

**31. Circular Dichroism of Tricarbonyl(diene)iron Complexes.
The Octant Rule Applied to Ketones Perturbed by Remote Fe(CO)₃ Groups.
Crystal Structure of (±)-Tricarbonyl[(1*R*,4*R*,5*R*,6*S*)-*C*,5,6,*C*- η -
(5,6,7,8-tetramethylidene-2-bicyclo[2.2.2]octanone)]iron**

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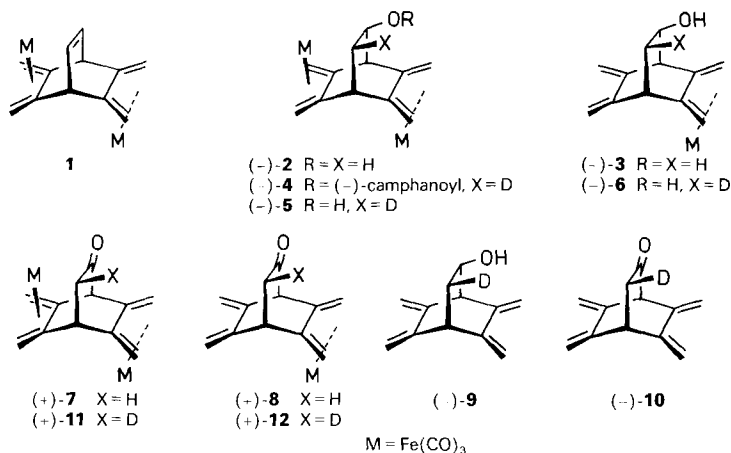
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The preparation and the CD spectra of optically pure (+)-*trans*- μ -[(1*R*,4*S*,5*S*,6*R*,7*R*,8*S*)-*C*,5,6,*C*- η :*C*,7,8,*C*- η -(5,6,7,8-tetramethylidene-2-bicyclo[2.2.2]octanone)]bis(tricarbonyliron) ((+)-**7**) and (+)-tricarbonyl[(1*S*,4*S*,5*S*,6*R*)-*C*-5,6,*C*- η -(5,6,7,8-tetramethylidene-2-bicyclo[2.2.2]octanone)]iron ((+)-**8**), and of its 3-deuterated derivatives (+)-*trans*- μ -[(1*R*,3*R*,4*S*,5*S*,6*R*,7*R*,8*S*)-*C*,5,6,*C*- η :*C*,7,8,*C*- η -(5,6,7,8-tetramethylidene(3-D)-2-bicyclo[2.2.2]octanone)]bis(tricarbonyliron) ((+)-**11**) and (+)-tricarbonyl[(1*S*,3*R*,4*S*,5*S*,6*R*)-*C*-5,6,*C*- η -(5,6,7,8-tetramethylidene(3-D)-2-bicyclo[2.2.2]octanone)]iron ((+)-**12**) are reported. The chirality in (+)-**7** and (+)-**8** is due to the Fe(CO)₃ moieties uniquely. The signs of the Cotton effects observed for (+)-**7** and (+)-**8** obey the octant rule (ketone $n \rightarrow \pi^*_{\text{C=O}}$ transition). Optically pure (-)-*(3R)*-5,6,7,8-tetramethylidene(3-D)-2-bicyclo[2.2.2]octanone ((-)-**10**) was prepared. Its CD spectrum showed an 'anti-octant' behaviour for the ketone $n \rightarrow \pi^*_{\text{C=O}}$ transition of the deuterium substituent. The CD spectra of the alcoholic derivatives (-)-*trans*- μ -[(1*R*,2*R*,4*S*,5*S*,6*R*,7*R*,8*S*)-*C*,5,6,*C*- η :*C*,7,8,*C*- η -(5,6,7,8-tetramethylidene-2-bicyclo[2.2.2]octanol)]bis(tricarbonyliron) ((-)-**2**) and (-)-tricarbonyl[(1*S*,2*R*,4*S*,5*S*,6*R*)-*C*,5,6,*C*- η -(5,6,7,8-tetramethylidene-2-bicyclo[2.2.2]octanol)]iron ((-)-**3**) and of the 3-deuterated derivatives (-)-**5** and (-)-**6** are also reported. The CD spectra of the complexes (-)-**2**, (-)-**3**, (+)-**7**, and (+)-**8** were solvent and temperature dependent. The 'endo'-configuration of the Fe(CO)₃ moiety in (±)-**8** was established by single-crystal X-ray diffraction.

Introduction. – There are only a few examples of optically pure, chiral tricarbonyl(diene)iron complexes reported in the literature [1] [2]. Reports on their circular-dichroism (CD) spectra are even more scarce [1b, d] [2]. We have shown [3] that 5,6,7,8-tetramethylidene-2-bicyclo[2.2.2]octanol and its mono- and dicomplexes **2** and **3** can be prepared easily. The corresponding ketones **7** and **8** [3] and the deuterated derivatives **5**, **6**, **11**, and **12** are also readily available [4]. In a preliminary communication [5], we reported on the optical resolution of these systems. The establishment of their absolute configuration has also been presented [6]. We describe here the CD spectra of these molecules. In the bicyclo[2.2.2]octanones **7** and **8**, the chirality is due exclusively to the Fe(CO)₃ groups. We have found that the octant rule [7] [8] can be applied to predict the sign of the Cotton effect of the $n \rightarrow \pi^*_{\text{C=O}}$ transition of the ketone chromophore in the monocomplex **8** and the dicomplex **7**. The Fe(CO)₃ moiety in **8** is *anti* to the C(2) centre ('endo'-complex), as demonstrated by X-ray crystallography. We report also the preparation and the CD spectrum of the optically pure monodeuterated ketone (-)-**10**.

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The signs given with each compound number corresponds to the $[\alpha]_D^{25}$ values measured for the configurations drawn here.

Results and Discussion. – Hydroboration followed by oxidative workup of the readily available dicomplex **1** gave the racemic mixture of alcohols (\pm)-**2** whose optical resolution was achieved in better than 98% optical purity by *Gerlach's* technique [6] [9].

Treatment of ($-$)-**2** (or ($+$)-**2**) with an excess of Me₃NO in anhyd. acetone (25°, 50 min) led to selective removal of the 'exo'-Fe(CO)₃ moiety (*syn* to C(2)) giving the monocomplex ($-$)-**3** (or ($+$)-**3**) in 78% yield [3]. The doubly complexed tetraenone ($+$)-**7** was obtained in 64% yield by oxidation of alcohol ($-$)-**2** with CrO₃/pyridine in CH₂Cl₂ (20°, 6–8 min). On treatment with Me₃NO, ($+$)-**7** afforded the monocomplexed tetraenone ($+$)-**8** in 50% yield together with the uncomplexed tetraenone (31%). The ketone ($+$)-**8** was also obtained by *Collins'* oxidation of alcohol ($-$)-**3** in 65% yield. The relative configuration of the Fe(CO)₃ moiety in ($+$)-**8** was given by the crystal structure of (\pm)-**8** described below.

