99. Cyclodimerization of 1-(Dimethoxymethyl)-5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene Induced by Nonacarbonyldiiron. Crystal Structure of (1*RS*,2*SR*,3*RS*,4*RS*,4a*RS*,9a*SR*)-Tricarbonyl[*C*,2,3,*C*-η-(1,4-epoxy-1,5-bis(dimethoxymethyl)-2,3-dimethylidene-1,2,3,4,4a,9,9a,10-octahydroanthracene)]iron[1])

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The transition-metal-carbonyl-induced cyclodimerization of 5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene is strongly affected by substitution at C(1). While 5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene-1-methanol (**7**) refused to undergo [4 + 2]-cyclodimerization in the presence of [$Fe_2(CO)_9$] in MeOH, 1-(dimethoxymethyl)-5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene (**8**) led to the formation of a 1.7:1 mixture of *'trans'* (**19**, **21**, **22**) *vs.* *'cis'* (**20**, **23**, **24**) products of cyclodimerization together with tricarbonyl[*C*,5,6,*C*-η-(1-(dimethoxymethyl)-5,6-dimethylidenecyclohexa-1,3-diene)]iron (**25**) and tricarbonyl[*C*,3,4,*C*-η-(methyl 5-(dimethoxymethyl)-3,4-dimethylidenecyclohexa-1,5-diene-1-carboxylate)]iron (**26**). The structures of products **19** (and of its *exo* (**21**) and *endo* (**22**) [$Fe(CO)_3$(1,3-diene)] complexes) and **20** (and of its *exo* (**23**) and *endo* (**24**) [$Fe(CO)_3$(1,3-diene)] complexes) were confirmed by X-ray diffraction studies of crystalline (1*RS*,2*SR*,3*RS*,4*RS*,4a*RS*,9a*SR*)-tricarbonyl[*C*,2,3,*C*-η-(1,4-epoxy-1,5-bis(dimethoxymethyl)-2,3-dimethylidene-1,2,3,4,4a,9,9a,10-octahydroanthracene)]iron (**21**). In the latter, the $Fe(CO)_3$(1,3-diene) moiety deviates significantly from the usual local C_s symmetry. Complex **21** corresponds to a 'frozen equilibrium' of rotamers with σ-alkyl,η^3-allyl bonding mode due to the acetal unit at the bridgehead centre C(1).

Introduction. – A few years ago, we reported the first example of a formal [4 + 2]-cycloaddition of a 1,3-diene to a monoolefin induced by a transition metal, namely, the cyclodimerization of 5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene (**1**) in the presence of [$Fe_2(CO)_9$] giving the partially deoxygenated dimer **2** and the corresponding *exo*- and *endo*-$Fe(CO)_3$ diene complexes **3** and **4** [1]. Later, we showed that the cyclodimerization of **1** can be assisted by other d^8-metal carbonyls such as [$Ru_3(CO)_{12}$] [2]. We also found that heating **1** with catalytical amounts of [$Os_3(CO)_{12}$] in MeOH afforded mixtures containing products **5** and **6** [2].

Since compounds **2**–**6** are potential precursors in the synthesis of antitumoral anthracyclines [3–5], we explored the possibility to obtain *C*-disubstituted derivatives of **2** through the induced cyclodimerization of 1-substituted 7-oxanorbornenes **7** and **8** [5] which are readily available from the inexpensive *Diels-Alder* adducts of maleic anhydride to furan-2-methanol and 2-(dimethoxymethyl)furan, respectively. Our results show that the [4 + 2]-cycloaddition is strongly affected by substitution at C(1) of the 5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene systems. Interestingly, the [4 + 2]-cyclodimerization of **8** shows a modest *'trans'* regioselectivity due to the dimethoxymethyl group.

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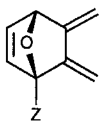
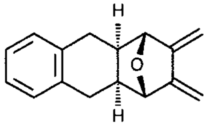
[1]) Part of the planned Ph. D. thesis of *Edia Bonfantini*, Ecole Polytechnique Fédérale de Lausanne.



1 Z=H
7 Z=CH_2OH
8 Z=$CH(OMe)_2$



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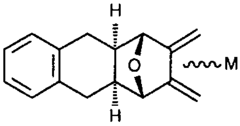
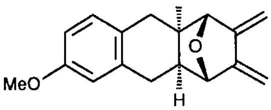


3 M=*exo*-$Fe(CO)_3$
4 M=*endo*-$Fe(CO)_3$



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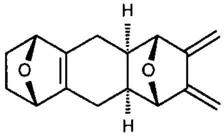

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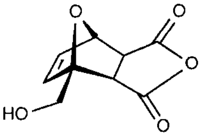
Results and Discussion. – The synthesis of triene **7** started with the *Diels-Alder* adduct **9** (85%) of maleic anhydride to furan-2-methanol. Reduction with $LiAlH_4$ in THF gave triol **10** (65%) which was esterified to **11** (71%) with CH_3SO_2Cl and pyridine. Treatment of **11** with a large excess of *t*-BuOK in CH_3CN afforded **12** (43%). Transalcoholysis with EtOH and KOH furnished **7** (73%). By treatment with KOH in MeOH (65°, 15 h), **7** (48%) can be obtained directly from **11**. The synthesis of triene-acetal **8** has already been described [5].



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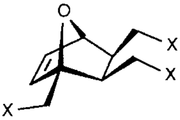
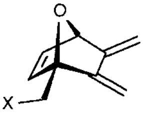
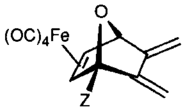


10 X=OH
11 X=OSO_2CH_3



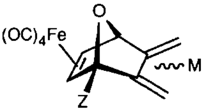
12 X = OSO_2CH_3
7 X = OH
8 X = $CH(OCH_3)_2$

On heating trienol **7** with various amounts of $[Fe_2(CO)_9]$ in MeOH for several days, slow decomposition was observed together with the formation of the corresponding complexes **13**–**15**. Less than 5% of possible dimeric products were present if any, thus demonstrating the defavourable influence of the CH_2OH group at C(1) on the cyclodimerization of the triene. Heating of **7** in MeOH with $[Ru_3(CO)_{12}]$ or $[Os_3(CO)_{12}]$ was not more successful and did not lead to any observable products of condensation.



