pentadeca-3,5,7,11,13-pentaene-2-ol]iron (**13**)*

Sodium borohydride (17.0 mg, 0.449 mmol) was added to a solution of **3** (100 mg, 0.286 mmol) in methanol (30 ml) at r.t. under nitrogen atmosphere. After stirring for 24 h, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2 as an eluent to afford **13** (96.0 mg, 95%). Pale yellow needles; m.p. 127.0–128.0 °C; IR (KBr) ν_{max} 3303 (m), 2040 (s), 1980 cm^{-1}; UV–vis (CH_3CN) λ_{max}, nm (log ε) 215 sh (4.57) and 287 sh (3.75); ^{1}H-NMR (600 MHz, $CDCl_3$) δ 6.64 (dd, $J = 10.9$, 5.9 Hz, H-5), 6.51 (dd, $J = 10.9$, 5.8, H-6), 6.21 (d, $J = 5.9$ Hz, H-4), 6.07 (ddd, $J = 9.6$, 5.8, 1.8 Hz, H-7), 5.59 (ddd, $J = 7.3$, 4.7, 1.6 Hz, H-12), 5.50 (dd, $J = 7.7$, 4.7 Hz, H-13), 5.33 (dd, $J = 9.6$, 4.5 Hz, H-8), 4.88 (m, H-2), 3.21 (t, $J = 7.7$ Hz, H-14), 3.07 (t, $J = 7.3$ Hz, H-11), 2.95 (dd, $J = 14.7$, 7.3 Hz, H-10), 2.13 (ddd, $J = 14.7$, 13.1, 6.6 Hz, H-1), 1.99 (m, H-9), 1.85 (ddd, $J = 13.1$, 7.7, 6.6 Hz, H-15), 1.36 (d, $J = 8.0$ Hz, OH) and 1.05 (t, $J = 13.1$ Hz, H-15); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 211.40 (Fe(*C*O)$_3$), 145.27 (C-3), 131.08 (C-5), 129.32 (C-6), 123.89 (C-7), 122.33 (C-8), 118.32 (C-4), 91.87 (C-12), 88.56 (C-13), 75.85 (C-2), 61.43 (C-11), 60.97 (C-14), 49.74 (C-1), 42.88 (C-9), 41.08 (C-10) and 20.74 (C-15); MS (70 eV) m/z 352 ([M^+], 0.6%), 268 (31), 204 (30), 194 (24), 176 (51), 165 (45), 148 (84), 141 (25), 120 (58), 112 (71), 91 (100), 84 (23), 70 (20) and 56 (31); Anal. Calc. for $C_{19}H_{16}FeO_4$: C, 61.39; H, 4.58. Found: C, 61.23; H, 4.63%.

*4.7. Tricyclo[8.5.0.0^{3,9}]pentadeca-3,5,7,11,13-pentaen-2-one (**14**)*

A solution of ceric ammonium nitrate (1.21 g, 2.21 mmol) in acetonitrile (20 ml) was added to a solution of [8 + 2] adduct **3** (274 mg, 0.783 mmol) in the same solvent (50 ml) at r.t. After stirring for 1 h, the reaction mixture was poured into water and extracted with ethyl acetate, dried over $MgSO_4$. After the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel with CH_2Cl_2 as an eluent to afford **14** (126 mg, 77%). Pale yellow crystals: m.p. 86.0–86.5 °C; IR (KBr) ν_{max} 1701 cm^{-1}; UV–vis (MeOH) λ_{max}, nm (log ε) 231 (4.27) and 321 (3.65); ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.09 (d, $J = 5.6$ Hz, H-4), 6.89 (dd, $J = 11.0$, 6.1 Hz, H-6), 6.83 (dd, $J = 11.0$, 5.6 Hz, H-5), 6.29 (ddd, $J = 9.5$, 6.1, 2.0 Hz, H-7), 6.17 (ddd, $J = 11.7$, 5.9, 1.9 Hz, H-12), 6.05 (dd, $J = 11.7$, 4.0 Hz, H-11), 6.02 (ddd, $J = 11.0$, 8.4, 3.9 Hz, H-14), 5.98 (ddd, $J = 11.0$, 5.9, 2.2 Hz, H-13), 5.75 (dd, $J = 9.5$, 5.0 Hz, H-8), 3.48 (m, H-10), 2.67 (ddd, $J =$ 11.7, 8.1, 1.9 Hz, H-1), 2.61 (ddd, $J = 7.5$, 5.0, 2.0 Hz, H-9), 2.48 (ddd, $J = 14.6$, 8.4, 2.2 Hz, H-15) and 2.16