Oxidative deuteration (NaBD₄/BF₃·Et₂O) of **1** gave alcohols (\pm)-**5** whose optical resolution was accomplished by using *Gerlach's* technique [5] [6] (\rightarrow ($-$)-**4**). *Collins'* oxidation [10] of ($-$)-**5** gave ($+$)-**11**. The product (\pm)-**11** was obtained on treating (\pm)-**7** with K₂CO₃ (1%) in anhyd. CD₃OD/CDCl₃ 1:1 (40°, 1 h) [4]. Prolonged heating of (\pm)-**7** in CD₃OD saturated with K₂CO₃ or containing 5–10% of CD₃ONa did not exchange the second H-atom at C(3) before decomposition of (\pm)-**7** (40°, 2–4 days). The high diastereoselectivity of the base-catalyzed monodeuteration (\pm)-**7** \rightarrow (\pm)-**11** can be attributed to a steric factor, *i.e.* protonation of the enolate intermediate occurs preferentially from its less hindered face. Oxidation of ($+$)-**11** with Me₃NO in acetone gave ($+$)-**12** (50%) and ($-$)-**10** (31%). Me₃NO oxidation of ($-$)-**5** (selective removal of the 'exo'-Fe(CO)₃ moiety) gave ($-$)-**6** which was then oxidized [10] to ketone ($+$)-**12**. These results demonstrated that the 'endo'-Fe(CO)₃ moiety in ($-$)-**3** and ($+$)-**8** did not migrate from one diene to the other during the oxidation reactions, thus confirming the absolute configurations given in the *Formulae*.

The 'endo'-complex (\pm)-**8** also gave the monodeuterated ketone (\pm)-**12** when treated in CD₃OD/CDCl₃ 1:1 containing K₂CO₃ or CD₃ONa. The exchange of the second H-atom at C(3) was also observed; at 35°, it occurred *ca.* 100 times more slowly than

reaction $(\pm)\text{-8} \rightarrow (\pm)\text{-12}$. On treating $(+)\text{-12}$ with an excess of Me_3NO in anh. acetone, the monodeuterated tetraenone $(-)\text{-10}$ was obtained. The latter was also prepared in the following way. The camphanate $(-)\text{-4}$ was oxidized with a large excess of Me_3NO (acetone, 25° , 20 h) and then saponified (CH_2Cl_2 , THF, H_2O , KOH) to give $(-)\text{-9}$. The latter was oxidized [10] to give $(-)\text{-10}$ (45% isolated yield from $(-)\text{-4}$).

The CD and UV/VIS spectrum of $(-)\text{-2}$ and $(-)\text{-3}$ are shown in *Figs. 1* (polar solvent) and 2 (non-polar solvent). The CD spectra were solvent and temperature dependent, thus indicating the importance of solvation and aggregation phenomena on the chiroptical properties of these molecules. This was not unexpected because of the alcoholic function [11]. At this time, we can say little about these spectra. It should be noted, however, that the two Cotton effects observed above 270 nm for $(-)\text{-2}$ and $(-)\text{-3}$ are significantly weaker than those observed for tricarbonyl(2,4-hexadienoic)iron [1b] and related complexes [1d]. The general shapes of the CD spectra of $(-)\text{-2}$ and $(-)\text{-3}$ are similar, although there are some differences in the positions of the maxima and minima. The latter also depend on solvent and temperature. If a through-space interaction between the two diene $\text{Fe}(\text{CO})_3$

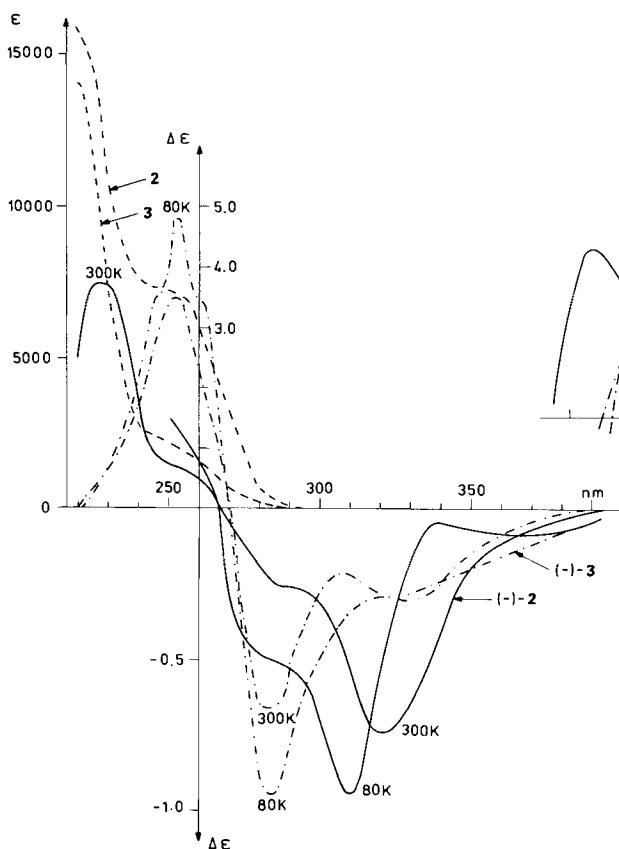


Fig. 1. UV/VIS (—) spectra of **2** and **3** in 95% EtOH. CD spectra of $(-)\text{-2}$ (---) and $(-)\text{-3}$ (----) in $\text{Et}_2\text{O}/\text{isopentane}/\text{EtOH}$ 5:5:2

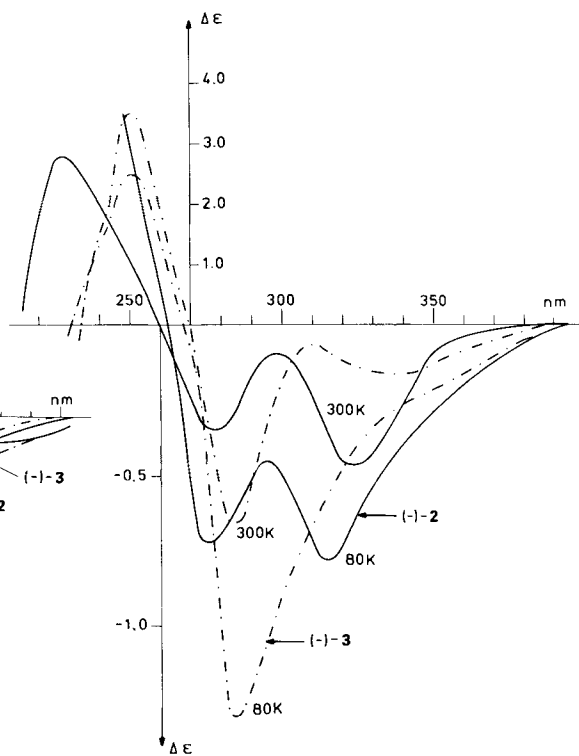


Fig. 2. CD spectra of $(-)\text{-2}$ (—) and $(-)\text{-3}$ (---) in isopentane/methylcyclohexane 4:1

chromophores [12] in (-)-**2** exists, little evidence for it is obtained from the comparison of the CD spectra of (-)-**2** and (-)-**3**.

The CD spectra of the monocomplexed tetraenone (+)-**8** and doubly complexed tetraenone (+)-**7** are given in *Figs. 3* (polar solvent) and *4* (non-polar solvent). The comparison of these spectra with those shown in *Figs. 1* and *2* for the corresponding