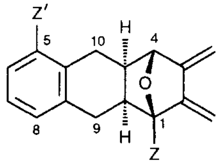
13 Z=CH_2OH

16 Z=$CH(OMe)_2$
27 Z=H

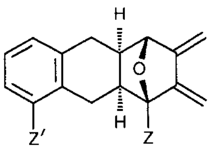


14 Z=CH_2OH, M=*exo*-$Fe(CO)_3$
15 Z=CH_2OH, M=*endo*-$Fe(CO)_3$
17 Z=$CH(OMe)_2$, M=*exo*-$Fe(CO)_3$
18 Z=$CH(OMe)_2$, M=*endo*-$Fe(CO)_3$

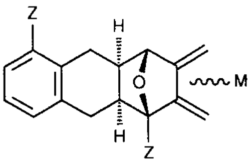
On heating triene-acetal **8** in MeOH with an excess of $[Fe_2(CO)_9]$ (40–70°, Ar), the monocomplex **16** was formed first which was then transformed into a mixture of dicomplexes **17** and **18**. Under these conditions, **16** gave also 18–30% of products of cyclodimerization **19** (2–5%) and **20** (1–3%) together with the corresponding *exo*- and *endo*-$Fe(CO)_3$ complexes **21** (6–10%), **22** (3–4%), **23** (3–5%), and **24** (2–4%) that were separated and isolated by column chromatography on silica gel. Their structures were given by their elemental analyses and their spectral data (see *Exper. Part*). They were confirmed by X-ray crystallography of **21** (see below) and by oxidative demetallations ($Ce(NH_4)_2(NO_3)_6$) of **21** and **22** into the *'trans'* adduct **27**, and of **23** and **24** into the *'cis'* isomer **28**. A regioselectivity of *ca.* 1.7:1 for the *'trans' vs. 'cis'* cycloadducts was thus determined.



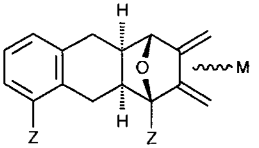
19 Z = $CH(OMe)_2$ = Z'
27 Z = $CH(OMe)_2$, Z' = CHO



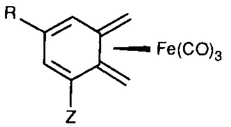
20 Z = $CH(OMe)_2$ = Z'
28 Z = $CH(OMe)_2$, Z' = CHO



21 M=*exo*-$Fe(CO)_3$, Z=$CH(OMe)_2$
22 M=*endo*-$Fe(CO)_3$, Z=$CH(OMe)_2$



23 M=*exo*-$Fe(CO)_3$, Z=$CH(OMe)_2$
24 M=*endo*-$Fe(CO)_3$, Z=$CH(OMe)_2$



25 Z=$CH(OMe)_2$, R=H
26 Z=$CH(OMe)_2$, R=$COOCH_3$

All our attempts (addition of CH_3CN, Ph_3P; change of the temperature: 40–80°; change of solvent: EtOH, i-PrOH, THF/H_2O; mode of addition and excess of $[Fe_2(CO)_9]$) to improve the overall yield of products of cyclodimerization were not met with success. The cyclodimerization was in fact inhibited by coordinating adjuvants such as CH_3CN. The relatively mediocre yield of products **19**–**24** was due to the competitive formation of the dicomplexes **17** and **18** which were transformed irreversibly into the *ortho*-quinodimethane complexes **25** and **26** [5]. The triene-acetal **8** did not react with $[Ru_3(CO)_{12}]$ (in toluene, 15 days, 65–70°) or $[Os_3(CO)_{12}]$ (MeOH, 7 days, 65°). Under these conditions, the unsubstituted triene **1** was found to undergo cyclodimerization.

When a 1:1 mixture of unsubstituted triene **1** and triene-acetal **8** was treated with $[Fe_2(CO)_9]$ in MeOH, only products of cyclodimerization of **1** were observed. Similarly, heating mixtures of (alkene)tetracarbonyliron complexes **16** and **27** in MeOH (50–70°) did not lead to the formation of products of cross-cyclodimerization. Products **2**–**4** resulting from the cyclodimerization of **27** were formed *ca.* 10 times faster than the decomposition of **16**, thus demonstrating the retarding effect of the (dimethoxy)methyl group of **16** on the [4 + 2]-cycloaddition.

In the presence of catalytical amounts of protic acids (*e.g.* HCl, AcOH), the bis-acetals **19**–**24** were converted selectively into the corresponding 1-(dimethoxymethyl)-anthracenecarbaldehydes.

Crystal Structure Determination of **21**. Cyclodimer **21** crystallizes as yellow parallelepipeds. X-Ray intensity data collection was carried out with an *Enraf-Nonius-CAD4* automatic diffractometer. The crystal data, intensity collection, structure solution, and refinement methods are summarized in *Table 1*. The structure was solved by direct methods. All H-atoms were located and, in the final least-squares refinement, non-H-atom anisotropic temperature factors included in the refinement, and H-atom isotropic temperature factors set to 1.3 times U(equiv.) of the bonding atom. All calculations were carried out on a *VAX-11/750*, using VAXSDP [7]. Scattering factors for the neutral atoms and anomalous dispersion coefficients were taken from [8]. Final atomic coordinates, tables of observed and calculated structure factors, temperature factors, and a detailed description of data collection, structure solution, and refinement are available as supplementary material from the authors upon request and are deposited with the *Cambridge Crystallographic Data Center*.

Table 1. *Crystal Data for* **21** ($C_{25}H_{28}FeO_8$), *Intensity Measurements, Structure Solution, and Refinement*

Crystal Data

Mol. wt.	512.34	Monoclinic space group $P2(1)/c$
$F(000)$	1072	$a = 12.548(1), b = 14.371(2), c = 13.603(1)$ Å
Crystal dimensions	0.32 × 0.22 × 0.14 mm	$\beta = 96.92(1)°$
Peak width at half-height	0.15°	$V = 2435.1$ Å^3
MoK_α radiation	$\lambda = 0.71073$ Å	$Z = 4$
Temp.	21 ● 1°	$\rho = 1.40$ g/cm^3, $\mu = 6.6$ cm^{-1}

Intensity Measurements

Instrument	*Enraf-Nonius-CAD4* diffractometer	Scan rate	1–7°/min (in ω)
Monochromator	graphite crystal, incident beam	Scan width, deg	0.8 + 0.34 tanθ
Attenuator	Zr foil, factor 19.5	Maximum 2θ	52.0°
Take-off angle	2.8°	No. of refl. measured	6090 total, 3979 unique
Detector aperture	1.6–1.7 mm horizontal, 4.0 mm vertical	Corrections	*Lorentz* polarization linear decay (from 0.976 to 1.061 on I) reflection averaging (agreement on $I = 1.5\%$)
Crystal-detector dist.	21 cm		
Scan type	$\omega - 2\theta$		

Structure Solution and Refinement

Solution	direct methods	Weighted agreement factor	0.044
Refinement	full-matrix least-squares	Esd. of obs. of unit weight	1.86
Minimization function	$\Sigma\omega(\lvert F_o\rvert - \lvert F_c\rvert)^2$	Convergence, largest shift	0.21
Least-squares weights	$4F_o^2/\sigma^2(F_o^2)$	High peak in final diff. map	0.27(4) e/Å^3
Anomalous dispersion	all non-H-atoms	Low peak in final diff. map	−0.23(4) e/Å^3
Reflections included	2592 with $F_o^2 > 3.0\,\sigma(F_o^2)$	Computer hardware	*VAX11/750*
Parameters refined	391	Computer software	SDP/VAX *(Enraf-Nonius & B. A. Frenz & Associates, Inc.)*
Unweighted agreement factor	0.034		

Calculated bond lengths, interatomic distances, bond angles, and selected torsional angles are given in *Tables 2–5*. Two perspective drawings of the molecule are shown in the *Figure*.

