15. Stereoselective Double Functionalization of Iron-Carbonyl Complexes of 5,6,7,8-Tetramethylidenebicyclo[2.2.2]oct-2-ene. Crystal Structure and Absolute Configuration of (−)-*trans*-*μ*-[(2*S*,5*R*,7*S*)-*C*,5,6,*C*-*η*:*C*,7,8,*C*-*η*-(6,7,8-trimethylidene-5-((*Z*)-2-oxopropylidene)-2-bicyclo[2.2.2]octyl acetate)]-bis(tricarbonyliron)

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The *Friedel-Crafts* monoacylation of *trans*-*μ*-[(1*RS*,2*RS*,4*SR*,5*SR*,6*RS*,7*RS*,8*SR*)-*C*,5,6,*C*-*η*:*C*,7,8,*C*-*η*-(5,6,7,8-tetramethylidene-2-bicyclo[2.2.2]octyl acetate)]-bis(tricarbonyliron) ((±)-**5**) is highly stereoselective and yields *trans*-*μ*-[(1*RS*,2*RS*,4*RS*,5*SR*,6*RS*,7*RS*,8*SR*)-*C*,6-*η*,*oxo*-*σ*:*C*,7,8,*C*-*η*-(6,7,8-trimethylidene-5-((*Z*)-2-oxopropylidene)-2-bicyclo[2.2.2]octyl acetate)]-bis(tricarbonyliron) ((±)-**8**) which equilibrates with the *trans*-*μ*-[(1*RS*,2*RS*,4*RS*,5*SR*,6*RS*,7*RS*,8*SR*)-*C*,5,6,*C*-*η*:*C*,7,8,*C*-*η*-(6,7,8-trimethylidene-5-((*Z*)-2-oxopropylidene)-2-bicyclo[2.2.2]octyl acetate)]-bis(tricarbonyliron) ((±)-**9**) on heating. Optically pure (−)-**9** has been prepared from the corresponding optically pure alcohol (+)-**4**. The structure and absolute configuration of (−)-**9** was established by single-crystal X-ray diffraction.

Introduction. – The tetraene **1** can be used to prepare various anthracycline precursors [1]. The principle of this strategy rests upon the fact that the rate constant for the *Diels-Alder* addition of **1** is much larger than that for the reaction of the corresponding monoadduct with the same nucleophile [2]. The utility of this synthesis[1]) would be greatly enhanced if (*i*) the regioselectivity of the two successive or 'tandem' cycloadditions could be controlled[2]), and (*ii*) optically pure adducts could be generated. With these goals in mind, we envisioned the preparation of an optically pure tetraene with an asymmetric bridge and substituted diene moieties. We report here our first results toward this objective.

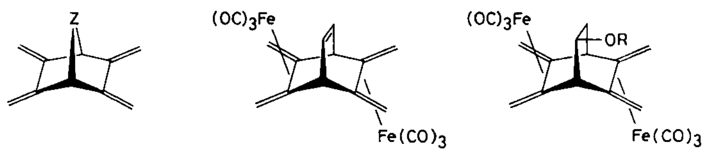
Results and Discussion. – The readily prepared pentaene **2** gives the bis(tricarbonyliron) complex **3** in good yield on heating with $Fe_2(CO)_9$ in hexane/MeOH [5]. The two $Fe(CO)_3$ groups in *trans* positions remove one of the two mirror planes in the free ligand. In terms of the reaction chemistry, they play the role of protecting groups

[1]) It has been called a 'doubly-doubly convergent' synthesis, see [3].

[2]) This has already been achieved with the 2,5-bis[(*Z*)-(2-nitrobenzenesulfenyl)methylene]-3,6-bis(methylene)-7-oxabicyclo[2.2.1]heptane, see [4].

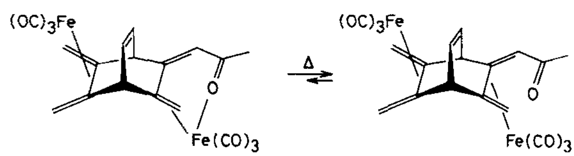
toward hydroboration of the diene moieties but leave one face of the endocyclic double bond at C(2),C(3) available for reaction. Thus, hydroboration followed by oxidative workup yields the corresponding alcohol (±)-**4** [6] from which the *'exo'*-$Fe(CO)_3$ group can be selectively removed on oxidation with Me_3NO [7]. Esterification of alcohol (±)-**4** with Ac_2O in pyridine gave complex (±)-**5** (98%, see *Exper. Part*).

Asymmetric induction in the hydroboration of **3** was not very successful. Using (−)-α-pinene and B_2H_6 led to a 20% yield of alcohol (+)-**4** with only 20% enantiomeric excess (e.e.). Treatment of **3** with monoisopinocampheylborane [8] in THF, followed by addition of KOH/H_2O_2 gave a better yield (67%) of optically active (+)-**4**, but with an e.e. of only 20%. *Gerlach*'s technique [9], however, was very successful in resolving the racemic alcohol (±)-**4** (*via* the camphanates, see *Exper. Part*), and gave (+)-**4** with e.e. > 98%.