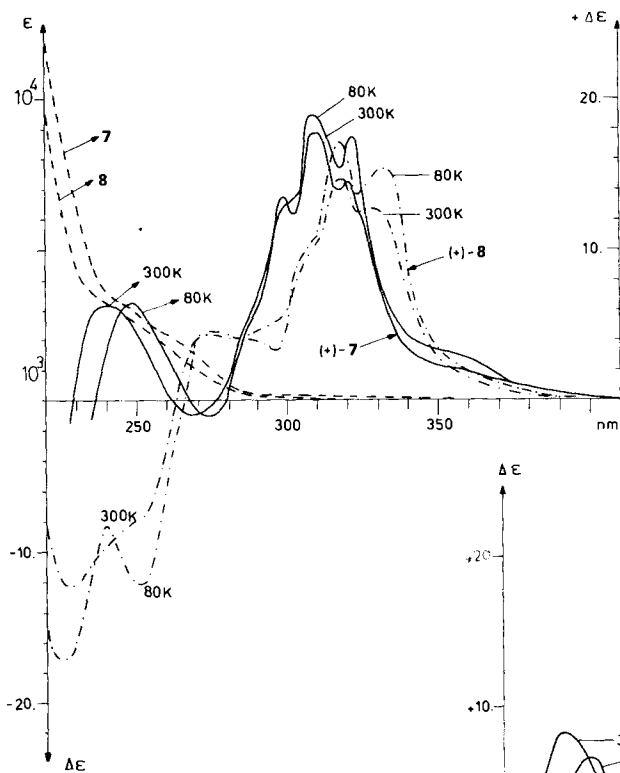


Fig. 3. UV/VIS (---) spectra of **7** and **8** in 95% EtOH. CD spectra of (+)-**7** (—) and (+)-**8** (---) in Et₂O/isopentane/EtOH 5:5:2

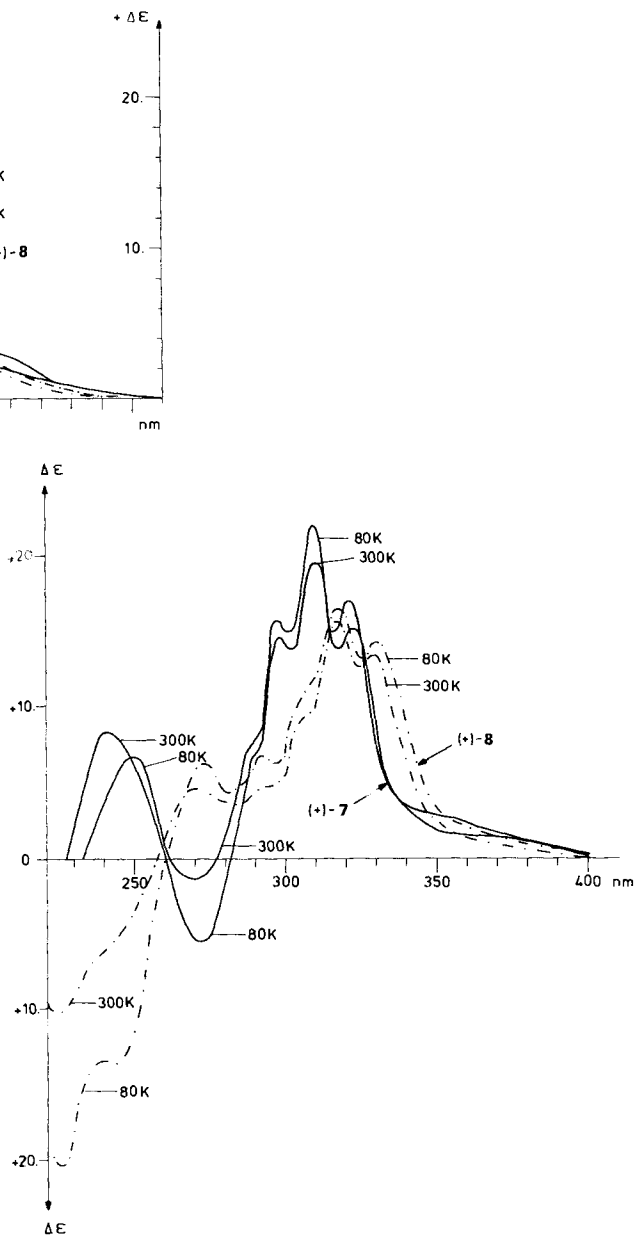


Fig. 4. CD spectra of (+)-**7** (—) and (+)-**8** (---) in isopentane/methylcyclohexane 4:1

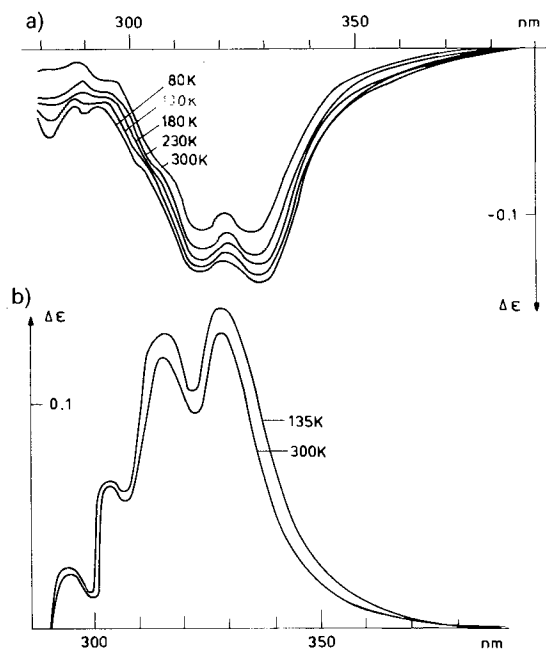


Fig. 5. CD spectra a) of (+)-**10** in $\text{Et}_2\text{O}/\text{isopentane}/\text{EtOH}$ 5:5:2 and b) of (-)-**10** in isopentane/methylcyclohexane 4:1 at various temperatures. (+)-**10** was prepared in the same fashion as (-)-**10** using the diastereoisomer (+)-**4'** prepared from (-)-camphanic acid and (\pm)-**5** [6].

alcohols (-)-**3** and (-)-**2**, respectively, suggests that the CD spectra of (+)-**7** and (+)-**8** correspond to the superposition of the relatively weak *Cotton* effects due to the $\text{Fe}(\text{diene})(\text{CO})_3$ chromophores and of those, much more intense, due to the $n \rightarrow \pi_{\text{CO}}^*$ transition of the ketone carbonyl groups. The position of the *Cotton* effects between 300 and 330 nm ($n \rightarrow \pi_{\text{CO}}^*$) in (+)-**7** and (+)-**8** is nearly the same as that observed for the monodeuterated, uncomplexed tetraenone (-)-**10** (see Fig. 5). The positive *Cotton* effect observed for the latter ketone corresponds to an 'anti-octant' behaviour of the deuterium substituent, as expected [13]. Due to instrumental limitation, the CD spectrum of (-)-**10** below 280 nm could not be recorded. The apparent dependence of this spectrum on temperature is too small to allow one to attribute it to a possible equilibrium of conformers. This tetraenone might well be a molecule belonging to a single minimum energy hypersurface as found for 7-deuterium- and 7-methyl-substituted 2,3,5,6-tetramethylidenebicyclo[2.2.2]octanes [5]. The temperature dependence observed for the CD spectrum of (+)-**10** (and (-)-**10**, Fig. 5) could be due to instrumental inaccuracy or/and to solvation and aggregation phenomena [14].

There is an apparent hypsochromic shift of about 7 nm for the maximum of the *Cotton* effect of (+)-**7** compared with that of (+)-**8**. Among the numerous explanations that can be proposed, one could invoke a steric repulsion between the CO groups of the 'exo'- $\text{Fe}(\text{CO})_3$ moiety and the ketone function in (+)-**7**. It is interesting to note that the influence of solvent and temperature on the *Cotton* effects of the ketone carbonyl chromophores of (+)-**7** and (+)-**8** is smaller than found for the *Cotton* effects attributed to the tricarbonyl(diene)iron chromophores.