(dddd, $J = 14.6$, 11.7, 3.9, 1.9 Hz, H-15); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 206.47 (C-2), 136.35 (C-6), 133.20 (C-11), 132.39 (C-14), 129.97 (C-5), 127.11 (C-12), 127.06 (C-8), 126.89 (C-13), 126.82 (C-3), 125.99 (C-7), 125.77 (C-4), 53.41 (C-1), 43.45 (C-9), 42.42 (C-10) and 33.21 (C-15); MS (70 eV) m/z 210 ([M^+], 39%), 118 (49) and 90 (100); Anal. Calc. for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.55; H, 6.54%.

4.8. Synthesis of tricarbonyl[(2,3,4,5-η)-11-acetoxy-1H-cyclohept[a]azulene]iron (15)

A solution of *o*-chloranil (35.0 mg, 0.142 mmol) in benzene (15 ml) was added to a solution of compound **12** (51.0 mg, 0.130 mmol) in the same solvent (15 ml) at r.t. After stirring for 1 min, reaction mixture was passed through cellulose powder. After the solvent was removed under reduced pressure, the residue was purified by chromatography on silica gel with CH_2Cl_2 as an eluent to afford **15** (40.0 mg, 79%). Green crystals; m.p. 171.0–173.0 °C; IR (KBr) ν_{max} 2033, 1985, 1971, 1954 and 1757 cm^{-1}; UV–vis (MeOH) λ_{max}, nm (log ε) 233 (4.41), 301 (4.54), 406 (4.06), 529 (2.83) and 710 (3.39); ^{1}H-NMR (600 MHz, $CDCl_3$) δ 8.17 (d, $J = 9.6$ Hz, H-6), 7.78 (d, $J = 9.6$ Hz, H-10), 7.40 (dd, $J = 10.0$, 9.7 Hz, H-8), 6.97 (dd, $J = 10.0$, 9.6 Hz, H-7), 6.90 (dd, $J = 9.7$, 9.6 Hz, H-9), 5.53 (ddt, $J = 8.0$, 4.9, 1.1 Hz, H-3), 5.49 (ddd, $J = 7.8$, 4.9, 1.4 Hz, H-4), 4.47 (dd, $J = 7.8$, 1.1 Hz, H-5), 3.53 (dddd, $J = 8.0$, 4.8, 2.7, 1.4 Hz, H-2), 3.28 (dd, $J = 21.7$, 4.8 Hz, H-1), 3.10 (dd, $J = 21.7$, 2.7 Hz, H-1) and 2.39 (s, Me); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 210.72 (Fe(*C*O)$_3$), 169.02 (O*C*O), 137.81 (C-8), 136.31 (C-11a), 135.22 (C-11), 132.17 (C-6), 130.99 (C-5b), 130.14 (C-10), 127.32 (C-5a or C-10a), 122.83 (C-10a or C-5a), 121.98 (C-9), 121.60 (C-7), 90.59 (C-4), 88.11 (C-3), 58.65 (C-2), 55.97 (C-5), 27.15 (C-1) and 20.56 (CH_3); MS (70 eV) m/z 390 ([M^+], 0.6), 250 (34), 208 (100), 191 (35), 178 (37) and 165 (25); Anal. Calc. for $C_{20}H_{14}FeO_5 \cdot 1/2H_2O$: C, 60.18; H, 3.79. Found: C, 60.15; H, 3.59%.