1 Z=O 3 4 R=H

2 Z=CH=CH 5 R=Ac



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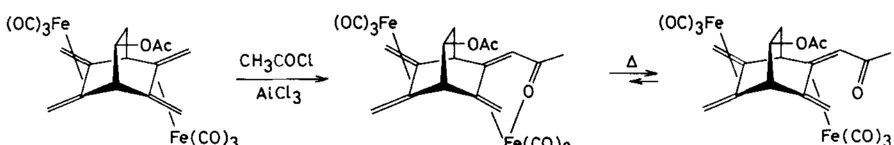

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The AcO group in (±)-**5** was found to direct subsequent electrophilic attack at only one of the four exocyclic C-atoms. We already reported that the parent bimetallic complex **3** can be monoacylated stereoselectively at the diene moiety coordinated to the *'endo'*-$Fe(CO)_3$ group yielding **6** [11]. Acylation under *Friedel-Crafts* conditions [10] of the diene moiety coordinated to the *'exo'*-$Fe(CO)_3$ group or of the endocyclic double bond were not observed. Under conditions of kinetic control, **6** was obtained pure; it could be isomerized into the more stable bis(tetrahapto) isomer **7** on heating [11]. A similar *Friedel-Crafts* acetylation of (±)-**5** ($AcCl/AlCl_3$) followed by quenching of the tetrachloroaluminate salt in sat. $NaHCO_3$/ice gave the kinetically favored, red product (±)-**8** (isolated yield: 56%); no other isomeric compounds could be isolated. The oxo group in (±)-**8** is *cis* with respect to C(5),C(6) as indicated by the ^{1}H-NMR pattern of the heterotriene moiety (see *Exper. Part*) which is very similar to that of **6** whose crystal structure has been determined [11]. The heterotriene is bonded to an $Fe(CO)_3$

group through one C,C-double bond and the O-atom of the oxo group. The unfunctionalized diene is η^4-bonded to the *'exo'*-$Fe(CO)_3$ group. Heating/cooling cycles of a solution of (±)-**8** in CH_2Cl_2 produced a reversible shift from red to yellow corresponding to the coordination equilibrium (±)-**8**⇆(±)-**9**. The ^{1}H- and ^{13}C-NMR spectra of the yellow solution indicated that the heterotriene moiety was now η^4-bonded to the *'endo'*-$Fe(CO)_3$ group through its two C,C-double bonds. Crystallization from the yellow solution gave the thermodynamically favored isomer (±)-**9** (97%).

Optically pure (–)-**9** was prepared by the above procedure starting with (+)-**4**. The crystal structure and absolute configuration of (–)-(2*S*,5*R*,7*S*)-**9** was established by X-ray crystallography (see below).

In the light of the stereoselective *Friedel-Crafts* acylation **3**→**6**, the preferential electrophilic substitution of the *'endo'*-$Fe(CO)_3$ coordinated diene moiety of **5** is no surprise. However, the regioselectivity (substitution of the 5-methylidene rather than the 6-methylidene group) of the reaction was not expected. There are several possible factors (*e.g.* steric, electronic, conformational effects, *etc.*) which could be responsible for the observed selectivity. Further experiments are required to distinguish them.

Preliminary experiments have suggested that either the *'endo'*-$Fe(CO)_3$ group in **8** or the *'exo'*-$Fe(CO)_3$ group in **9** can be removed selectively on treatment with an appropriate oxidant. This opens interesting possibilities for synthetic applications of system **9**, and they will be discussed in a forthcoming paper [12].

Crystal Structure and Absolute Configuration of (–)-9. – Single crystal diffraction intensities were collected on a *Syntex P2₁* autodiffractometer. An absorption correction based on the *Gaussian* integration method was applied. *Table 1* gives the crystallographic data and data collection procedure using the 'X-Ray 72 System' of programs [14]. Atomic scattering factors for neutral C, O, Fe [15], and H [16], and anomalous coefficients for Fe [17] were included in the structure factor calculations. The Fe-atoms were located on the *Patterson* map and the remaining non-H-atoms were identified on successive *Fourier* maps. All H-atoms were found on a difference *Fourier* synthesis after preliminary refinement to $R = 0.056$. The calculated positions of the H-atoms were included in the structure factor and refined with an isotropic temperature factor fixed at $U_{ij} = 0.08$.

Table 1. *Summary of Crystal Data of (–)-***9***, Intensity Collection, and Refinement*

Formula	(–)-[$(CO)_3Fe(C_{16}H_{18}O_3)Fe(CO)_3$]	Radiation	Mo-K_α, Nb-filtered (λ = 0.71069 Å)
Molecular mass	538.07	μ [cm^{-1}]	13.3
Dimensions [mm]	0.29 × 0.017 × 0.015	Min. and max. transmission	0.810 and 0.840
Crystal system	Orthorhombic	Scan method	2θ–θ
Space group	$P2_12_12$	Background from	Scan profile interpretation [13]
a [Å]	15.303(8)	$(\sin\theta/\lambda)_{max}$	0.54 Å^{-1}
b [Å]	15.790(9)	Data collected	$+h, +k, +l$ $-h, -k, -l$
c [Å]	9.621(4)	No. of unique reflections	3546
V [Å^3]	2325	No. of reflections ($I < 3\sigma$)	2676
Z	4		
d_{obs} (g · cm^{-3})	1.54(1) (ZnI_2 solution)	Resolution method	*Patterson* and *Fourier*
d_{calc} (g · cm^{-3})	1.54	Refinement method	Block-diagonal least-squares
F_{000}	1096	Function minimized	$\Sigma 1/\sigma^2(\lvert F_0\rvert - \lvert F_c\rvert)^2$
Systematic extinctions	$h00: h = 2n + 1$ $0k0: k = 2n + 1$	R	0.034
		R_W	0.026
		Goodness of fit	1.73