The chirality of ketones (+)-**7** and (+)-**8** is due uniquely to coordination to $\text{Fe}(\text{CO})_3$ moieties. Projections of these molecules in a plane perpendicular to the ketone C=O axis

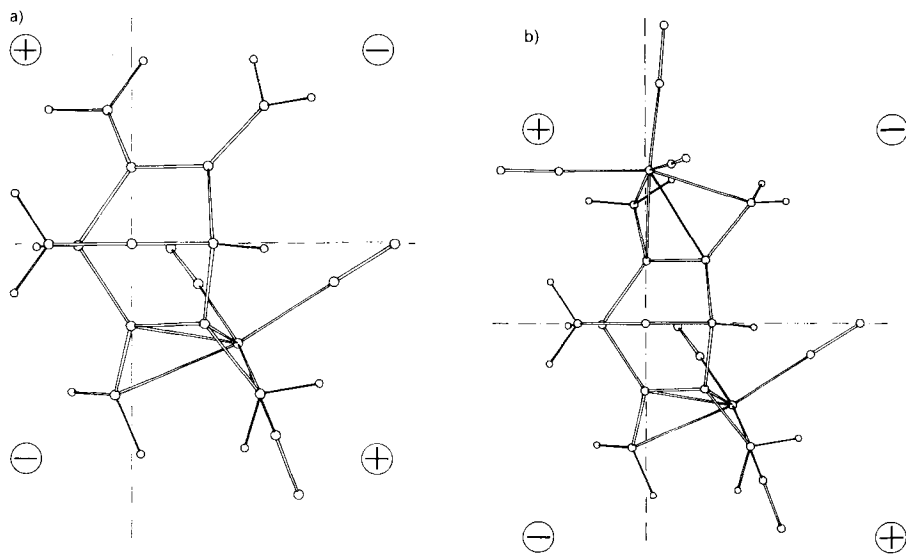


Fig. 6. Application of the octant rule a) to (+)-**8** and b) to (+)-**7**. Crystalline structures of (\pm)-**8** and of *trans*- μ -[C:5,6,C- η :C:7,8,C- η -(5,6,7,8-tetramethylidenebicyclo[2.2.2]oct-2-ene)]bis(tricarbonyliron) [22] were used for these projections perpendicular to the C=O axis.

are shown in Fig. 6. According to the octant rule [7] [8], a positive Cotton effect is predicted for the ketone $n \rightarrow \pi_{\text{CO}}^*$ transition of (+)-**8** due to the 'endo'-Fe(CO)₃ moiety, as observed. In the case of the dicomplex (+)-**7**, the contribution by the 'exo'-Fe(CO)₃ moiety (*syn* to C(2)) to the Cotton effect of the ketone is expected to be small since the Fe-atom lies almost in the 'vertical' nodal plane of the CO chromophore. Furthermore, the positive contribution of one of the CO ligand (basal ligand) is expected to be compensated by the negative contributions of the two other CO ligands (one basal and the apical ligands), in agreement with our observations (see Figs. 3 and 4).

Crystal Structure of (\pm)-8**.** - The ketone (\pm)-**8** crystallizes as tiny irregular orange plates from EtOH. The crystal used for data collection was the largest single crystal found. X-Ray intensity data collection was carried out at room temperature with an *Enraf-Nonius CAD-4* automatic diffractometer. The crystal data, intensity collection, structure solution, and refinement methods are summarized in Table 1. The measured intensities were not corrected for absorption due to loss of the crystal. The variances of the intensities were derived from counting statistics and the fluctuations of three periodically measured check reflections. The computer programs used for data reduction and structure solution were taken from the 'XRAY-72' program system [15]. The scattering factors for the neutral non-H-atoms were taken from *Cromer and Mann* [16], and for the H-atoms from *Stewart et al.* [17]. Anomalous dispersion coefficients were taken from *Cromer and Liberman* [18]. The structure was solved in the centric space group $C2/c$ by *Patterson and Fourier* methods. Refinement by full matrix least squares to $R = 0.103$ followed by a difference *Fourier* synthesis revealed all the H-atoms and refinement was continued to $R = 0.054$. In the last cycles the non-H-atoms were refined anisotropically and H-atoms of the same type constrained to have the same isotropic temperature factor. Although the other H-atoms refined correctly, H(2) and H(3) refined to unreasonable positions and were hence constrained to ideal positions on C(2) at a distance of 0.97 Å. The final atomic coordinates are reported in Table 2. Calculated bond lengths, bond angles, and torsion angles are reported in Table 3. A perspective drawing of the molecule prepared by the program ORTEP [19] is shown in Fig. 7 and angles between planes, in Fig. 8. The H-atoms are drawn with an artificial temperature factor of 0.004 Å² for clarity. A list of observed and calculated structure factors as well as tables of temperature factors are available as supplementary material.

Table 1. Summary of Crystal Data for (\pm)-8, Intensity Measurements, Structure Solution, and Refinement

Formula	$C_{15}H_{12}FeO_4$	λ [Å]	0.56087
Molecular weight	312.1	μ [cm ⁻¹]	5.7
Crystal system	Monoclinic	Scan method	2 θ - θ
a [Å]	30.759(4)	($\sin\theta/\lambda$) _{max}	0.60
b [Å]	7.872(2)	No. of unique reflections	2700
c [Å]	12.274(2)	No. of reflections $< 3\sigma$	1775
β [°]	107.39(1)	No. of observations (No. of variables)	12.6(8.1) ^{a)}
U [Å ³]	2836.1	Structure solution	Patterson and Fourier
Z	8	Refinement method	Full matrix least squares
d_{obs} [g·cm ⁻³]	1.43	Function minimized	$\Sigma w(F_o - F_c)^2$
d_{calc} [g·cm ⁻³]	1.46	w	$1/\sigma^2$
F_{000}	1280	R	0.054
Space group	$C2/c$	R_w	0.028
Radiation	Ag- $K\alpha$	Goodness of fit	1.26

^{a)} Only those reflections with $I < 3\sigma$ with $|F_c| > |F_o|$ were included in the refinement.

Table 2. Final Atomic Coordinates for $C_{15}H_{12}O_4Fe$

Atom ^{a)}	x	y	z
Fe	0.17702(4)	0.1965(1)	0.10006(8)
C(1)	0.1060(2)	0.314(1)	0.2330(5)
C(2)	0.0709(2)	0.199(1)	0.2597(6)
C(3)	0.0489(2)	0.0682(9)	0.1698(5)
C(4)	0.0725(3)	0.098(1)	0.0740(7)
C(5)	0.1233(2)	0.0694(8)	0.1307(5)
C(6)	0.1412(2)	0.1886(9)	0.2162(5)
C(7)	0.0819(2)	0.4013(9)	0.1216(6)
C(8)	0.0632(2)	0.278(1)	0.0288(6)
C(9)	0.1514(3)	-0.0516(9)	0.1054(6)
C(10)	0.1878(3)	0.179(1)	0.2775(6)
C(11)	0.0777(3)	0.565(1)	0.1115(7)
C(12)	0.0403(3)	0.311(1)	-0.0774(6)
C(13)	0.1524(2)	0.204(1)	-0.0514(5)
C(14)	0.2327(3)	0.1242(9)	0.1086(6)
C(15)	0.1867(3)	0.420(1)	0.1028(7)
O(1)	0.0606(2)	0.2090(7)	0.3465(4)
O(2)	0.1366(2)	0.2029(8)	-0.1472(4)
O(3)	0.2681(2)	0.0756(8)	0.1133(6)
O(4)	0.1934(2)	0.5606(6)	0.1024(6)
H(1)	0.122(1)	0.387(5)	0.288(3)
H(2)	0.054(2)	-0.046(6)	0.200(4)
H(3)	0.016(2)	0.087(8)	0.140(5)
H(4)	0.063(2)	0.030(6)	0.021(4)
H(5)	0.141(2)	-0.118(6)	0.038(4)
H(6)	0.180(2)	-0.088(6)	0.177(4)
H(7)	0.201(2)	0.284(7)	0.323(4)
H(8)	0.203(2)	0.085(7)	0.304(5)
H(9)	0.086(2)	0.651(6)	0.165(4)
H(10)	0.059(2)	0.608(7)	0.056(5)
H(11)	0.024(2)	0.220(7)	-0.139(4)
H(12)	0.036(2)	0.428(6)	-0.111(4)

^{a)} For practical reasons, the atom numbering of the centres that are not part of the bicyclo[2.2.2]octanone skeleton does not follow the IUPAC rules (see Fig. 7).