The molecular structure of **21** *(Fig.)* displays a few unexpected features which deserve comments. Out of the two possible staggered conformations of the (dimethoxy)-methyl group at the bridgehead centre C(1) of the 7-oxanorbornane moiety, the one leading to interactions with the $Fe(CO)_3$ moiety is preferred *(Fig., b)*. This interaction imposes a rotation of the $Fe(CO)_3$ tripod from the usual local C_s symmetry observed in

Table 2. *Bond Distances* [Å]a)

Fe–C(13)	2.043(3)	O(4)–C(23)	1.433(5)	C(5)–C(6)	1.388(5)
Fe–C(14)	2.079(3)	O(5)–C(24)	1.148(4)	C(6)–C(7)	1.391(5)
Fe–C(16)	2.127(3)	O(6)–C(25)	1.154(4)	C(7)–C(8)	1.390(4)
Fe–C(17)	2.136(4)	O(7)–C(26)	1.133(5)	C(8)–C(9)	1.401(5)
Fe–C(24)	1.776(3)	O(15)–C(1)	1.443(3)	C(8)–C(21)	1.512(4)
Fe–C(25)	1.766(4)	O(15)–C(12)	1.452(3)	C(9)–C(10)	1.499(4)
Fe–C(26)	1.788(3)	C(1)–C(2)	1.559(4)	C(10)–C(11)	1.532(4)
O(1)–C(18)	1.397(3)	C(1)–C(14)	1.529(4)	C(11)–C(12)	1.532(4)
O(1)–C(19)	1.431(4)	C(1)–C(18)	1.518(4)	C(12)–C(13)	1.512(4)
O(2)–C(18)	1.405(3)	C(2)–C(3)	1.546(4)	C(13)–C(14)	1.401(4)
O(2)–C(20)	1.438(3)	C(2)–C(11)	1.565(4)	C(13)–C(16)	1.415(4)
O(3)–C(21)	1.413(3)	C(3)–C(4)	1.513(4)	C(14)–C(17)	1.421(4)
O(3)–C(22)	1.430(5)	C(4)–C(5)	1.377(4)		
O(4)–C(21)	1.399(4)	C(4)–C(9)	1.401(4)		

a) Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 3. *Interatomic Distances* [Å]

C(24)–O(2)	2.890	O(2)–O(5)	2.932
C(24)–C(20)	3.302	O(5)–C(20)	3.108
C(24)–H(19)a)	3.416	O(5)–H(19)a)	2.903
C(24)–H(20)a)	2.986	H(20)a)	3.001
C(24)–H(21)a)	> 4	H(21)a)	> 4

a) H(19), H(20), and H(21) are the H-atoms on C(20) (one methyl group of the dimethyl acetal).

Table 4. *Bond Angles* [°]

C(13)–Fe–C(14)	39.7(1)	C(1)–O(15)–C(12)	96.4(2)	C(2)–C(11)–C(12)	100.9(2)
C(13)–Fe–C(16)	39.6(2)	O(15)–C(1)–C(2)	101.2(2)	C(10)–C(11)–C(12)	113.0(2)
C(13)–Fe–C(17)	71.7(1)	O(15)–C(1)–C(14)	101.9(3)	O(15)–C(12)–C(11)	102.3(3)
C(13)–Fe–C(24)	132.5(1)	O(15)–C(1)–C(18)	111.2(3)	O(15)–C(12)–C(13)	102.8(3)
C(13)–Fe–C(25)	126.6(1)	C(2)–C(1)–C(14)	105.9(3)	C(11)–C(12)–C(13)	105.6(2)
C(13)–Fe–C(26)	92.9(1)	C(2)–C(1)–C(18)	115.7(2)	Fe–C(13)–C(12)	126.2(2)
C(14)–Fe–C(16)	71.2(1)	C(14)–C(1)–C(18)	118.6(2)	Fe–C(13)–C(14)	71.6(2)
C(14)–Fe–C(17)	39.4(2)	C(1)–C(2)–C(3)	114.3(2)	Fe–C(13)–C(16)	73.4(2)
C(14)–Fe–C(24)	101.5(1)	C(1)–C(2)–C(11)	101.2(2)	C(12)–C(13)–C(14)	104.7(2)
C(14)–Fe–C(25)	131.2(1)	C(3)–C(2)–C(11)	111.0(2)	C(12)–C(13)–C(16)	134.5(3)
C(14)–Fe–C(26)	121.3(1)	C(2)–C(3)–C(4)	110.1(2)	C(14)–C(13)–C(16)	120.9(3)
C(16)–Fe–C(17)	83.6(1)	C(3)–C(4)–C(5)	123.2(3)	Fe–C(14)–C(1)	128.0(2)
C(16)–Fe–C(24)	172.1(1)	C(3)–C(4)–C(9)	116.2(3)	Fe–C(14)–C(13)	68.8(2)
C(16)–Fe–C(25)	88.5(1)	C(5)–C(4)–C(9)	120.5(3)	Fe–C(14)–C(17)	72.5(2)
C(16)–Fe–C(26)	92.1(1)	C(4)–C(5)–C(6)	119.8(3)	C(1)–C(14)–C(13)	104.1(2)
C(17)–Fe–C(24)	92.6(1)	C(5)–C(6)–C(7)	120.1(3)	C(1)–C(14)–C(17)	135.8(3)
C(17)–Fe–C(25)	96.1(1)	C(6)–C(7)–C(8)	120.6(3)	C(13)–C(14)–C(17)	120.2(2)
C(17)–Fe–C(26)	160.5(1)	C(7)–C(8)–C(9)	119.1(3)	Fe–C(16)–C(13)	67.0(2)
C(24)–Fe–C(25)	98.8(1)	C(7)–C(8)–C(21)	121.1(3)	Fe–C(17)–C(14)	68.2(2)
C(24)–Fe–C(26)	89.3(1)	C(9)–C(8)–C(21)	119.8(3)	O(1)–C(18)–O(2)	108.3(2)
C(25)–Fe–C(26)	102.8(2)	C(4)–C(9)–C(8)	119.7(3)	O(1)–C(18)–C(1)	104.6(3)
C(18)–O(1)–C(19)	114.0(3)	C(4)–C(9)–C(10)	114.9(2)	O(2)–C(18)–C(1)	113.5(2)
C(18)–O(2)–C(20)	114.1(2)	C(8)–C(9)–C(10)	125.3(3)	O(3)–C(21)–O(4)	111.8(2)
C(21)–O(3)–C(22)	115.4(3)	C(9)–C(10)–C(11)	109.4(2)	O(3)–C(21)–C(8)	113.6(2)
C(21)–O(4)–C(23)	112.7(3)	C(2)–C(11)–C(10)	112.4(2)	O(4)–C(21)–C(8)	108.6(2)
Fe–C(24)–O(5)	175.3(3)	Fe–C(25)–O(6)	177.5(3)	Fe–C(26)–O(7)	177.7(3)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 5. *Selected Torsional Angles* [°]