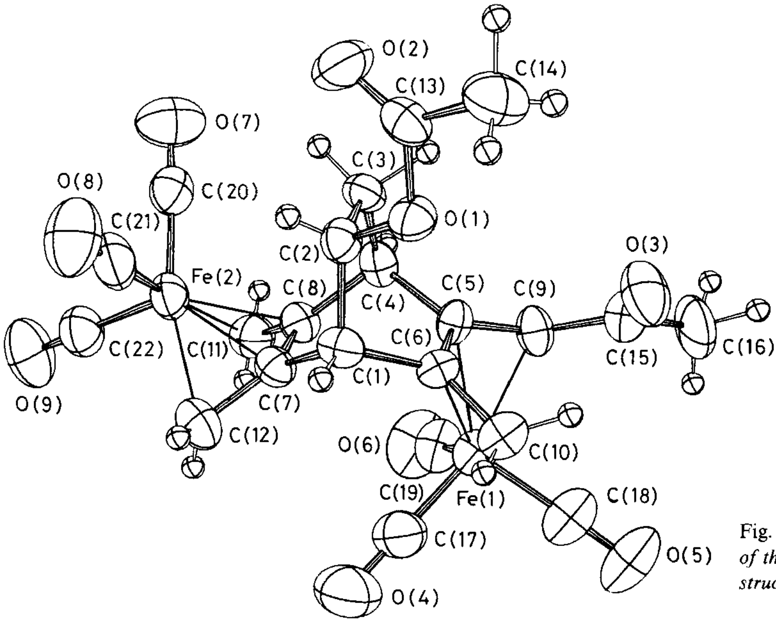

Fig. *A perspective view of the molecular structure of (−)-***9**

The absolute configuration of the molecule was determined from a comparison of two separate refinements with opposite signs of the atomic positional parameters. The parameters of *Table 2* give the better agreement ($R = 0.034$, $R_W = 0.026$, and $G_oF = 1.73$) compared with $R = 0.047$, $R_W = 0.042$, and $G_oF = 2.64$ for the inverse structure. On the basis of *Hamilton*'s test [18], the inverted structure can be rejected with a confidence level of more than 99.999%. The largest peaks in the final difference synthesis are *ca.* $1e^-/Å^3$ in the vicinity of the heavy atoms[3]).

Calculated bond lengths and angles are listed in *Tables 3* and *4*, respectively. A view of the molecular structure prepared by the program ORTEP [19] is given in the *Figure* where the numbering scheme is indicated. The two $Fe(CO)_3$ groups are in the *trans* position with respect to the roof-shaped ligand as in **3** [6] indicating that isomerization of the metal (*'exo' vs. 'endo'*) in a [$Fe(CO)_3$(1,3-diene)] complex does not occur in the presence of electrophiles of the *Friedel-Crafts* type. The arrangement of ligands about the Fe-atoms is tetragonal pyramidal. Four coordination sites are occupied by 2 CO and the midpoints of the outer C,C-bonds of the diene systems. The apex-to-base angles are 100° for the carbonyl groups and 110° for the C,C-bond midpoints. The basal angles are 92, 94, and 64°, the small angle being that subtended by the two outer C,C-bonds of the dienes. The dienes are perpendicular to the corresponding basal planes, and the Fe-atoms lie 0.5 Å above them. The geometrical features of the coordinated dienes are quite comparable to those already discussed for analogous [$Fe(CO)_3$(exocyclic 1,3-diene)] complexes [20]. The relative positions found for the acetyl and acetate substituents confirm unambiguously those proposed on the basis of the NMR spectra of (±)-**9**.

We thank the *Swiss National Science Foundation, Hoffmann-La Roche & Co. AG*, Basel, and the *Fondation Herbette*, Lausanne, for generous financial support.

[3]) List of observed and calculated structure factors are available on request from *R. R.*

Table 2. *List of Atomic Parameters for Complex (–)-(2S,5R,7S)-***9**[a])