Table 3. Bond Lengths (Å) and Angles (°) for $C_{15}H_{12}O_4Fe$ ((±)-**8**) with Estimated Standard Deviations in Parentheses^a

Distances			
Fe–C(5)	2.059(7)	C(3)–C(4)	1.57(1)
Fe–C(6)	2.047(7)	C(4)–C(5)	1.53(1)
Fe–C(9)	2.115(8)	C(4)–C(8)	1.52(1)
Fe–C(10)	2.107(7)	C(5)–C(6)	1.393(9)
Fe–C(13)	1.786(6)	C(5)–C(9)	1.38(1)
Fe–C(14)	1.779(9)	C(6)–C(10)	1.409(9)
Fe–C(15)	1.781(8)	C(7)–C(8)	1.47(1)
C(1)–C(2)	1.52(1)	C(7)–C(11)	1.30(1)
C(1)–C(6)	1.53(1)	C(8)–C(12)	1.310(9)
C(1)–C(7)	1.511(9)	C(13)–O(2)	1.130(7)
C(2)–C(3)	1.51(1)	C(14)–O(3)	1.14(1)
C(2)–O(1)	1.202(9)	C(15)–O(4)	1.127(9)
Angles			
C(2)–C(1)–C(6)	102.7(6)	C(5)–Fe–C(9)	38.6(3)
C(2)–C(1)–C(7)	106.2(5)	C(5)–Fe–C(10)	70.6(3)
C(6)–C(1)–C(7)	110.3(6)	C(5)–Fe–C(13)	95.3(3)
C(1)–C(2)–C(3)	116.3(6)	C(5)–Fe–C(14)	130.2(3)
C(1)–C(2)–O(1)	123.0(7)	C(5)–Fe–C(15)	127.9(4)
C(3)–C(2)–O(1)	120.7(7)	C(6)–Fe–C(9)	70.6(3)
C(2)–C(3)–C(4)	103.6(6)	C(6)–Fe–C(10)	39.6(3)
C(3)–C(4)–C(5)	106.0(6)	C(6)–Fe–C(13)	125.2(3)
C(3)–C(4)–C(8)	109.5(7)	C(6)–Fe–C(14)	131.3(3)
C(5)–C(4)–C(8)	111.1(6)	C(6)–Fe–C(15)	98.0(4)
C(4)–C(5)–C(6)	111.3(6)	C(9)–Fe–C(10)	81.5(3)
C(4)–C(5)–C(9)	128.5(6)	C(9)–Fe–C(13)	91.0(3)
C(6)–C(5)–C(9)	120.2(6)	C(9)–Fe–C(14)	93.7(3)
C(5)–C(6)–C(1)	113.8(5)	C(9)–Fe–C(15)	166.5(4)
C(5)–C(6)–C(10)	118.4(7)	C(10)–Fe–C(13)	164.7(3)
C(1)–C(6)–C(10)	127.8(6)	C(10)–Fe–C(14)	93.8(3)
C(1)–C(7)–C(8)	112.0(6)	C(10)–Fe–C(15)	94.1(3)
C(1)–C(7)–C(11)	122.9(6)	C(13)–Fe–C(14)	100.0(3)
C(8)–C(7)–C(11)	125.0(6)	C(13)–Fe–C(15)	90.2(4)
C(7)–C(8)–C(4)	110.1(6)	C(14)–Fe–C(15)	99.3(4)
C(7)–C(8)–C(12)	127.5(7)	Fe–C(13)–O(2)	177.6(7)
C(4)–C(8)–C(12)	122.3(7)	Fe–C(14)–O(3)	178.9(7)
C(5)–Fe–C(6)	39.6(3)	Fe–C(15)–O(4)	178.3(9)
Torsion angles			
C(8)–C(4)–C(1)–C(7)	1.0(9)	C(5)–C(4)–C(1)–C(6)	0.5(9)
C(3)–C(4)–C(1)–C(2)	0.6(9)	C(4)–C(3)–C(2)–O(1)	–179.2(9)

^a) See Footnote a in Table 2.

The crystal structure of (±)-**8** does not provide us with an explanation based on ground-state properties of this molecule for the stereoselectivity of the H/D exchange **8**→**12** [11] and the stereoselective hydride reductions of (±)-**8** [20]. Our results suggest in fact that the face of the ketone function *syn* to the complexed diene moiety is less available on steric grounds than the other face. This is shown by the angles between average planes reported in Fig. 8. These data confirm that electronic factors may well play a dominant role in controlling the stereoselectivity of reaction **8**→**12**. If a dipole/dipole interaction

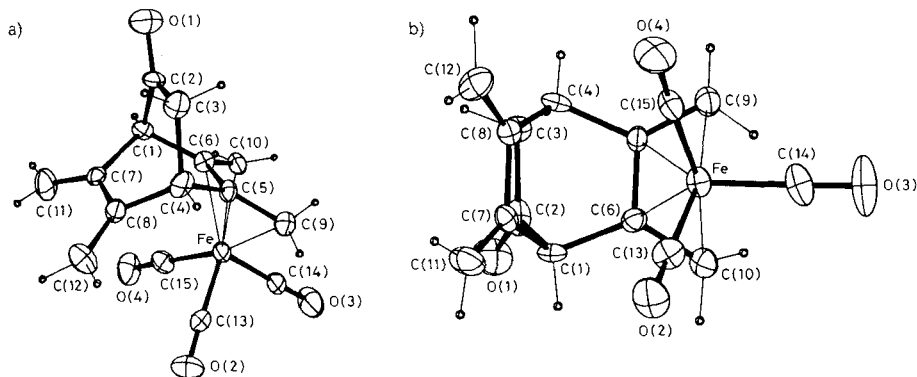


Fig. 7. ORTEP representations of (\pm)-8. a) Perspective view. b) Projection onto plane C(1),C(4),C(5),C(6).

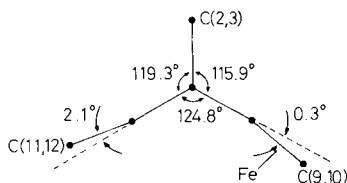


Fig. 8. Angles between least-squares planes in (\pm)-8

between the carbonyl groups of the ketone function at C(2) and the $\text{Fe}(\text{CO})_3$ moiety in (\pm)-8 exists, it is not manifested by a significant deformation (see Fig. 7b) of the tricarbonyl(diene)iron (*e.g.*: twist of the $\text{Fe}(\text{CO})_3$ tripod, deformation of the diene $\text{Fe}(\text{CO})_3$ moiety into an allyl(alkyl) $\text{Fe}(\text{CO})_3$ structure [2]).

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Experimental Part

General. See [21]. Optical resolution of alcohol (\pm)-2, see [6]. $[\alpha]_D$: thermostated Perkin-Elmer-141 polarimeter. CD spectra (λ ($\Delta\epsilon$)): Roussel-Jouan (Jobin-Yvon) Dichrographic III instrument, equipped with an Oxford-Instruments-DN704 cryostat and an Oxford-Instruments-DTC2 temperature controller. CD solvents: isopentane/methylcyclohexane 4:1 (A); Et_2O /isopentane/ EtOH 5:5:2 (B).