C(2)–C(1)–C(14)–C(13)	71.50(0.26)	C(7)–C(8)–C(21)–O(3)	–121.63(0.28)
C(2)–C(1)–C(14)–C(17)	–110.03(0.35)	C(7)–C(8)–C(21)–O(4)	3.44(0.35)
C(2)–C(1)–C(18)–O(1)	61.86(0.28)	C(9)–C(8)–C(21)–O(3)	60.26(0.33)
C(2)–C(1)–C(18)–O(2)	179.56(0.21)	C(9)–C(8)–C(21)–O(4)	–174.67(0.24)
C(14)–C(1)–C(18)–O(1)	–65.75(0.29)	C(19)–O(1)–C(18)–C(1)	–169.69(0.24)
C(14)–C(1)–C(18)–O(2)	51.95(0.32)	C(20)–O(2)–C(18)–C(1)	91.36(0.28)
C(11)–C(2)–C(3)–C(4)	48.85(0.30)	C(22)–O(3)–C(21)–C(8)	59.87(0.34)
C(1)–C(2)–C(11)–C(12)	0.12(0.25)	C(4)–C(9)–C(10)–C(11)	54.25(0.32)
C(3)–C(2)–C(11)–C(10)	1.20(0.31)	C(9)–C(10)–C(11)–C(2)	–52.11(0.29)
C(2)–C(3)–C(4)–C(9)	–50.99(0.33)	C(2)–C(11)–C(12)–C(13)	71.97(0.25)
C(3)–C(4)–C(5)–C(6)	–176.46(0.28)	C(11)–C(12)–C(13)–C(14)	–76.17(0.26)
C(9)–C(4)–C(5)–C(6)	2.16(0.45)	C(11)–C(12)–C(13)–C(16)	103.42(0.36)
C(3)–C(4)–C(9)–C(10)	–1.94(0.37)	C(23)–O(4)–C(21)–C(8)	175.36(0.26)
C(5)–C(4)–C(9)–C(8)	–2.36(0.43)	C(12)–O(15)–C(1)–C(2)	–57.69(0.22)
C(4)–C(5)–C(6)–C(7)	0.16(0.46)	C(12)–O(15)–C(1)–C(14)	51.47(0.22)
C(5)–C(6)–C(7)–C(8)	–2.30(0.45)	C(1)–O(15)–C(12)–C(11)	58.67(0.22)
C(6)–C(7)–C(8)–C(9)	2.07(0.41)	C(1)–O(15)–C(12)–C(13)	–50.74(0.23)
C(6)–C(7)–C(8)–C(21)	–176.05(0.26)	C(14)–C(1)–C(2)–C(11)	–70.84(0.24)
C(7)–C(8)–C(9)–C(4)	0.24(0.41)	C(12)–C(13)–C(14)–C(1)	1.81(0.28)
C(7)–C(8)–C(9)–C(10)	178.34(0.26)	C(16)–C(13)–C(14)–C(17)	3.38(0.42)

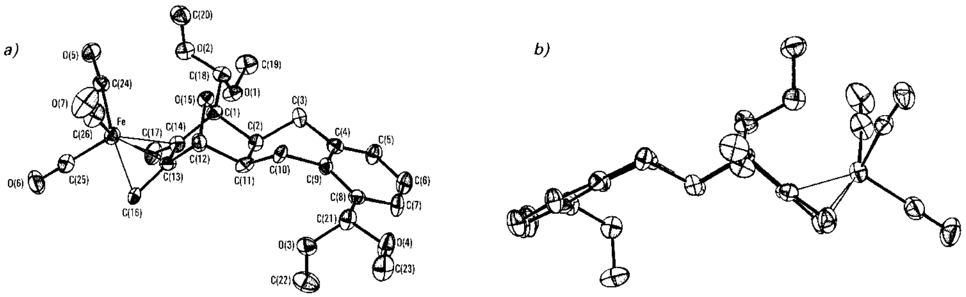
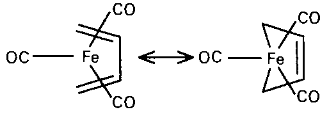


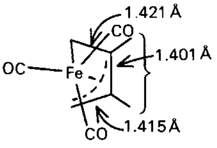
Figure. *ORTEP representation* [9] *of* **21**. For reason of simplicity, the atom numbering does not follow the IUPAC rules. Heavy atoms are reproduced with 50% thermal ellipsoids, the H-atoms have been omitted for clarity.

the crystalline state of a large number of [Fe(CO)$_3$(1,3-diene)] complexes [10] and for which the two valence-bond representations **28**↔**29** have been widely used to describe the iron-diene bonding [11].

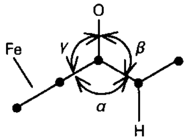
With the help of variable-temperature circular dichroism of optically pure [Fe(CO)$_3$(diene)] complexes [12] [13], we have shown that these complexes involve in fact equilibria between pairs of rapidly interconverting rotamers of diastereoisomeric species



28 **29**



21'



α = 109.7°
β = 122.1°
γ = 128.3°

having a σ-alkyl,η^3-allyl type of bonding. The acetal group at C(1) in **21** lifts the degeneracy or near-degeneracy of that equilibrium favouring only one of the two possible asymmetric structures in which not only the $Fe(CO)_3$ tripod has been rotated but also the bond lengths of the diene unit are not equivalent (see *Formula* **21'**) and deviate from the average bond lengths determined for C_s symmetrical derivatives [10]. If the rotation of the $Fe(CO)_3$ tripod had been demanding in energy, it would have led to a rotation of the $(MeO)_2CH{-}C(1)$ group from its nearly perfectly staggered conformation with respect to the 7-oxanorbornane skeleton *(Fig., b)*. Thus, our results demonstrate the great ease for the $Fe(CO)_3$ tripod to deviate from the local C_s symmetry [14].

The distance (2.89 Å) between atoms C(24) and O(2) of the interacting carbonyl and methoxy groups, respectively, is not greater than the sum of the *van der Waals* radii for C and O atoms. This leaves the possibility for a weak, stabilizing interaction between the carbonyl and methoxy functions which can be assigned to an electrostatic effect due to their dipole moments. This hypothesis is confirmed by the slight bending of 4.7° measured for the concerned Fe=C=O unit. Thus, without that stabilizing interaction, it is not excluded that the deviation of the $Fe(CO)_3$ tripod from the local C_s symmetry could be even larger.

Another remarkable feature of the structure of **21** are the angles α,β, and γ between the average planes of its 7-oxanorbornane skeleton (see above). X-Ray data of a large number of bicyclo[2.2.1]heptanes and bicyclo[2.2.1]hept-2-enes have shown that the introduction of an endocyclic double bond into the bicyclic system pushes the $CH_2(7)$ or O(7) bridge away from the unsaturated centres [15]. Force-field and quantum calculations [16] have suggested that this is due to the shortening of bond C(2)–C(3) when going from norbornanes to norborn-2-enes. In agreement with that interpretation, we find for **21** that the O-bridge is 'repelled' by the C(13)–C(14) bond of the butadiene moiety (angle $\gamma >$ angle β), because it is shorter (1.401 Å) than bond C(2)–C(11) (1.565 Å).