Atom	x	y	z	U_{11} (or U)	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	0.0699(3)	0.1102(3)	0.7089(5)	0.039(3)	0.031(3)	0.047(3)	– 0.006(2)	0.008(3)	– 0.003(2)
C(2)	0.1387(3)	0.0571(2)	0.6342(5)	0.043(3)	0.040(3)	0.034(3)	0.000(3)	– 0.005(3)	– 0.002(3)
C(3)	0.2209(3)	0.1083(3)	0.6080(5)	0.036(3)	0.052(3)	0.037(3)	0.001(3)	0.007(3)	– 0.002(3)
C(4)	0.2082(3)	0.1983(3)	0.6658(5)	0.033(3)	0.052(3)	0.039(3)	– 0.017(3)	– 0.003(3)	0.008(2)
C(5)	0.1281(3)	0.2327(2)	0.5890(4)	0.036(3)	0.035(3)	0.040(3)	– 0.007(2)	– 0.009(2)	0.005(2)
C(6)	0.0534(2)	0.1850(2)	0.6112(4)	0.031(3)	0.028(2)	0.040(3)	– 0.001(2)	– 0.003(2)	– 0.005(2)
C(7)	0.1091(3)	0.1448(2)	0.8428(5)	0.043(3)	0.036(2)	0.036(3)	– 0.003(2)	0.003(3)	– 0.002(2)
C(8)	0.1829(3)	0.1944(3)	0.8190(4)	0.043(3)	0.042(3)	0.031(3)	– 0.001(2)	– 0.006(2)	– 0.010(2)
C(9)	0.1260(3)	0.3033(3)	0.4977(5)	0.056(3)	0.042(3)	0.038(3)	– 0.013(3)	– 0.004(3)	0.008(3)
C(10)	– 0.0279(3)	0.2098(3)	0.5557(6)	0.041(3)	0.039(3)	0.060(4)	– 0.002(3)	– 0.005(4)	– 0.002(3)
C(11)	0.2251(4)	0.2330(4)	0.9341(6)	0.057(4)	0.065(3)	0.054(4)	0.009(3)	0.000(4)	– 0.004(3)
C(12)	0.0804(4)	0.1341(3)	0.9819(5)	0.066(4)	0.053(3)	0.047(3)	– 0.009(3)	0.010(3)	0.004(3)
C(13)	0.1435(3)	– 0.0371(3)	0.4430(5)	0.052(3)	0.039(3)	0.040(3)	– 0.007(3)	0.011(3)	– 0.003(3)
C(14)	0.1003(4)	– 0.0589(3)	0.3068(6)	0.071(4)	0.064(4)	0.058(5)	0.006(4)	0.009(4)	– 0.019(3)
C(15)	0.0957(3)	0.3032(3)	0.3517(5)	0.058(3)	0.051(3)	0.051(3)	– 0.003(3)	– 0.010(3)	0.004(3)
C(16)	0.1041(5)	0.3879(5)	0.2766(7)	0.124(7)	0.083(5)	0.049(4)	0.010(5)	0.007(4)	0.034(4)
C(17)	– 0.0300(4)	0.2925(3)	0.8021(6)	0.058(4)	0.059(3)	0.078(4)	0.005(3)	0.010(4)	0.004(3)
C(18)	– 0.0368(3)	0.3862(3)	0.5714(5)	0.058(3)	0.043(3)	0.087(4)	– 0.005(3)	– 0.022(4)	– 0.001(3)
C(19)	0.1000(4)	0.3809(3)	0.7487(6)	0.075(4)	0.043(3)	0.067(4)	– 0.006(3)	– 0.013(3)	– 0.005(3)
C(20)	0.3199(3)	0.0849(3)	0.9103(5)	0.063(4)	0.050(3)	0.047(3)	0.001(3)	– 0.009(3)	– 0.004(3)
C(21)	0.1873(3)	– 0.0073(3)	0.9543(5)	0.079(4)	0.065(3)	0.041(3)	– 0.001(3)	0.003(4)	0.009(4)
C(22)	0.2350(3)	0.1140(3)	1.1436(6)	0.060(4)	0.076(4)	0.050(4)	0.000(3)	– 0.004(3)	0.005(4)
Fe(1)	0.03162(4)	0.31251(4)	0.65610(7)	0.0481(4)	0.0396(4)	0.0520(4)	– 0.0015(4)	– 0.0079(4)	– 0.0049(4)
Fe(2)	0.21244(5)	0.10136(4)	0.96421(7)	0.0564(5)	0.0512(4)	0.0346(4)	+ 0.0007(4)	– 0.0022(4)	0.0036(4)

O(1)	0.0998(2)	0.0275(2)	0.5053(3)	0.051(2)	0.036(2)	0.044(2)	0.008(2)	– 0.004(2)	– 0.008(1)
O(2)	0.2049(2)	– 0.0700(2)	0.4916(3)	0.064(2)	0.079(2)	0.071(3)	0.036(2)	– 0.014(2)	– 0.013(2)
O(3)	0.0674(2)	0.2411(2)	0.2938(3)	0.110(3)	0.068(2)	0.045(2)	– 0.004(2)	– 0.009(2)	– 0.007(2)
O(4)	– 0.0724(3)	0.2782(3)	0.9013(4)	0.100(3)	0.094(3)	0.104(4)	0.022(3)	0.034(3)	– 0.002(3)
O(5)	– 0.0828(2)	0.4333(2)	0.5178(4)	0.075(3)	0.075(3)	0.132(4)	0.011(2)	– 0.037(3)	0.018(3)
O(6)	0.1435(3)	0.4277(2)	0.8114(5)	0.118(3)	0.074(3)	0.115(4)	– 0.014(2)	– 0.039(3)	– 0.022(3)
O(7)	0.3930(3)	0.0732(2)	0.8777(4)	0.063(2)	0.095(3)	0.103(3)	0.003(2)	– 0.002(3)	– 0.032(3)
O(8)	0.1701(2)	– 0.0785(2)	0.9498(5)	0.122(3)	0.056(2)	0.098(3)	– 0.011(2)	– 0.012(3)	0.017(3)
O(9)	0.2511(3)	0.1252(3)	1.2586(4)	0.132(4)	0.135(4)	0.039(2)	– 0.002(3)	– 0.016(3)	0.003(3)
H(1)	0.024(3)	0.079(3)	0.732(5)	0.0800					
H(2)	0.151(3)	0.009(3)	0.675(4)	0.0800					
H(3A)	0.276(3)	0.081(2)	0.645(5)	0.0800					
H(3S)	0.236(3)	0.115(3)	0.495(4)	0.0800					
H(4)	0.251(3)	0.230(3)	0.661(5)	0.0800					
H(9E)	0.168(3)	0.344(3)	0.514(5)	0.0800					
H(10E)	– 0.070(3)	0.185(3)	0.588(5)	0.0800					
H(10Z)	– 0.027(3)	0.227(3)	0.456(5)	0.0800					
H(11E)	0.290(3)	0.251(3)	0.916(5)	0.0800					
H(11Z)	0.189(3)	0.248(3)	0.975(6)	0.0800					
H(12E)	0.048(3)	0.097(3)	0.989(5)	0.0800					
H(12Z)	0.075(3)	0.187(2)	1.049(4)	0.0800					
H(141)	0.038(3)	– 0.079(2)	0.331(5)	0.0800					
H(142)	0.142(3)	– 0.097(2)	0.258(5)	0.0800					
H(143)	0.103(4)	– 0.018(3)	0.249(5)	0.0800					
H(161)	0.068(3)	0.426(3)	0.323(5)	0.0800					
H(162)	0.147(3)	0.390(4)	0.228(6)	0.0800					
H(163)	0.081(3)	0.373(3)	0.171(5)	0.0800					