(-)-Tricarbonyl[(1*S*,2*R*,4*S*,5*S*,6*R*)-*C*,5,6, *C*- η -(5,6,7,8-tetramethylidene-2-bicyclo[2.2.2]octanol)]iron ((-)-3). Freshly distilled Me_3NO (2.7 g, 36 mmol) was added portionwise to a stirred soln. of (-)-2 (0.8 g, 1.76 mmol) in anhyd. acetone (100 ml). After stirring at 25° for 50 min, the mixture was filtered. CH_2Cl_2 (300 ml) and H_2O (100 ml) were added. The org. phase was washed with H_2O (100 ml, 3 times). The aq. layers were extracted with CH_2Cl_2 (850 ml). The org. extracts were united and dried (MgSO_4). After solvent evaporation, the residue was purified by column chromatography on silica gel (25 g, AcOEt /hexane 1:1). The crude (-)-3 was recrystallized from CH_2Cl_2 yielding 430 mg (78%) of yellow crystals, m.p. 91–92°. Spectral data were the same as those for (\pm)-3 [3]. $[\alpha]_D^{25} = -2.2^\circ$, $[\alpha]_{378}^{25} = -4.3^\circ$, $[\alpha]_{346}^{25} = -4.9^\circ$, $[\alpha]_{336}^{25} = -8.6^\circ$, $[\alpha]_{365}^{25} = -9.5^\circ$ ($c = 2$, CHCl_3). CD ($c = 0.0072$, A, 25°; see Fig. 2): 400 (0), 337 (-0.17), 283 (-0.66), 270 (0), 251 (+3.5), 233 (0). CD ($c = 0.0062$, B, 25°; see Fig. 1): 400 (0), 327 (-0.30), 283 (-0.66), 270 (0), 252 (+3.5), 220 (0). Anal. calc. for $\text{C}_{13}\text{H}_{14}\text{FeO}_4$ (314.12): C 57.38, H 4.49; found: C 57.42, H 4.55.

(-)-2: CD ($c = 0.0076$, A , 25°): 390 (0), 323 (-0.48), 277 (-0.36), 260 (0), 227 (+2.8). CD ($c = 0.0084$, B , 25°): 400 (0), 321 (-0.75), 290 (-0.26, sh), 266 (0), 227 (+3.7; see Fig. 1).

trans- μ -[(1RS,2RS,3RS,4SR,5SR,6RS,7RS,8SR)-C.5.6,C- η :C.7,8,C- η -(5.6,7,8-Tetramethylidene(3-D)-2-bicyclo[2.2.2]octanol)]bis(tricarbonyliron) ((\pm)-5). $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (2 g, 14 mmol) was added dropwise to a vigorously stirred suspension of NaBD_4 (800 mg, 21 mol) in anh. THF (30 ml) containing **1** (3 g) at 0° . After stirring at 20° for 3 h, the mixture was cooled to 0° and H_2O was added dropwise (1.6 g, 89 mmol), then 3N aq. KOH soln. (1.6 g), and H_2O (3 g, 89 mmol). After stirring at 20° for 16 h, the mixture was extracted with CH_2Cl_2 (20 ml, 3 times). After drying (MgSO_4) the org. extract, the solvent was evaporated and the residue purified by column chromatography on silica gel (90 g, CH_2Cl_2). The crude (\pm)-5 was recrystallized from CH_2Cl_2 yielding 2.2 g (70%) of yellow crystals, m.p. 157-158°. IR (CHCl_3): 3610, 3420, 3050, 3000, 2960, 2040, 1985, 1460, 1450, 1290, 1140, 1080, 1020, 935, 905, 855. $^1\text{H-NMR}$ (CDCl_3): 4.62 (ddd, $J = 8, 6, 3$, H-C(2)); 3.49 (d , $J = 3$, H-C(1)); 3.42 (d , $J = 3$, H-C(4)); 2.61 (dd , $J = 8, 3$, H-C(3)); 1.94 (d , $J = 6$, OH); 2.14, 2.09, 1.90, 1.81, 0.67, 0.61, 0.37, 0.31 (8d, $J = 3$). MS (70 eV): 455 (1), 427 (12), 399 (31), 371 (24), 343 (10), 315 (96), 287 (100). Anal. calc. for $\text{C}_{18}\text{H}_{13}\text{DFe}_2\text{O}_7$ (455.01): C 47.52, H + D 3.32; found: C 47.66, H + D 3.28.

Optical Resolution of (\pm)-5. Same procedure as for the optical resolution of (\pm)-2 [6]. The diastereoisomeric camphanate with the largest R_f is (+)-4', m.p. 197-198°. $[\alpha]_{\text{D}}^{25} = +74^\circ$, $[\alpha]_{\text{D}}^{25} = +78^\circ$, $[\alpha]_{\text{D}}^{25} = +90^\circ$, $[\alpha]_{\text{D}}^{25} = +12^\circ$ ($c = 2$, CHCl_3).

Data for (-)-4 (smaller R_f): m.p. 198-199°. $[\alpha]_{\text{D}}^{25} = -80^\circ$, $[\alpha]_{\text{D}}^{25} = -84^\circ$, $[\alpha]_{\text{D}}^{25} = -98^\circ$, $[\alpha]_{\text{D}}^{25} = -15^\circ$ ($c = 2$, CHCl_3).

To a soln. of 100 mg (0.16 mmol) of (-)-4 in 5 ml of $\text{MeOH}/\text{CH}_2\text{Cl}_2/\text{THF}$ 3:1:1, 1.5N KOH (3 ml) was added and the mixture stirred at 20° . The mixture was extracted with CH_2Cl_2 (3 ml, 3 times) and the extracts washed with H_2O (5 ml, 3 times). After drying (MgSO_4), the solvent was evaporated and the crude (-)-5 recrystallized from $\text{CHCl}_3/\text{hexane}$ 1:1 yielding 61 mg (85%) of yellow crystals.

Selective oxidation of the 'exo'-Fe(CO)₃ moiety in (-)-5 following the procedure given above for the preparation of (-)-3 afforded the alcohol (-)-6.

(+)-trans- μ -[(1R,4S,5S,6R,7R,8S)-C.5.6,C- η :C.7,8,C- η -(5.6,7,8-Tetramethylidene-2-bicyclo[2.2.2]octanone)]bis(tricarbonyliron) ((+)-7). Same procedure as that reported for the preparation of (\pm)-7, starting with (-)-2 [3]. $[\alpha]_{\text{D}}^{25} = +313^\circ$, $[\alpha]_{\text{D}}^{25} = +331^\circ$, $[\alpha]_{\text{D}}^{25} = +404^\circ$, $[\alpha]_{\text{D}}^{25} = +18^\circ$, $[\alpha]_{\text{D}}^{25} = +17^\circ$ ($c = 2$, CHCl_3). CD ($c = 0.0059$, A , 25°): 410 (0), 355 (+2.0, sh), 321 (+15.2), 310 (+19.6), 299 (+14.4), 290 (+7.4, sh), 276 (0), 269 (-1.4), 261 (0), 241 (8.4), 228 (0; see Fig. 4). CD ($c = 0.0054$, B): 410 (0), 355 (+2.0, sh), 321 (+14.6), 309 (+17.9), 301 (+13.2, sh), 290 (+6.7, sh), 276 (0), 268 (-1.0), 261 (0), 241 (+6.5), 229 (0; see Fig. 3). Anal. calc. for $\text{C}_{18}\text{H}_{12}\text{FeO}_7$ (451.99): C 47.83, H 2.68; found: C 47.93, H 2.62.