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Experimental Part

General. See [17]. None of the procedures reported has been optimized.

*1-(Hydroxymethyl)-7-oxabicyclo[2.2.1]hept-5-ene-2-*exo,*3-*exo*-dicarboxylic Anhydride* (**9**). Furan-2-methanol (82.4 g, 0.84 mol) was added dropwise to a soln. of maleic anhydride (107 g, 1.1 mol) in Et_2O (1100 ml). After staying 6 days at 20°, the precipitate was washed with cold Et_2O, yielding 139.5 g (85%), white powder, M.p. 71–78° (dec.). IR (KBr): 3370, 3100, 1860, 1790, 1235, 1225, 1210, 1150, 1090, 1050, 1035, 995, 980, 925. ^1H-NMR (360 MHz, $CDCl_3$): 6.65 (*d*, $^3J = 5.5$, H–C(6)); 6.62 (*dd*, $^3J = 5.5$, 1.7, H–C(5)); 5.44 (*d*, $^3J = 1.7$, H–C(4)); 4.23, 4.17 (2*d*, $^2J = 12.5$, CH_2OH); 3.35, 3.27 (2*d*, $^3J = 7$, H–C(2), H–C(3)). MS (70 eV): 196 (1, $M^{+\cdot}$), 100 (18), 99 (18), 98 (34), 97 (77), 81 (98), 54 (98), 53 (100). Anal. calc. for $C_9H_8O_5$ (196.158): C 55.11, H 4.11; found: C 54.94, H 4.10.

*7-Oxabicyclo[2.2.1]hept-5-ene-1,2-*exo,*3-*exo*-trimethanol* (**10**). A soln. of **9** (30 g, 0.153 mol) in anh. THF (230 ml) was added slowly to a stirred suspension of $LiAlH_4$ (14 g, 0.37 mol) in anh. THF (280 ml) cooled to 0° under N_2. After stirring at 0° for 2 h, the mixture was heated under reflux for 3 h. After cooling to 20°, H_2O (70 ml) was added dropwise under vigourous stirring. This operation was repeated twice. After the addition of EtOH (200 ml), the soln. was heated under reflux for 1 h and filtered through silica gel. The precipitate/silica gel was washed with hot EtOH (200 ml, 3 times). The EtOH extracts were evaporated, and the residue was crystallized from EtOH, yielding 18.5 g (65%), colourless crystals. M.p. 146–147.5°. IR (KBr): 3280, 3180, 2960, 2920, 1475, 1460, 1375, 1320, 1250, 1180, 1105, 1035, 1015, 980, 960, 940, 915. ^1H-NMR (360 MHz, CD_3OD): 6.49 (*s*, H–C(5), H–C(6)); 4.89 (*s*, H–C(4)); 4.12, 3.97 (2*d*, $^2J = 12$, CH_2–C(1)); 3.92–3.57 (4*m*, CH_2–C(2), CH_2–C(3)); 2.07 (*m*, H–C(2), H–C(3)). ^{13}C-NMR (90.55 MHz, CD_3OD): 138.3, 136.7 (2*d*, $^1J(C,H) = 175$, C(5), C(6)); 92.2 (*s*, C(1)); 81.6 (*d*, ^{1}J(C,H) = 160, C(4)); 62.4, 61.4, 60.5 (3*t*, ^{1}J(C,H) = 140, 3 CH_2OH); 45.9, 44.5 (2*d*, ^{1}J(C,H) = 135, C(2),C(3)). MS (70 eV): 107 (12), 98 (100), 97 (62), 91 (22), 81 (54), 79 (36), 77 (53), 70 (88). Anal. calc. for $C_9H_{14}O_4$ (186.196): C 58.05, H 7.58; found: C 57.97, H 7.54.

*7-Oxabicyclo[2.2.1]hept-5-ene-1,2-*exo*,3-*exo*-trimethyl Trimethanesulfonate* (**11**). Methanesulfonyl chloride (41 ml, 525 mmol) was added dropwise under stirring and N_2 to a soln. of **10** (12.7 g, 68.2 mmol) in anh. pyridine (115 ml) cooled to 0°. After stirring at 0° for 2 h, the mixture was allowed to stay at 20° for 4 days. The mixture was poured into a vigourously stirred mixture H_2O/ice. The precipitate was triturated with CH_2Cl_2 and washed with ice-cold H_2O and then with CH_2Cl_2. The org. layer was washed with H_2O, dried ($MgSO_4$), and evaporated. The residue was crystallized from CH_3CN yielding 20.5 g (71%), white solid. M.p. 134–137° (dec.). IR (KBr): 3100, 3040, 2940, 1470, 1425, 1340, 1175, 995, 955, 860, 825. ^{1}H-NMR (360 MHz, CD_3CN): 6.50 (*dd*, ^{3}J = 6.0, 2, H–C(5)); 6.40 (*d*, ^{3}J = 6.0, H–C(6)); 4.90 (*d*, ^{3}J = 2, H–C(4)); 4.80, 4.58 (2*d*, ^{2}J = 12, CH_2–C(1)); 4.42–4.15 (4*m*, CH_2–C(2), CH_2–C(3)); 3.10, 3.076, 3.069 (3*s*, CH_3); 2.33 (*m*, H–C(2), H–C(3)). ^{13}C-NMR (90.55 MHz, CD_3CN): 138.1, 137.5 (2*d*, ^{1}J(C,H) = 175, C(5),C(6)); 90.4 (*s*, C(1)); 81.7 (*d*, ^{1}J(C,H) = 165, C(4)); 71.0, 69.4, 69.1 (3*t*, ^{1}J(C,H) = 150, 3 CH_2O); 43.7, 43.4 (2*d*, ^{1}J(C,H) = 140, C(2),C(3)); 38.6, 38.3, 38.2 (3*q*, ^{1}J(C,H) = 140, 3 Me). MS (70 eV): 176 (23), 133 (8), 121 (3), 109 (4), 98 (8), 97 (100), 96 (21), 95 (8), 91 (4), 81 (39), 80 (14), 79 (80). Anal. calc. for $C_{12}H_{20}O_{10}S_3$ (420.474): C 34.28, H 4.79; found: C 34.39, H 4.76.