4.9. 11-Acetoxy-1H-cyclohept[a]azulene (16)

DDQ (125 mg, 0.55 mmol) was added to a solution of compound **3** (97.7 mg, 0.248 mmol) in benzene (30 ml) at reflux temperature. After stirring at the same temperature for 12 h, the reaction mixture was chromatographed by a short column on silica gel with benzene and separated by GPC with $CHCl_3$ to afford **15** (9.60 mg, 10%) and compound **16** (11.1 mg, 18%) along with recovered **3** (56.8 mg, 58%). **16**: Green needles; m.p. 109.0–109.5 °C; IR (KBr) ν_{max} 1752 and 1717 cm^{-1}; UV–vis (CH_2Cl_2) λ_{max}, nm (log ε) 318 (4.48), 401 (3.94), 631 (2.47) and 688 sh (2.37); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.35 (d, $J = 9.8$ Hz, H-6), 8.00 (d, $J = 9.8$ Hz, H-10), 7.53 (dd, $J = 10.5$, 10.1 Hz, H-8), 7.48 (d, $J = 11.3$ Hz, H-5), 7.14 (dd, $J = 10.5$, 9.8 Hz, H-7), 7.05 (dd, $J = 10.1$, 9.8 Hz, H-9), 6.33 (dd, $J = 11.3$, 6.0 Hz, H-4), 6.13 (dd, $J = 10.5$, 6.0 Hz, H-3), 5.59 (dt, $J = 10.5$, 6.1 Hz, H-2), 3.37 (d, $J = 6.1$ Hz, H-1 and H-1) and 2.48 (s, Me); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 169.69 (O*C*O), 139.32 (C-10a), 137.65 (C-6), 134.10 (C-1), 129.42 (C-11a), 128.48 (C-8), 124.68 (C-7), 124.26 (C-3), 123.50 (C-9), 123.38 (C-4), 123.01 (C-6a), 122.64 (C-2), 26.46 (C-10), and 20.67 (OCO*C*H$_3$); MS (70 eV) m/z 250 ([M^+], 11), 208 (100) and 178 (26); Anal. Calc. for $C_{17}H_{14}O_2 \cdot 1/2H_2O$: C, 78.74; H, 5.83. Found: C, 78.46; H, 5.73%.

4.10. 10-Acetoxy-4-formylbenzo[a]azulene (17)

A solution of trimethylamine *N*-oxide (191 mg, 2.54 mmol) and compound **15** (48.0 mg, 0.123 mmol) in benzene (30 ml) was stirred at reflux temperature under nitrogen atmosphere for 20 min. After reaction mixture was passed through the cellulose powder, the solvent was removed. The residue was purified by column chromatography on silica gel with CH_2Cl_2 to afford **17** (13.0 mg, 48%). Dark green crystals; m.p. 131.0–132.5 °C; IR (KBr) ν_{max} 1743 cm^{-1}; UV–vis (CH_2Cl_2) λ_{max}, nm (log ε) 253 (4.26), 319 (3.68), 370 (3.68), 390 (3.54), 411 (4.53), 566 (3.69) and 615 (3.72); ^{1}H-NMR (600 MHz, $CDCl_3$) δ 10.46 (s, C*H*O), 9.82 (dd, $J = 8.8$, 1.0 Hz, H-5), 8.04 (dd, $J = 7.3$, 1.0 Hz, H-3), 7.95 (dd, $J = 7.9$, 1.0 Hz, H-1), 7.86 (dd, $J = 7.9$, 7.3 Hz, H-2), 7.76 (dd, $J = 10.9$, 1.0 Hz, H-9), 7.28 (ddt, $J = 11.1$, 8.3, 1.0 Hz, H-7), 7.13 (ddd, $J = 11.1$, 8.8, 0.7 Hz, H-6), 6.90 (ddd, $J = 10.9$, 8.3, 0.7 Hz, H-8) and 2.54 (s, Me); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 193.65(*C*HO), 169.15 (O*C*O), 137.83 (C-5), 137.09 (C-7), 135.93 (C-4), 135.67 (C-10), 134.68, 133.43, 133.10 (C-3), 130.07 (C-9), 127.37 (C-2), 126.75 (C-6), 126.59, 125.28, 124.70 (C-8), 123.25 (C-1) and 20.70 (OCO*C*H$_3$); MS (70 eV) m/z 264 ([M^+], 17%), 222 (100) and 165 (31); Anal. Calc. for $C_{17}H_{12}O_3 \cdot 1/2H_2O$: C, 74.71; H, 4.79; Found: C, 74.54; H, 4.82%.