(+)-Tricarbonyl[(1S,4S,5S,6R)-C.5.6,C- η -(5.6,7,8-tetramethylidene-2-bicyclo[2.2.2]octanone)]iron ((+)-8). Same procedure as that reported for the preparation of (\pm)-8, starting with (+)-7; m.p. 118-119°. $[\alpha]_{\text{D}}^{25} = +435^\circ$, $[\alpha]_{\text{D}}^{25} = +438^\circ$, $[\alpha]_{\text{D}}^{25} = +536^\circ$, $[\alpha]_{\text{D}}^{25} = +1240^\circ$, $[\alpha]_{\text{D}}^{25} = +24^\circ$ ($c = 0.5$, CHCl_3). CD ($c = 0.006$, A , 25°): 400 (0), 330 (13.1), 317 (15.3), 307 (9.3, sh), 295 (4.6, sh), 282 (3.7), 270 (4.4), 259 (0), 240 (-6.0, sh), 225 (-10.1), 212 (0; see Fig. 4). CD ($c = 0.0063$, B , 25°): 400 (0), 329 (+12.7), 317 (14.7), 308 (9.6, sh), 295 (+4.9, sh), 274 (4.4), 263 (0), 239 (-9.2, sh), 227 (-12.4), 213 (0; see Fig. 3). Anal. calc. for $\text{C}_{15}\text{H}_{12}\text{FeO}_4$ (312.11): C 57.73, H 3.88; found: C 57.61, H 3.74.

(-)-(3R)-5.6,7,8-Tetramethylidene(3-D)-2-bicyclo[2.2.2]octanone ((-)-10). A mixture of camphanate (-)-4 (400 mg, 0.63 mmol), Me_3NO (2 g, 27 mmol), and anh. acetone (200 ml) was stirred at 25° for 20 h. After filtration, the solvent was evaporated and H_2O (50 ml) added. The mixture was extracted with CH_2Cl_2 (50 ml, 3 times) and the extract dried (MgSO_4) and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (5 g, CH_2Cl_2) yielding 180 mg of colourless oil. The latter was dissolved in 9 ml of $\text{MeOH}/\text{CH}_2\text{Cl}_2/\text{THF}$ 5:2:2, 1.5N KOH (3 ml) was added and the mixture stirred at 25° for 1 h. The mixture was extracted with CH_2Cl_2 (5 ml, 3 times) and the org. phase washed with H_2O (5 ml, 3 times), dried (MgSO_4), and evaporated. The residue was purified by column chromatography on silica gel (10 g, CH_2Cl_2) yielding 75 mg of (-)-9, colourless crystals. CrO_3 (343 mg, 3.43 mmol) was added in small portions to a stirred mixture of anh. pyridine (531 mg, 6.72 mmol) and anh. CH_2Cl_2 (6 ml) at 0° and under N_2 . After stirring at 20° for 10 min, (-)-9 (75 mg, 0.43 mmol) in anh. CH_2Cl_2 (0.5 ml) was added dropwise. After stirring at 20° for 8 min, the mixture was filtered through silica gel (2 g), the silica gel washed with anh. CH_2Cl_2 (5 ml), and the filtrate concentrated *in vacuo*. The crude oil was purified by column chromatography on silica gel (1.5 g, $\text{CH}_2\text{Cl}_2/\text{hexane}$ 1:1) yielding 49 mg (45%) of (-)-10, colourless crystals, m.p. 55-56°. $^1\text{H-NMR}$ (360 MHz, CDCl_3): 5.38 (s, 2H); 5.32 (s, 2H); 4.98 (s, 4H); 3.75 (s, H-C(1)); 3.40 (d , $J = 3$, H-C(4)); 2.40 (m, H-C(3)). Degree of monodeuteration: > 95%. MS (70 eV): 173 (80, M^+), 149 (74), 131 (42), 130 (100), 129 (96), 127 (62). $[\alpha]_{\text{D}}^{25} = -7.1^\circ$, $[\alpha]_{\text{D}}^{25} = -7.3^\circ$, $[\alpha]_{\text{D}}^{25} = -9.3^\circ$, $[\alpha]_{\text{D}}^{25} = -26.7^\circ$, $[\alpha]_{\text{D}}^{25} = -9.2^\circ$ ($c = 2$, CHCl_3). CD ($c = 0.017$, A , 25°): 390 (0), 330 (+0.12), 316 (+0.12), 304 (+0.07), 294 (+0.03), 285 (+0.02). CD ($c = 0.016$, B , 25°):

410 (0), 328 (+0.14), 316 (+0.13), 304 (+0.06, sh), 293 (+0.03), 285 (+0.03; see Fig. 5). Anal. calc. for $C_{12}H_{11}DO$ (173.24): C 83.20, H + D 7.56; found: C 83.15, H + D 7.30.

(±)-trans-μ-(1RS,3RS,4SR,5SR,6RS,7RS,8SR)-C,5,6,C-η:C,7,8,C-η-(5,6,7,8-Tetramethylidene(3-D)-2-bicyclo[2.2.2]octanone)bis(tricarboyliron) ((±)-11). a) Same procedure as that reported for the preparation of (±)-7, starting with (±)-5 [3]. b) A mixture of (±)-7 (100 mg, 0.58 mmol), anh. K_2CO_3 (10 mg) in $CDCl_3$ (0.5 ml), and CD_3OD (0.5 ml) was stirred for 1 h at 40°. After filtration, the soln. was evaporated and the residue dissolved in CH_2Cl_2 (5 ml). The CH_2Cl_2 soln. was washed with ice-cold H_2O (5 ml, 2 times) and dried ($MgSO_4$). After solvent evaporation, the crude (±)-11 was recrystallized from CH_2Cl_2 /hexane yielding 95 mg (95%) of yellow crystals, m.p. 159–160°. 1H -NMR ($CDCl_3$): 3.88 (s, H-C(1)); 3.60 (d, $J = 3$, H-C(4)); 2.71 (m, H-C(3)); 2.15, 2.05, 2.04, 1.86, 0.67, 0.59, 0.50, 0.40 (8d, $J = 3$). MS (70 eV): 453 (1, M^+), 425 (8), 397 (21), 369 (14), 341 (11), 314 (8), 313 (42), 286 (15), 285 (100), 282 (15), 259 (14), 258 (8), 257 (10), 229 (11), 199 (8), 149 (12), 112 (23). Anal. calc. for $C_{18}H_{11}DFe_2O_7$ (452.99): C 47.73, H + D 2.89; found: C 47.88, H + D 2.78.

(+)-trans-μ-(1R,3R,4S,5S,6R,7R,8S)-C,5,6,C-η:C,7,8,C-η-(5,6,7,8-Tetramethylidene(3-D)-2-bicyclo[2.2.2]octanone)bis(tricarboyliron) ((+)-11). Same procedure as that reported for the preparation of (±)-11, using (–)-5 [3]; m.p. 159–160°. $[\alpha]_D^{25} = +285^\circ$, $[\alpha]_{578}^{25} = +304^\circ$, $[\alpha]_{536}^{25} = +372^\circ$, $[\alpha]_{336}^{25} = +875^\circ$, ($c = 0.5$, $CHCl_3$). CD ($c = 0.007$, A , 25°): 410 (0), 355 (+2.0, sh), 322 (+15.0), 310 (+19.5), 299 (+14.4), 290 (+7.6, sh), 277 (0), 269 (–1.3), 261 (0), 242 (+8.5), 229 (0). Anal. calc. for $C_{18}H_{11}DFe_2O_7$ (452.99): C 47.73, H + D 2.89; found: C 47.82, H + D 2.55.