5,6-Dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene-1-methyl Methanesulfonate (**12**). Compd. **11** (1 g, 2.38 mmol) was dissolved in hot CH_3CN (40 ml). After cooling to 20° under N_2, *t*-BuOK (4 g, 35.5 mmol) was added portionwise. After stirring at 20° for 20 min, H_2O (100 ml) was added. The mixture was extracted with CH_2Cl_2 (40 ml, 4 times). The extract was dried ($MgSO_4$), evaporated, and purified by chromatography on silica gel (100 g, AcOEt/CH_2Cl_2 1:9) yielding 225 mg (47%), colourless solid which could be recrystallized from Et_2O at –20°. M.p. 54–55°. UV (95% EtOH): 205 (13500), 221 (sh, 9400), 231 (8800). IR (KBr): 3080, 3020, 2960, 2930, 1415, 1340, 1280, 1165, 1060, 990, 960. ^{1}H-NMR (360 MHz, $CDCl_3$): 6.53 (*dd*, ^{3}J = 5.7, 1.7, H–C(3)); 6.37 (*d*, ^{3}J = 5.7, H–C(2)); 5.37, 5.30, 5.16, 5.03 (4*s*, CH_2=C(5), CH_2=C(6)); 5.21 (*s*, H–C(4)); 4.90, 4.76 (2*d*, ^{2}J = 12.5, CH_2O); 3.10 (*s*, Me). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 143.3, 142.3 (2*s*, C(5),C(6)); 137.1, 134.3 (2*d*, ^{1}J(C,H) = 180, C(2),C(3)); 103.0, 102.4 (2*t*, ^{1}J(C,H) = 160, CH_2=C(5), CH_2=C(6)); 88.8 (*s*, C(1)); 82.2 (*dm*, ^{1}J(C,H) = 168, C(4)); 66.3 (*t*, ^{1}J(C,H) = 150, CH_2–C(1)); 37.9 (*q*, ^{1}J(C,H) = 140, Me). MS (70 eV): 228 (0.2, $M^{+\cdot}$), 199 (0.3), 176 (3), 132 (11), 104 (53), 97 (42), 91 (100). Anal. calc. for $C_{10}H_{12}O_4S$ (228.266): C 52.62, H 5.30; found: C 52.21, H 5.29.

5,6-Dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene-1-methanol (**7**). A mixture of **12** (467 mg, 2.04 mmol) in anh. EtOH (10 ml) and KOH (1.5 g, 26.7 mmol) was stirred at 60° for 5 h. After the addition of H_2O (50 ml), the mixture was extracted with CH_2Cl_2 (110 ml, 4 times). The combined extracts were washed with H_2O (200 ml), dried ($MgSO_4$) and evaporated. The residue was purified by column chromatography on silica gel (AcOEt/CH_2Cl_2 1:5) yielding 225 mg (73%), colourless oil that crystallized from toluene and CH_2Cl_2 at –20°. M.p. 58–59°. IR (KBr): 3460, 3060, 3000, 2940, 2910, 2180, 1640, 1600, 1405, 1320, 1285, 1255, 1230, 1145, 1075, 1040, 995, 965, 900. UV (95% EtOH): 205 (12200), 222 (sh, 8800), 232 (8300). ^{1}H-NMR (360 MHz, $CDCl_3$): 6.51 (*dd*, ^{3}J = 5.5, 2, H–C(3)); 6.36 (*d*, ^{3}J = 5.5, H–C(2)); 5.35, 5.28, 5.12, 5.0 (4*s*, CH_2=C(5), CH_2=C(6)); 5.19 (*s*, H–C(4)); 4.26, 4.17 (2*d*, ^{2}J = 12.5, CH_2–C(1)). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 144.5, 143.1 (2*s*, C(5),C(6)); 137.1, 135.6 (2*d*, ^{1}J(C,H) = 180, C(2),C(3)); 102.3, 102.0 (2*t*, ^{1}J(C,H) = 160, CH_2=C(5), CH_2=C(6)); 91.7 (*s*, C(1)); 82.0 (*dm*, ^{1}J(C,H) = 165, C(4)); 60.3 (*t*, ^{1}J(C,H) = 145, CH_2–C(1)). CI-MS (NH_3): 168 (100, $M^+ + NH_4$), 151 (13, $M^+ + H$), 150 (16, $M^{+\cdot}$), 133 (10), 123 (6), 105 (10), 96 (16), 91 (98). Anal. calc. for $C_9H_{10}O_2$ (150.177): C 71.98, H 6.71; found: C 71.92, H 6.67.

Cyclodimerization of 1-(Dimethoxymethyl)-5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene (**8**). [$Fe_2(CO)_9$] (7.3 g, 20.1 mmol) was added portionwise to a soln. of **8** [5] (2.2 g, 11.2 mmol) in MeOH, heated to 70°, and gently degassed by a flow (5 ml/min) of Ar. After 26 h at 70°, the mixture was cooled to 20° and filtered. The soln. was evaporated and purified by filtration on a short column of *Florisil* (AcOEt/petroleum ether 1:4). The solvent was evaporated and the residue separated into *Fractions A, B,* and *C* by column chromatography on silica gel (*Lobar*, column *C*, AcOEt/petroleum ether 1:5). *Fraction A* was separated into **17** (0.5–1%), **16** (5–7%), and **25** (20–35%) [5] (silica gel, *Lobar*, column *B*, AcOEt/petroleum ether 1:15). *Fraction B* was separated into **16** (0.4%), **21** (8–12%), **26** (1.5%) [5], and **23** (1–2%) (silica gel, *Lobar*, column *B*, AcOEt/petroleum ether 1:5). *Fraction C* was separated into **23** (2–3%), **8** (2–6%), and two fractions *C-1* and *C-2* (silica gel, *Lobar*, column *B*, AcOEt/petroleum ether 1:4). *Fraction C-1* was separated into a product of hydrolysis of **25** [6], **24** (2–4%), and **19** (2–5%) (silica gel, *Lobar*, column *B*, AcOEt/CH_2Cl_2 1:15). *Fraction C-2* was separated into **22** (3–4%) and **20** (1–3%). Products **19**–**26** were all recrystallized from MeOH at –20°.

*(1*RS*,4*SR*,4a*SR*,9a*RS*)-1,5-Bis(dimethoxymethyl)-1,4-epoxy-1,2,3,4,4a,9,9a,10-octahydro-2,3-dimethylideneanthracene* (**19**). White crystals. M.p. 94–95°. IR (KBr): 3010, 2990, 2960, 2940, 2925, 2910, 2840, 1470, 1460, 1450, 1400, 1375, 1210, 1205, 1195, 1115, 1100, 1085, 1065, 960, 930, 910. ^{1}H-NMR (360 MHz, $CDCl_3$): 7.32, 7.11