[a]) The temperature factor has the form e^{-T} where $T = 2\pi^2 \Sigma h_i h_j U_{ij} a_i^* a_j^*$ for anisotropic atoms and $T = 8\pi^2 U \sin^2\theta/\lambda^2$ for isotropic atoms. These coordinates give the correct configuration of the molecule in a right-hand coordinate system. The e.s.d. of the last significant digit is given in parentheses.

[b]) C-atom numbering, see *Fig.* H-atom numbering follows C-atom numbering; A refers to *anti*, S to *syn*, with respect to the bond C(5), C(6); E means *trans* and Z *cis* with respect to the bond C(5), C(6) or C(7), C(8).

Table 3. *Bond Lengths (Å) in (−)-9*[a])

Fe(1)–C(5)	2.046(4)	C(1)–C(2)	1.525(6)	C(1)–H(1)	0.89(4)
Fe(1)–C(6)	2.086(4)	C(2)–O(1)	1.453(5)	C(2)–H(2)	0.88(4)
Fe(1)–C(9)	2.105(5)	C(2)–C(3)	1.516(6)	C(3)–H(3A)	1.01(4)
Fe(1)–C(10)	2.096(5)	C(3)–C(4)	1.538(6)	C(3)–H(3S)	1.12(4)
Fe(1)–C(17)	1.721(6)	C(4)–C(5)	1.531(6)	C(4)–H(4)	0.83(4)
Fe(1)–C(18)	1.766(5)	C(5)–C(6)	1.386(6)	C(9)–H(9E)	0.92(5)
Fe(1)–C(19)	1.748(5)	C(6)–C(1)	1.531(6)	C(10)–H(10E)	0.82(4)
Fe(2)–C(7)	2.083(4)	C(1)–C(7)	1.522(6)	C(10)–H(10Z)	1.00(5)
Fe(2)–C(8)	2.077(4)	C(4)–C(8)	1.525(6)	C(11)–H(11E)	1.05(5)
Fe(2)–C(11)	2.108(6)	C(7)–C(8)	1.392(6)	C(11)–H(11Z)	0.72(5)
Fe(2)–C(12)	2.093(5)	C(5)–C(9)	1.419(6)	C(12)–H(12E)	0.77(4)
Fe(2)–C(20)	1.744(5)	C(6)–C(10)	1.409(6)	C(12)–H(12Z)	1.06(4)
Fe(2)–C(21)	1.761(6)	C(7)–C(12)	1.419(7)	C(14)–H(141)	1.03(4)
Fe(2)–C(22)	1.771(5)	C(8)–C(11)	1.420(7)	C(14)–H(142)	0.99(4)
C(17)–O(4)	1.176(7)	C(9)–C(15)	1.478(7)	C(14)–H(143)	0.86(5)
C(18)–O(5)	1.145(6)	C(13)–O(1)	1.359(5)	C(16)–H(161)	0.93(5)
C(19)–O(6)	1.164(7)	C(13)–O(2)	1.171(6)	C(16)–H(162)	0.80(6)
C(20)–O(7)	1.177(7)	C(13)–C(14)	1.508(8)	C(16)–H(163)	1.10(5)
C(21)–O(8)	1.155(6)	C(15)–O(3)	1.208(6)		
C(22)–O(9)	1.148(6)	C(15)–C(16)	1.526(9)		

[a]) The e.s.d. of the last significant digit is given in parentheses.
[b]) For numbering of atoms, see *Footnote b* in *Table 2*.

Table 4. *Bond Angles (°) in (−)-9*[a])[b])