4.11. Tricarbonyl[(2,3,4,5-η)-1H-cyclohept[a]azulene-11-yl]iron cyclohexa-1,3,5-triene-7-carboxylate] (18)

A solution of *o*-chloranil (120 mg, 0.529 mmol) in benzene (15 ml) was added to a solution of **3** (192 mg, 0.409 mmol) in the same solvent (30 ml) at r.t. After stirring for 1 min, reaction mixture was passed through the cellulose powder. After the solvent was removed, the residue was purified by column chromatography on silica gel with CH_2Cl_2 as an eluent to afford **18** (141 mg, 57%). Green crystals; m.p. 160 °C (dec.); IR (KBr) ν_{max} 2043, 1972, 1946 and 1746 cm^{-1}; UV–vis (CH_2Cl_2) λ_{max}, nm (log ε) 306 (4.73), 408 (4.09), 529 (2.24) and 651 (2.47); ^{1}H-NMR (600 MHz, $CDCl_3$) δ 8.19 (d, $J = 9.7$ Hz, H-6), 7.79 (d, $J = 9.6$ Hz, H-10),

7.41 (dd, $J = 10.0$, 9.9 Hz, H-8), 6.99 (dd, $J = 9.9$, 9.7 Hz, H-7), 6.91 (dd, $J = 10.0$, 9.6 Hz, H-9), 6.74 (m, H-3′ and H-4′), 6.39 (m, H-2′ and H-5′), 5.62 (m, H-1′ and H-6′), 5.54 (ddd, $J = 7.9$, 4.9, 1.0 Hz, H-3), 5.50 (ddd, $J = 7.7$, 4.9, 1.3 Hz, H-4), 4.48 (dd, $J = 7.7$, 1.0 Hz, H-5), 3.54 (dddd, $J = 7.9$, 4.9, 2.7, 1.3 Hz, H-2), 3.31 (dd, $J = 21.7$, 4.8 Hz, H-1), 3.13 (dd, $J = 21.7$, 2.7 Hz, H-1) and 2.98 (tt, $J = 4.7$, 1.1 Hz, H-7′); ^{13}C-NMR ($CDCl_3$), δ 210.70 (Fe(*C*O)$_3$), 171.18 (O*C*O), 137.87 (C-8), 136.23, 134.95, 132.23 (C-6), 131.08, 131.06 (C-4′ or C-3′), 131.04 (C-3′ or C-4′), 130.13 (C-10), 127.33, 126.16 (C-5′ or C-2′), 126.15 (C-2′ or C-5′), 122.86, 122.07 (C-9), 121.68 (C-7), 116.01 (C-1′ and C-6′), 90.64 (C-4), 88.12 (C-3), 58.61 (C-2), 55.89 (C-5), 43.67 (C-7′) and 27.22 (C-1); MS (70 eV) m/z 466 ([M$^+$], 0.24), 326 (22), 207 (50), 178 (23) and 91 (100); Anal. Calc. for $C_{26}H_{18}FeO_5 \cdot 1/2H_2O$: C, 65.71; H, 3.82. Found: C, 65.98; H, 3.99%.

*4.12. Dicarbonyl[(11,12,13,14-η)-tricyclo[8.5.0.0^{3,9}]-pentadeca-3,5,7,11,13-pentaen-2-one]-(triphenylphosphine)iron (**20a**)*