(2*d*, $^3J = 7.5$, H–C(6), H–C(8)); 7.15 (*t*, $^3J = 7.5$, H–C(7)); 5.47, 5.32, 5.30, 5.18 (4*s*, CH_2=C(2), CH_2=C(3)); 4.94, 4.79 (2*s*, 2 C*H*$(OMe)_2$); 4.57 (*s*, H–C(4)); 3.69, 3.66, 3.40, 3.34 (4*s*, 4 MeO); 3.4–3.34 (*m*, 1 H), 2.93 (*dd*, $^2J = 13.5$, $^3J = 6$, H_{endo}–C(9), H_{endo}–C(10)); 2.68, 2.40 (*dd*, $^2J = 13.5$, $^3J = 11.7$, H_{exo}–C(9), H_{exo}–C(10)); 2.23–2.07 (*m*, H–C(4a), H–C(9a)). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 149.0, 147.1 (2*s*, C(2), C(3)); 139.3, 136.7, 133.8 (3*s*, C(8a), C(10a), C(5)); 127.6, 125.3, 125.0 (3*d*, ^1J(C,H) = 160, C(6), C(7), C(8)); 106.4, 102.5 (2*d*, ^1J(C,H) = 160, 2 *C*H$(OMe)_2$); 102.8, 99.7 (2*t*, ^1J(C,H) = 160, *C*H_2=C(2), *C*H_2=C(3)); 91.5 (*s*, C(1)); 85.7 (*d*, ^1J(C,H) = 160, C(4)); 58.1, 57.3, 53.0 (3*q*, ^1J(C,H) = 142, 4 MeO); 46.2, 45.1 (2*d*, ^1J(C,H) = 140, C(4a), C(9a)); 29.5, 27.3 (2*t*, ^1J(C,H) = 130, C(9), C(10)). MS (70 eV): 372 (0.2, $M^{+\cdot}$), 341 (6), 340 (7), 325 (4), 308 (5), 171 (18), 138 (55), 137 (30), 75 (100). Anal. calc. for $C_{22}H_{28}O_5$ (372.461): C 70.94, H 7.58; found: C 70.41, H 7.76.

*(1*RS*,4*SR*,4a*SR*,9a*RS*)-1,8-Bis(dimethoxymethyl)-1,4-epoxy-1,2,3,4,4a,9,9a,10-octahydro-2,3-dimethylideneanthracene* (**20**). White crystals. M.p. 122–125°. IR (KBr): 3000, 2960, 2950, 2880, 2840, 1455, 1355, 1195, 1190, 1115, 1100, 1085, 1055, 975, 930, 905, 800. ^{1}H-NMR (360 MHz, $CDCl_3$): 7.39, 7.19–7.11 (3*m*, $^3J = 7.3$, H–C(5), H–C(6), H–C(7)); 5.54, 5.37, 5.35, 5.21 (4*s*, CH_2=C(2), CH_2=C(3)); 4.97, 4.74 (2*s*, 2 C*H*$(OMe)_2$); 4.61 (*s*, H–C(4)); 3.67, 3.65, 3.34 (3*s*, 4 MeO); 3.37, 2.88 (2*dd*, $^2J = 13.5$, $^3J = 5.6$, H_{endo}–C(9), H_{endo}–C(10)); 2.72, 2.41 (2*dd*, $^2J = 13.5$, $^3J = 11.8$, H_{exo}–C(9), H_{exo}–C(10)); 2.3–2.2, 2.15–2.05 (2*m*, H–C(4a), H–C(9a)). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 149.0, 146.6 (2*s*, C(2), C(3)); 139.1, 137.0, 134.3 (3*s*, C(8), C(8a), C(10a)); 127.1, 125.3, 124.8 (3*d*, ^1J(C,H) = 160, C(5), C(6), C(7)); 106.3, 102.8 (2*d*, ^1J(C,H) = 160, 2 *C*H$(OMe)_2$); 103.1, 99.6 (2*t*, ^1J(C,H) = 160, *C*H_2=C(2), *C*H_2=C(3)); 91.6 (*s*, C(1)); 85.7 (*d*, ^1J(C,H) = 160, C(4)); 58.2, 57.4, 53.9, 53.1 (4*q*, ^1J(C,H) = 142, 4 MeO); 46.4, 45.1 (2*d*, ^1J(C,H) = 138, C(4a), C(9a)); 32.5, 24.0 (2*t*, ^1J(C,H) = 128, C(9); C(10)). MS (70 eV): 372 (0.1, $M^{+\cdot}$), 340 (12), 171 (11), 138 (33), 137 (25), 75 (100). Anal. calc. for $C_{22}H_{28}O_5$ (372.461): C 70.94, H 7.58; found: C 70.98, H 7.66.

*(1*RS*,2*SR*,3*RS*,4*RS*,4a*RS*,9a*SR*)-[C,2,3,C-η-(1,5-Bis(dimethoxymethyl)-1,4-epoxy-1,2,3,4,4a,9,9a,10-octahydro-2,3-dimethylideneanthracene)]tricarbonyliron* (**21**). Yellow crystals. M.p. 102–103°. IR (KBr): 3010, 2950, 2840, 2040, 1985, 1970, 1455, 1360, 1110, 1085, 1070, 1055, 970, 955, 945, 935. ^{1}H-NMR (360 MHz, $CDCl_3$): 7.37, 7.18–7.12 (3*m*, H–C(6), H–C(7), H–C(8)); 5.52, 4.75 (2*s*, C*H*$(OMe)_2$); 4.62 (*s*, H–C(4)); 3.63, 3.59, 3.35, 3.34 (4*s*, 4 MeO); 3.49, 3.05 (*dd*, $^2J = 14$, $^3J = 5.8$, H_{endo}–C(9), H_{endo}–C(10)); 2.90, 2.59 (*dd*, $^2J = 14$, $^3J = 11.7$, H_{exo}–C(9), H_{exo}–C(10)); 2.55–2.48, 2.44–2.31 (2*m*, H–C(4a), H–C(9a)); 2.17 (*dd*, $^2J = 2.4$, $^4J = 0.8$[2]), H of CH_2=C(3) *trans* to C(2)); 1.97 (*d*, $^2J = 2.5$, H of CH_2=C(2) *trans* to C(3)); 0.39 (*d*, $^2J = 2.4$, H of CH_2=C(3) *cis* to C(2)); 0.20 (*d*, $^2J = 2.5$, $^5J = 0.5$[2]), H of CH_2=C(2) *cis* to C(3)). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 211.3 (*s*, 3 CO); 140.0, 137.0, 134.0 (3*s*, C(5), C(8a), C(10a)); 127.7, 125.4, 125.1 (3*d*, ^1J(C,H) = 162, C(6), C(7), C(8)); 109.4, 108.5 (2*s*, C(2), C(3)); 105.8, 102.8 (2*d*, ^1J(C,H) = 161, 2 *C*H$(OMe)_2$); 89.4 (*s*, C(1)); 82.8 (*d*, ^1J(C,H) = 165, C(4)); 57.8, 57.4, 53.2 (3*q*, ^1J(C,H) = 144, 4 MeO); 44.25, 44.2 (2*d*, ^1J(C,H) = 140, C(4a), C(9a)); 32.8, 30.9 (2*t*, ^1J(C,H) = 164, *C*H_2=C(2), *C*H_2=C(3)); 30.5, 28.2 (2*t*, ^1J(C,H) = 130, C(9), C(10)). MS (70 eV): 456 (16, $M^{+\cdot} - 2$ CO), 428 (47, $M^{+\cdot} - 3$ CO), 413 (29), 368 (29), 338 (16), 278 (9), 141 (21), 137 (29), 75 (26), 28 (100). Anal. calc. for $C_{25}H_{28}FeO_8$ (512.338): C 58.61, H 5.51; found: C 58.71, H 5.62.