C(5)–Fe(1)–C(6)	39.2(2)	C(3)–C(4)–C(8)	110.1(3)	H(2)–C(2)–O(1)	101(3)
C(5)–Fe(1)–C(9)	39.9(2)	C(5)–C(4)–C(8)	106.1(3)	H(3A)–C(3)–C(2)	114(2)
C(6)–Fe(1)–C(10)	39.4(2)	C(4)–C(5)–C(6)	113.1(3)	H(3A)–C(3)–C(4)	112(2)
C(17)–Fe(1)–C(18)	99.9(2)	C(4)–C(5)–C(9)	126.6(4)	H(3A)–C(3)–H(3S)	102(3)
C(17)–Fe(1)–C(19)	91.4(3)	C(6)–C(5)–C(9)	120.2(4)	H(3S)–C(3)–C(2)	113(2)
C(18)–Fe(1)–C(19)	100.6(2)	C(1)–C(6)–C(5)	112.2(3)	H(3S)–C(3)–C(4)	107(2)
C(7)–Fe(2)–C(8)	39.1(2)	C(1)–C(6)–C(10)	126.4(4)	H(4)–C(4)–C(3)	116(3)
C(7)–Fe(2)–C(12)	39.7(2)	C(5)–C(6)–C(10)	121.2(4)	H(4)–C(4)–C(5)	113(3)
C(8)–Fe(2)–C(11)	39.7(2)	C(1)–C(7)–C(12)	129.3(4)	H(4)–C(4)–C(8)	106(3)
C(20)–Fe(2)–C(21)	92.6(2)	C(8)–C(7)–C(12)	118.2(4)	H(9E)–C(9)–C(5)	115(3)
C(20)–Fe(2)–C(22)	97.0(2)	C(1)–C(7)–C(8)	112.5(4)	H(9E)–C(9)–C(15)	112(3)
C(21)–Fe(2)–C(22)	101.8(2)	C(4)–C(8)–C(7)	112.8(4)	H(10E)–C(10)–C(6)	115(3)
Fe(1)–C(17)–O(4)	179.4(5)	C(4)–C(8)–C(11)	128.3(4)	H(10E)–C(10)–H(10Z)	120(4)
Fe(1)–C(18)–O(5)	178.5(4)	C(7)–C(8)–C(11)	118.8(4)	H(10Z)–C(10)–C(6)	116(3)
Fe(1)–C(19)–O(6)	178.1(5)	C(5)–C(9)–C(15)	126.5(4)	H(11E)–C(11)–C(8)	115(3)
Fe(2)–C(20)–O(7)	178.1(4)	O(1)–C(13)–O(2)	123.5(4)	H(11Z)–C(11)–C(8)	103(4)
Fe(2)–C(21)–O(8)	178.9(4)	O(1)–C(13)–C(14)	109.8(4)	H(11E)–C(11)–H(11Z)	137(5)
Fe(2)–C(22)–O(9)	177.3(5)	O(2)–C(13)–C(14)	126.7(4)	H(12E)–C(12)–C(7)	112(4)
C(2)–O(1)–C(13)	114.6(3)	O(3)–C(15)–C(9)	123.5(5)	H(12Z)–C(12)–C(7)	120(2)
C(2)–C(1)–C(6)	104.4(3)	O(3)–C(15)–C(16)	121.5(5)	H(12E)–C(12)–H(12Z)	121(4)
C(2)–C(1)–C(7)	108.9(3)	C(9)–C(15)–C(16)	115.0(5)	H(141)–C(14)–C(13)	106(3)
C(6)–C(1)–C(7)	107.9(3)			H(142)–C(14)–C(13)	105(3)
C(1)–C(2)–C(3)	110.9(3)	H(1)–C(1)–C(2)	111(3)	H(143)–C(14)–C(13)	112(3)
C(1)–C(2)–O(1)	107.2(3)	H(1)–C(1)–C(6)	117(3)	H(161)–C(16)–C(15)	107(3)
O(1)–C(2)–C(3)	111.7(3)	H(1)–C(1)–C(7)	108(3)	H(162)–C(16)–C(15)	112(4)
C(2)–C(3)–C(4)	109.1(3)	H(2)–C(2)–C(1)	114(4)	H(163)–C(16)–C(15)	102(2)
C(3)–C(4)–C(5)	104.7(3)	H(2)–C(2)–C(3)	111(3)		

[a]) The e.s.d. of the last significant digit is given in parentheses.
[b]) For numbering of atoms, see *Footnote b* in *Table 2*.

Experimental Part

1. *General Remarks.* See [21].

2. *Preparation of Complexes.* The following compounds were obtained by published procedures: **2** [7] and (±)-**4** [6].

Preparation of **3**. The original procedure [5] has been optimalized in the following way: A suspension of $Fe_2(CO)_9$ (20 g, 55 mmol) and **2** (3.0 g, 1.93 mmol) in hexane (200 ml)/MeOH (30 ml) was stirred at r.t. for 14 h under Ar flux, then at 45° for 24 h. The solv. was evaporated *i.v.*, and the residue was taken up in hexane (300 ml) and filtered. Acid alumina (grade I, *Merck;* 50 g) was added to the green soln. to decompose $Fe_3(CO)_{12}$. The filtered soln. was evaporated *i.v.*, and the brown residue was chromatographed on silica gel with petroleum ether. Recrystallization from hexane at –25° gave **3** (4.8 g, 57%) and its *cis*-μ-isomer (6%) (see [5]).