A solution of tropyl carboxylic acid chloride (295 mg, 1.91 mmol) in dry benzene (50 ml) was added dropwise at r.t. to a solution of dicarbonyl[(1,2,3,4-η)-1,3,5-cycloheptatriene](triphenylphosphine)iron (**19a**) (393 mg, 0.843 mmol) and triethylamine (232 mg, 2.29 mmol) in the same solvent (50 ml) over a period of 6 h under nitrogen atmosphere. After stirring for another 30 min, triethylammonium chloride was filtered and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2 as an eluent to afford **20a** (183 mg, 37%) along with recovered **19a** (121 mg, 31%). **20a**: Yellow crystals; m.p. 117–118 °C (dec.); IR (KBr) ν_{max} 1965, 1905 and 1709 cm^{-1}; UV–vis (CH_3CN) λ_{max}, nm (log ε) 227 sh (4.64) and 314 sh (3.81); ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.44 (6H), 7.39 (9H), 6.72 (d, $J = 5.2$ Hz, H-4), 6.15 (dd, $J = 11.1$, 6.7 Hz, H-6), 6.06 (dd, $J = 11.1$, 6.6 Hz, H-5), 5.74 (dd, $J = 9.6$, 6.7 Hz, H-7) 4.93 (d, $J = 9.6$ Hz, H-8), 4.78 (broad s, H-12 and H-13), 3.72 (d, $J = 2.8$ Hz, H-9), 2.97 (broad s, H-10), 2.47 (braod s, H-14), 2.33 (broad s, H-15), 2.16 (m, H-15), 2.11 (m, H-1), 2.02 (broad s, H-11); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 215.05 (Fe(*C*O)$_2$), 205.20 (Fe(*C*O)$_2$), 135.24 (Ph), 135.14 (C-6), 134.92 (Ph), 134.88 (Ph), 133.23 (Ph), 133.16 (Ph), 130.50 (C-8), 129.74 (Ph), 129.73 (Ph), 128.76 (C-4), 128.32 (Ph), 128.26 (Ph), 127.90 (C-5), 126.30 (C-7), 90.34 (C-13 or C-12), 87.70 (C-12 or C-13), 53.38 (C-14), 50.59 (C-1 and C-11), 46.56 (C-9), 41.32 (C-10) and 25.63 (C-15); MS (70 eV) m/z 528 ([M$^+$], 3), 277 (5), 262 (100), 210 (23) and 183 (47); Anal. Calc. for $C_{35}H_{29}FeO_3P$: C, 71.93; H, 5.00. Found: C, 72.47; H, 5.15%.

*4.13. Dicarbonyl[(11,12,13,14-η)-tricyclo[8.5.0.0^{3,9}]-pentadeca-3,5,7,11,13-pentaen-2-one](triphenyl phosphite)iron (**20b**)*

A solution of tropyl carboxylic acid chloride (272 mg, 1.76 mmol) in dry benzene (50 ml) was added dropwise at r.t. to a solution of cycloheptatriene-Fe(CO)$_2$P(OPh)$_3$ (**19b**) (430 mg, 0.837mmol) and triethylamine (220 mg, 2.17 mmol) in the same solvent (50 ml) over a period of 6 h under nitrogen atmosphere. After stirring for another 30 min, triethylammonium chloride was filtered and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2 as an eluent to afford **20b** (179 mg, 34%) along with recovered **19b** (235 mg, 55%). **20b**: Yellow crystals; m.p. 135.5–136.0 °C; UV–vis (CH_3CN) λ_{max}, nm (log ε) 233 sh (4.53), 268 sh (3.93) and 328 sh (3.65); IR (KBr) ν_{max} 1991, 1935 and 1707 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.34 (6H), 7.20 (9H), 6.72 (dd, $J = 6.6$, 2.2 Hz, H-4), 6.18 (dd, $J = 11.2$, 6.8 Hz, H-6), 6.07 (dd, $J = 11.2$, 6.6 Hz, H-5), 5.88 (ddd, $J = 11.0$, 6.8, 2.3 Hz, H-7), 5.26 (d, $J = 11.0$ Hz, H-8), 4.65 (m, H-12 and H-13), 3.79 (dddd, $J = 5.9$, 2.8, 2.3, 2.2 Hz, H-9), 2.84 (m, H-10), 2.76 (ddd, $J = 7.0$, 6.1, 5.1 Hz, H-14), 2.56 (m, H-11), 2.32 (dd, $J = 13.6$, 6.1 Hz, H-15) and 1.97 (m, H-1 and H-15); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 204.68 (C-2), 151.38 (OPh), 135.27 (C-6), 134.73 (C-3), 130.21 (C-8), 129.75 (OPh), 129.22 (C-4), 127.96 (C-5), 126.88 (C-7), 124.93 (OPh), 121.20 (OPh), 89.50 (C-12 or C-13), 86.47 (C-12 or C-13), 57.27 (C-11), 54.91 (C-14), 50.13 (C-1), 46.58 (C-9), 41.08 (C-10) and 24.90 (C-15); MS (70 eV) m/z 632 ([M$^+$], 0.2), 311 (35) and 211 (100); Anal. Calc. for $C_{35}H_{29}FeO_6P \cdot 1/2H_2O$: C, 65.54; H, 4.71. Found: C, 65.37; H, 4.62%.