(+)-Tricarboyl[(1S,3R,4S,5S,6R)-C,5,6,C-η-(5,6,7,8-tetramethylidene(3-D)-2-bicyclo[2.2.2]octanone)]-iron ((+)-12). To a soln. of anh. pyridin (810 mg, 10.2 mmol) in anh. CH_2Cl_2 (10 ml) cooled to 0°, CrO_3 (515 mg, 5.1 mmol) was added portionwise under N_2 . After stirring at 20° for 10 min, (–)-6 (170 mg, 0.54 mmol) in anh. CH_2Cl_2 (2 ml) was added dropwise, the mixture filtered through silical gel (1 g), and the silica gel washed with CH_2Cl_2 (10 ml). The solvent was evaporated and the residue purified by column chromatography on silica gel (8 g, CH_2Cl_2 /hexane 1:1). The crude (+)-12 was recrystallized from hexane yielding 110 mg (65%) of yellow crystals, m.p. 118–119°. $[\alpha]_D^{25} = +402^\circ$, $[\alpha]_{578}^{25} = +430^\circ$, $[\alpha]_{536}^{25} = +522^\circ$, $[\alpha]_{336}^{25} = +1438^\circ$, ($c = 0.5$, $CHCl_3$). CD ($c = 0.0084$, A , 25°): 400 (0), 330 (+13.0), 317 (+15.2), 307 (+9.3, sh), 295 (+4.7, sh), 282 (+3.7), 271 (+4.4), 259 (0), 240 (–6.0), 225 (–10.5), 213 (0). CD ($c = 0.0065$, B , 25°): 400 (0), 329 (+12.5), 317 (+14.5), 307 (+9.3, sh), 295 (+4.8, sh), 274 (+4.6), 263 (0), 239 (–9.4, sh), 227 (–12.1), 212 (0). 1H -NMR ($CDCl_3$): 5.45, 5.35, 5.01, 4.95 (4s); 3.72 (s, H-C(1)); 3.45 (m, H-C(4)); 2.58 (m, H-C(3)); 1.91, 1.80, 0.39, 0.23 (4d, $J = 3$). MS (70 eV): 313 (5, M^+), 285 (26), 257 (64), 229 (100), 201 (10), 199 (38).

REFERENCES

- [1] a) G. Paiaro, R. Palumbo, A. Musco, A. Pannuzi, *Tetrahedron Lett.* **1965**, 1067; A. Musco, G. Paiaro, R. Palumbo, *Chim. Ind.* **1968**, *50*, 669; b) A. Musco, R. Palumbo, G. Paiaro, *Inorg. Chim. Acta* **1971**, *5*, 157; c) R. H. Grubbs, R. A. Grey, *J. Chem. Soc., Chem. Commun.* **1973**, 76; E. K. G. Schmidt, *Chem. Ber.* **1974**, *107*, 2440; *ibid.* **1975**, *108*, 1598; S. Litman, A. Gedanken, Z. Goldschmidt, Y. Bakal, *J. Chem. Soc., Chem. Commun.* **1978**, 983; A. J. Birch, W. D. Raverty, G. R. Stephenson, *Tetrahedron Lett.* **1980**, *21*, 197; A. J. Birch, B. M. R. Bandara, *ibid.* **1980**, *21*, 2981; A. Monpert, J. Martelli, R. Gree, R. Carrié, *ibid.* **1981**, *22*, 1961; d) M. Green, R. P. Hughes, *J. Chem. Soc., Dalton Trans.* **1976**, 1907; see also: D. L. Reger, *J. Inorg. Nucl. Chem.* **1977**, *39*, 1095.
- [2] Ch. Barras, R. Roulet, P. Vogel, *Inorg. Chim. Acta* **1984**, *82*, L1.
- [3] R. Gabioud, P. Vogel, *Helv. Chim. Acta* **1983**, *66*, 1134.
- [4] R. Gabioud, P. Vogel, *Tetrahedron Lett.* **1983**, *24*, 1983.
- [5] R. Gabioud, P. Vogel, *Tetrahedron Lett.* **1984**, *25*, 1729.
- [6] E. Tagliaferri, Ph. Campiche, R. Roulet, R. Gabioud, P. Vogel, G. Chapuis, *Helv. Chim. Acta* **1985**, *68*, 126.
- [7] W. Moffitt, R. B. Woodward, A. Moscowitz, W. Klyne, C. Djerassi, *J. Am. Chem. Soc.* **1961**, *83*, 4013; P. Crabbé, 'Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry', Holden Day, San Francisco, California, USA, 1965; L. Velluz, M. Legrand, M. Grosjean, 'Optical Circular Dichroism', Verlag Chemie, 1965; D. A. Lightner, D. E. Jackman, *J. Chem. Soc., Chem. Commun.* **1974**, 344; D. A. Lightner, T. C. Chang, *J. Am. Chem. Soc.* **1974**, *96*, 3015; D. A. Lightner, B. V. Crist, N. Kalyanam, L. M. May, D. E. Jackman, *J. Org. Chem.* **1985**, *50*, 3867.
- [8] Y. H. Rao, D. P. Santry, *J. Am. Chem. Soc.* **1966**, *88*, 4157; C. Djerassi, R. Records, E. Bunnenberg, K. Mislow, A. Moscowitz, *ibid.* **1962**, *84*, 870; C. Coulombeau, A. Rassat, *Bull. Soc. Chim. Fr.* **1971**, 516; D. A. Lightner, G. D. Christiansen, *Tetrahedron Lett.* **1972**, 883; T. D. Bouman, D. A. Lightner, *J. Am. Chem. Soc.*

- 1976, 98, 3145.
- [9] H. Gerlach, *Helv. Chim. Acta* **1968**, 51, 1587.
- [10] J. R. Holum, *J. Org. Chem.* **1961**, 26, 4814; R. Ratcliffe, R. Rodehorst, *ibid.* **1970**, 35, 4000.
- [11] M. Sheves, B. Kohne, N. Friedman, Y. Mazur, *J. Am. Chem. Soc.* **1984**, 106, 5000.
- [12] G. Granozzi, E. Lorenzoni, R. Roulet, J.-P. Dandey, D. Ajo, *Organometallics* **1985**, 4, 836.
- [13] G. Barth, C. Djerassi, *Tetrahedron* **1981**, 37, 4123; L. A. Gorthey, M. Vairamani, C. Djerassi, *J. Org. Chem.* **1984**, 49, 1511 and ref. cit. therein; see also: D. A. Lightner, B. V. Crist, *Tetrahedron* **1985**, 41, 3021.
- [14] C. Coulombeau, A. Rassat, *Bull. Soc. Chim. Fr.* **1966**, 3752; J. Allinger, N. L. Allinger, *Tetrahedron* **1958**, 2, 64.
- [15] J. M. Stewart, F. A. Kundell, J. C. Baldwin, 'XRAY-72', version of June 1972, technical report TR-192 of the Computing Science Center, University of Maryland (as modified by D. Schwarzenbach).
- [16] D. T. Cromer, J. B. Mann, *Acta Crystallogr., Sect. A* **1968**, 24, 321.
- [17] R. F. Stewart, E. R. Davidson, W. T. Simpson, *J. Phys. Chem.* **1965**, 42, 3175.
- [18] D. T. Cromer, D. Liberman, *J. Chem. Phys.* **1970**, 53, 1891.
- [19] C. K. Johnson, ORNL-3794, Oak-Ridge National Laboratory, 1971.
- [20] J.-C. Zwick, P. Vogel, *Angew. Chem., Int. Ed.* **1985**, 24, 787.
- [21] J. Tamariz, P. Vogel, *Tetrahedron* **1984**, 22, 4560.
- [22] Ph. Narbel, A. A. Pinkerton, E. Tagliaferri, J. Wenger, R. Roulet, R. Gabioud, P. Vogel, D. Schwarzenbach, *J. Organomet. Chem.* **1981**, 208, 335.