trans-*μ-[(1*RS,*2*RS,*4*SR,*5*SR,*6*RS,*7*RS,*8*SR*)-C,5,6,C-η:C,7,8,C-η-(5,6,7,8-tetramethylidene-2-bicyclo-[2.2.2]octyl acetate)]-bis(tricarbonyliron) ((±)-***5***).* Alcohol (±)-**4** (0.55 g, 1.21 mmol) was stirred with pyridine (3 g) in Ac_2O (6 g) at 20° for 5 h. After addition of H_2O (100 ml), the mixture was extracted with hexane (100 ml), and the org. extracts were washed with H_2O (3 × 100 ml) and dried over $MgSO_4$. Evaporation *i.v.* gave an oil which yielded yellow crystals of (±)-**5** in hexane at –25° (0.585 g, 98%). M.p. 89–91°. IR: 2065, 1990, 1980, 1975 (CO), 1730 (C=O). ^{1}H-NMR (80 MHz, $CDCl_3$): 5.45 (*m*, H–C(2)); 3.75 (*d*, H–C(1)); 3.50 (*dd*, H–C(4)); 2.63 (*m*, H_{anti}–C(3)); 2.13 (*m*, H_{syn}–C(3)); 2.10 (*s*, CH_3); 1.95, 1.90 (2*d*, 4H, CH=C *trans* to C(5),C(6) and to C(7),C(8)); 0.66, 0.63, 0.43, 0.36 (4*d*, 4H, CH=C *cis* to C(5),C(6) and to C(7),C(8)); $J(1,2) = 3.5$, $J(2,3_{anti}) = 8.0$, $J(2,3_{syn}) < 2.0$, $J(3_{anti},3_{syn}) = 14.0$, $J(3,4) = 2.6$, $J_{gem} = 3.0$, $J(1,3) \approx J(2,4) < 1$. MS: 496 (10, M^+), 468 (19), 440 (77), 412 (19), 384 (12), 356 (25), 328 (100, $M^+ - 6$ CO), 116 (50), 112 (96), 84 (88), 56 (63). Anal. calc. for $C_{20}H_{16}Fe_2O_8$ (496.04): C 48.43, H 3.25; found: C 48.43, H 3.39.

trans-*μ-[(1*RS,*2*RS,*4*RS,*5*SR,*6*RS,*7*RS,*8*SR*)-C,6-η,* oxo-*σ:C,7,8,C-η-(6,7,8-trimethylidene-5-((*Z*)-2-oxopropylidene)-2-bicyclo[2.2.2]octyl acetate)]-bis(tricarbonyliron)*[4]*) ((±)-***8***).* AcCl (2 ml) was syringed into a flask containing (±)-**5** (0.6 g, 1.21 mmol), then $AlCl_3$ (0.40 g, 3 mmol) was slowly added. After stirring at 20° for 10 min, the mixture was poured into a vigorously stirred sat. $NaHCO_3$ (60 g)/ice (40 g) mixture. The quenched product turned deep red and was extracted with Et_2O (3 × 50 ml) at 0°. Column chromatography on *Florisil* with hexane/CH_2Cl_2 1:2 at –10° brought down a single red band. Recrystallization from hexane at –25° gave (±)-**8** as red needles (0.37 g, 57%). M.p.: isomerizes into (±)-**9** on heating. IR: 2060 1990, 1985, 1972 (CO), 1730 (C=O). ^{1}H-NMR (80 MHz, $CDCl_3$, –10°): 6.01 (*s*, H–C=C(5)); 5.23 (*m*, H–C(2)); 3.73 (*d*, H–C(1)); 3.37 (*m*, H–C(4)); 2.88 (*d*, 1H, CH=C(6) *trans* to C(5),C(6)); 2.45 (*m*, H_{anti}–C(3)); 2.14, 2.03 (2*s*, 2CH_3); 1.94, 0.49 (2*d*, 4H, CH=C *trans* and *cis* to C(7),C(8)); 1.82 (*m*, H_{syn}–C(3)); 1.16 (*d*, 1H, CH=C(6) *cis* to C(5),C(6)); $J(1,2) = 3.5$, $J(2,3_{anti}) \approx 8$, $J(2,3_{syn}) \approx 2$, $J(3_{anti},3_{syn}) = 14.0$, $J(3,4) = 2.8$, $J_{gem} = 3.0$. MS: 538 (< 1, M^+), 510 (8), 482 (10), 454 (19), 426 (15), 398 (11), 370 (85, $M^+ - 6$ CO), 238 (100), 149 (56), 56 (67).

trans-*μ-[(1*RS,*2*RS,*4*RS,*5*SR,*6*RS,*7*RS,*8*SR*)-C,5,6,C-η:C,7,8,C-η-(6,7,8-trimethylidene-5-((*Z*)-2-oxo-propylidene)-2-bicyclo[2.2.2]octyl acetate)]-bis(tricarbonyliron)*[4]*) ((±)-***9***).* On heating at 40° for 3 h, the red soln. of (±)-**8** (0.36 g, 0.67 mmol) in CH_2Cl_2 (30 ml) turned yellow. Column chromatography on silica gel with CH_2Cl_2 at 20° brought down a single yellow band. Recrystallization from Et_2O/hexane at –25° gave **9** as pale yellow microcrystals (0.35 g, 97%). M.p. 152°. IR: 2070, 2063, 1995, 1988, 1974 (CO), 1730, 1668 (C=O). ^{1}H-NMR (380 MHz, $CDCl_3$): 5.35 (*m* [42] (relative shift induced by addition of Eu(fod)$_3$), H–C(2)); 3.75 (*d* [33], H–C(1)); 3.53 (*s* [34], H–C=C(5)); 3.35 (*dd* [27], H–C(4)); 2.70, 2.54 (2*m* [23], H_{anti}–C(3), H_{syn}–C(3)); 2.45 (*d*, 1H [28], CH=C(6) *trans* to C(5),C(6)); 2.15 (*s* [17 and 53], 2 CH_3); 1.94, 1.88 (2*d*, 2H [9 and 12], CH=C *trans* to C(7),C(8)); 1.73 (*d*, 1H [100], CH=C *cis* to C(5),C(6)); 0.35, 0.28 (2*d*, 2H [3 and 5], CH=C *cis* to C(7),C(8)); $J(1,2) = 3.6$, $J(2,3_{anti}) = 8.1$, $J(2,3_{syn}) = 2.0$, $J(3_{anti},3_{syn}) = 13.8$, $J(3,4) = 2.7$, $J_{gem} = 3.0$. ^{13}C-NMR (90.55 MHz, $CDCl_3$): 212.5, 208.6, 206.7 (3*s*, CO); 199.0 (*s*, C=O); 170.6 (*s*, OCO); 112.8, 111.0, 108.7, 106.1 (4*s*, C(5), C(6), C(7), C(8)); 73.1 (*d*, *J* = 159, C(2)); 56.5 (*d*, *J* = 150, H–*C*=C(5)); 47.2, 43.3 (2*d*, *J* = 150, 143, C(1), C(4)); 44.5 (*t*, *J* = 162, H_2*C*=C(6)); 38.0 (*t*, *J* = 135, C(3)); 36.7, 36.5 (2*t*, *J* = 160, =CH_2); 29.2, 21.0 (2*q*, *J* = 128, 130, CH_3). MS: 538 (< 1, M^+), 510 (5), 482 (9), 454 (16), 426 (12), 398 (9), 370 (67, $M^+ - 6$ CO), 314 (33), 238 (100), 56 (Fe^+). Anal. calc. for $C_{22}H_{18}Fe_2O_9$ (538.07): C 49.11, H 3.77; found: C 49.25, H 3.39.