References

[1] T. Asao, N. Morita, Y. Kitahara, J. Am. Chem. Soc. 94 (1972) 3655.

[2] (a) N. Morita, T. Asao, Y. Kitahara, Tetrahedron Lett. (1975) 2821;
(b) Y. Kitahara, Pure Appl. Chem. 44 (1975) 833.

[3] C. Falshaw, A. Lakoues, G. Taylor, J. Chem. Res. (S) 106 (1985).

[4] (a) Z. Goldschmidt, S. Antebi, Tetrahedron Lett. (1978) 271;
(b) Z. Goldschmidt, S. Antebi, D. Cohen, J. Organomet. Chem. 273 (1984) 347.

[5] (a) Z. Goldschmidt, H.E. Gottieb, E. Genizi, D. Cohen, J. Organomet. Chem. 301 (1986) 337;
(b) Z. Goldschmidt, S. Antebi, H.E. Gottieb, D. Cohen, J. Organomet. Chem. 282 (1985) 369;
(c) S.K. Chopra, M.J. Hynes, P. McArdle, J. Chem. Soc. Dalton (1981) 586;
(d) J. Weaver, P. Woodward, J. Chem. Soc. (A) (1971) 3521.

[6] (a) E.A.K. von Gustorf, F.-W. Grevels, I. Fischler (Eds.), The Organic Chemistry of Iron, vols. 1 and 2, Academic Press, New York, 1978 and 1981;

(b) A.J. Deeming, in: G. Wilkinson (Ed.), Comprehensive Organometallic Chemistry, vol. 4, Pergamon Press, Oxford, 1982, pp. 377–512;
(c) R.C. Kerber, in: G. Wilkinson (Ed.), Comprehensive Organometallic Chemistry II, vol. 7, Pergamon Press, Oxford, 1995, pp. 101–229 References cited therein.

[7] (a) N. Morita, Y. Kitahara, T. Asao, Tetrahedron Lett. (1982) 1575;
(b) N. Morita, S. Ito, T. Asao, H. Sotokawa, M. Hatano, A. Tajiri, Chem. Lett. (1990) 1639;
(c) N. Morita, M. Kurita, S. Ito, T. Asao, C. Kabuto, M. Ueno, T. Sato, H. Sotokawa, M. Watanabe, A. Tajiri, Enantiomer 3 (1998) 453.

[8] (a) N. Morita, Y. Kitahara, T. Asao, Tetrahedron Lett. (1972) 869;
(b) T. Asao, N. Morita, Y. Kitahara, Synth. Commun. 2 (1972) 353;
(c) T. Asao, N. Morita, C. Kabuto, Y. Kitahara, Tetrahedron Lett. (1972) 4379;
(d) N. Morita, T. Asao, N. Iwagame, Y. Kitahara, Chemistry Lett. (1973) 67;
(e) N. Morita, T. Asao, Y. Kitahara, Tetrahedron Lett. (1974) 2083.

[9] (a) G. Maier, Angew. Chem. Int. Ed. Engl. 6 (1967) 402;
(b) T. Toda, J. Synth. Org. Chem. Jpn. 20 (1972) 412;
(c) W.J. le Noble, Highlights of Organic Chemistry, Marcel Dekker, New York, 1974, pp. 402–406;
(d) W. Grimme, H.G. Köser, J. Am. Chem. Soc. 103 (1981) 5919.

[10] (a) J.E. Mahler, R. Pettit, J. Am. Chem. Soc. 85 (1963) 3955;
(b) M.A. Hashmi, J.D. Munro, P.C. Pauson, J.M. Williamson, J. Chem. Soc. A (1967) 240;
(c) R. Hoffman, P. Hofmann, J. Am. Chem. Soc. 98 (1976) 598;
(d) A.J. Peason, Transition Met. Chem. 6 (1981) 67.

[11] R. Burton, L. Pratt, G. Wilkinson, J. Chem. Soc. (1960) 4290.

[12] M. Yasunami, T. Amemiya, K. Takase, Tetrahedron Lett. 24 (1983) 69.

[13] F.M. Chaudhari, P.L. Pauson, J. Organomet. Chem. 5 (1966) 73.

[14] A.J. Pearson, K. Chang, J. Chem. Soc. Chem. Commun. (1991) 394.