*(1*RS*,2*RS*,3*SR*,4*RS*,4a*RS*,9a*SR*)-[C,2,3,C-η-(1,5-Bis(dimethoxymethyl)-1,4-epoxy-1,2,3,4,4a,9,9a,10-octahydro-2,3-dimethylideneanthracene)]tricarbonyliron* (**22**). Yellow crystals. M.p. 157–158° (dec.). Instable compound at 20° in soln. ^{1}H-NMR (360 MHz, $CDCl_3$): 7.42 (*t*, $^3J = 5.5$, H–C(7)); 7.19 (*d*, $^3J = 5.5$, H–C(6), H–C(8)); 5.52, 4.90, 4.78 (3*s*, 2 C*H*$(OMe)_2$, H–C(4)); 3.67, 3.65, 3.33, 3.28 (4*s*, 4 MeO); 3.54 (*m*), 2.98 (*dd*, $^2J = 13.3$, $^3J = 5.5$, H_{endo}–C(9), H_{endo}–C(10)); 2.65 (*dd*, $^2J = 13.3$, $^3J = 11.8$, H_{exo}–C(9) or H_{exo}–C(10)); 2.55–2.39 (*m*, H_{exo}–C(10) or H_{exo}–C(9), H–C(4a), H–C(9a)); 2.30 (*d*, $^2J = 3.3$, 1 H); 1.98 (*d*, $^2J = 3.6$, 1 H); 0.50 (*d*, $^2J = 3.6$, 1 H); 0.44 (*d*, $^2J = 3.3$, 1 H). MS (70 eV): 512 (0.3, $M^{+\cdot}$), 484 (13, $M^{+\cdot}$ – CO), 456 (13, $M^{+\cdot} - 2$ CO), 428 (100, $M^{+\cdot} - 3$ CO), 413 (56), 368 (70), 338 (42), 171 (39), 141 (70), 137 (67), 115 (48), 87 (56), 75 (94).

*(1*RS*,2*SR*,3*RS*,4*RS*,4a*RS*,9a*SR*)-[C,2,3,C-η-(1,8-Bis(dimethoxymethyl)-1,4-epoxy-1,2,3,4,4a,9,9a,10-octahydro-2,3-dimethylideneanthracene)]tricarbonyliron* (**23**). Yellow crystals. M.p. 129–130°. IR (KBr): 3000, 2960, 2940, 2840, 2040, 1975, 1450, 1195, 1110, 1075, 1045, 945, 785. ^{1}H-NMR (360 MHz, $CDCl_3$): 7.39, 7.16 (2*m*, H–C(5), H–C(6), H–C(7)); 5.51, 4.79 (2*s*, 2 C*H*$(OMe)_2$); 4.60 (*s*, H–C(4)); 3.68, 3.60, 3.40, 3.37 (4*s*, 4 MeO); 3.53, 3.02 (2*dd*, $^2J = 13.5$, $^3J = 5.5$, H_{endo}–C(9), H_{endo}–C(10)); 2.79, 2.57 (2*dd*, ^2J13.5, $^3J = 11.8$, H_{exo}–C(9), H_{exo}–C(10)); 2.51–2.37 (*m*, H–C(4a), H–C(9a)); 2.21 (*dd*, $^2J = 2.3$, $^4J = 0.8$[2]), H of CH_2=C(3) *trans* to C(2)); 1.93 (*d*, $^2J = 2.5$, H of CH_2=C(2) *trans* to C(3)); 0.40 (*d*, $^2J = 2.3$, H of CH_2=C(3) *cis* to C(2)); 0.18 (*dd*, $^2J = 2.5$, $^5J = 0.5$[2]), H of CH_2=C(2) *cis* to C(3)). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 211.3 (*s*, 3 CO); 139.4, 137.5, 134.8 (3*s*, C(8), C(8a), C(10a)); 127.2, 125.4, 124.9 (3*d*, ^1J(C,H) = 160, C(5), C(6), C(7)); 109.2, 108.2 (2*s*, C(2), C(3)); 105.6, 102.8 (2*d*, ^1J(C,H) = 160, 2 *C*H$(OMe)_2$); 89.6 (*s*, C(1)); 82.8 (*d*, ^1J(C,H) = 166, C(4)); 57.9, 57.4, 53.8, 53.4 (4*q*,

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[2] These long-range coupling constants with the adjacent bridgehead protons H–C(4) are typical for *exo*-$Fe(CO)_3$ complexes only [18].

^1J(C,H) = 144, 4 MeO); 44.6, 44.4 (2*d*, ^1J(C,H) = 140, C(4a), C(9a)); 33.3, 25.0 (2*t*, ^1J(C,H) = 130, C(9), C(10)); 33.0, 30.4 (2*t*, ^1J(C,H) = 162, *C*H_2=C(2), *C*H_2=C(3)). MS (70 eV): 484 (9, $M^{+\cdot}$ – CO), 456 (11, $M^{+\cdot}$ – 2 CO), 428 (99, $M^{+\cdot}$ – 3 CO), 413 (54), 368 (57), 171 (12), 137 (78), 75 (100). Anal. calc. for $C_{25}H_{28}O_8Fe$ (512.338): C 58.61, H 5.51; found: C 58.51, H 5.62.

*(1*RS*,2*RS*,3*SR*,4*RS*,4a*RS*,9a*SR*)-[C,2,3,C-η-(1,8-Bis(dimethoxymethyl)-1,4-epoxy-1,2,3,4,4a,9,9a,10-octahydro-2,3-dimethylideneanthracene)]tricarbonyliron* (**24**). Yellow oil. ^{1}H-NMR (360 MHz, $CDCl_3$): 7.37 (*m*, 1 H); 7.23–7.14 (2*m*, H–C(5), H–C(6), H–C(7)); 5.46, 4.87, 4.82 (3*s*, 2 C*H*$(OMe)_2$, H–C(4)); 3.73, 3.69, 3.35, 3.352 (4*s*, 4 MeO); 3.58, 3.06 (2*dd*, ^2J = 13.4, ^3J = 5.5, H_{endo}–C(9), H_{endo}–C(10)); 2.63, 2.35 (2*dd*, ^2J = 13.5, ^3J = 12, H_{exo}–C(9), H_{exo}–C(10)); 2.56–2.37 (*m*, H–C(4a), H–C(9a)); 2.36 (*d*, ^2J = 3.0, 1 H); 2.00 (*d*, ^2J = 3.5, 1 H); 0.52 (*d*, ^2J = 3.5, 1 H); 0.47 (*d*, ^2J = 3.0, 1 H).

Oxidative Demetallation of the [Fe(CO)$_3$(1,3-diene)] Complexes. To a soln. of **21**–**24** (36 mg, 0.07 mmol) in acetone (3 ml), anh. $(NH_4)_2Ce(NO_3)_6$ (82–100 mg, 0.15–0.18 mmol) was added portionwise under stirring. After 30 min at 20°, H_2O (15 ml) was added and the mixture extracted with pentane (30 ml, 4 times). The combined extracts were dried ($MgSO_4$) and evaporated yielding 21–22 mg (92–96%) of **27** (when starting with **21** or **22**) or **28** (when using **23** or **24**).

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