*Optical Resolution of (±)-***4**. Camphanoyl chloride (*Fluka;* $[\alpha]^{20}_{546} = -23 \pm 2°$ ($c = 2$, CCl_4); 550 mg, 2.5 mmol) was slowly added to a solution of (±)-**4** (900 mg, 2 mmol) in anh. pyridine (4 ml) at 0°. After stirring for 16 h at 20°, the mixture was poured into ice/H_2O (15 g), then extracted with CH_2Cl_2 (3 × 10 ml). The extracts were dried over $MgSO_4$ and evaporated *i.v.* Recrystallization from Et_2O gave 1.15 g (91%) of the camphanate diastereoisomers. Anal. calc. for $C_{28}H_{26}Fe_2O_{10}$: C 53.02, H 4.13; found: C 52.90, H 4.03.

The diastereoisomers (50 mg, 0.5 ml AcOEt/hexane 1:1) were separated by HPLC (25 cm × 21.2 mm column, 7-μ silica gel) with AcOEt/hexane 8:92 at 500–800 psi and recrystallized from Et_2O (global yield: 95%;

[4]) For better comparison, the bridging ligand in (±)-**8** and (±)-**9** is numbered in the same way as in (±)-**5**.

optical purity > 98% by 360-MHz ^{1}H-NMR (δ_H of the CH_3-groups)). (+)-Camphanate (larger R_f value): m.p. 197–8°; $[\alpha]_D^{25} = +75°$. (−)-Camphanate (smaller R_f value): m.p. 198–9°; $[\alpha]_D^{25} = -82°$ ($c = 2$, $CHCl_3$).

A 1.5N aq. soln. of KOH (2 ml) was then added to a solution of (+)-camphanate (100 mg, 0.16 mmol) in $MeOH/CH_2Cl_2$/THF 3:1:1. After stirring for 1 h at 20°, the solution was extracted with CH_2Cl_2 (3 × 3 ml). The extracts were dried over $MgSO_4$ and evaporated *i.v.* Recrystallization from $CHCl_3$/hexane gave 61 mg (85%) of (+)-**4** of e.e. > 98%, by *Mosher*'s technique [22] (δ_F ($CDCl_3$, 30°): −74.5 for (+)-**4** and −74.3 ppm for (−)-**4**). M.p. 144–5°. $[\alpha]_D^{25} = +25°$ ($c = 2$, $CHCl_3$). Anal. calc. for $C_{18}H_{14}Fe_2O_7$ (454.00): C 47.62, H 3.11; found: C 47.78, H 3.11.

Same procedure for the preparation of (−)-**4**. M.p. 144–5°. $[\alpha]_D^{25} = -25°$, $[\alpha]_{578}^{25} = -26°$, $[\alpha]_{546}^{25} = -31°$, $[\alpha]_{436}^{25} = -2°$, $[\alpha]_{365}^{25} = 0°$[5]). Anal. calc. for $C_{18}H_{14}Fe_2O_7$ (454.00): C 47.62, H 3.11; found: C 47.76, H 3.08.

Preparation of (−)-9. Alcohol (+)-**4** (500 mg) was converted to the corresponding acetate following the procedure used for the preparation of (±)-**5**; yield: 520 mg (95%). The latter (250 mg) was acetylated under the *Friedel-Crafts* conditions used for the preparation of (±)-**8** followed by thermal isomerization to (−)-**9**; yield: 140 mg (52%). Single crystals of (−)-**9** were grown by slow cooling of a solution in hexane/Et_2O at −25°. $[\alpha]_D^{25} = -100°$, $[\alpha]_{578}^{25} = -107°$, $[\alpha]_{546}^{25} = -126°$, $[\alpha]_{436}^{25} = +21°$, $[\alpha]_{365}^{25} = +19°$ ($c = 2$, $CHCl_3$).

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[5]) For the circular dichroism of the corresponding uncoordinated alcohol, see [23].