91. Structure of Tricarbonyl(diene)iron Complexes in Solution. Variable-Temperature Circular Dichroism of *trans*-*μ*-(2,3,5,6-Tetramethylidenebicyclo[2.2.2]octane)bis(tricarbonyliron) Complexes

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Optically pure (–)-*trans*-*μ*-[(1*R*,2*R*,3*S*,4*S*,5*S*,6*R*)-*C*,2,3,*C*-*η*:*C*,5,6,*C*-*η*-(2,3,5,6,7-pentamethylidenebicyclo[2.2.2]octane)]bis(tricarbonyliron) ((–)-**9**), (–)-*trans*-*μ*-[(1*R*,2*R*,3*S*,4*S*,5*S*,6*R*,7*S*)-*C*,2,3,*C*-*η*:*C*,5,6,*C*-*η*-(7-methyl-2,3,5,6-tetramethylidenebicyclo[2.2.2]octane)]bis(tricarbonyliron) ((–)-**10**), and (–)-*trans*-*μ*-[(1*R*,2*R*,3*S*,4*S*,5*S*,6*R*,7*R*)-*C*,2,3,*C*-*η*:*C*,5,6,*C*-*η*-(2,3,5,6-tetramethylidene(7D)bicyclo[2.2.2]octane)]bis(tricarbonyliron) ((–)-**16**) have been prepared. Their CD spectra were solvent- and concentration-independent, but temperature-dependent, in accord with the existence of equilibria between rapidly interconverting diastereoisomeric species which can be interpreted as arising from distortions of the tricarbonyl(diene)iron units from the C_s symmetry.

Introduction. – The structure of (butadiene)tricarbonyliron has been determined by single-crystal X-ray diffraction [1] and by gas-phase electron diffraction [2]. The overall structural features are the same as found for other tricarbonyl(1,3-diene)iron derivatives [3] [4]. The C-atoms of the diene unit are invariably planar, and the Fe-atom is about 1.64 Å from this plane. The most common description of the coordination geometry is square pyramidal with one apical CO; the diene is perpendicular to the basal plane with three statistically equal C–C distances and two equal Fe-C(terminal) distances [4]. The basal plane is defined by the two equivalent CO ligands and the mid-points of the outer C–C bonds of the diene. Hence, the two valence-bond representations **1**↔**2** have been widely used to describe the iron-diene interaction [5].

1 (C_s) **2** (C_s)

Recently, several arguments have been advanced [6] for a representation **3**⇄**3'** which involves an equilibrium between a pair of rapidly interconverting enantiomers having a σ-alkyl,η^3-allyl bonding mode. An alternative hypothesis which also involves two rapidly interconverting enantiomeric structures would be an equilibrium between the rotamers **4** and **4'**. Vibrational spectra of (butadiene)tricarbonyliron in the liquid state were consistent with the latter hypothesis [7]. In the limit, hypotheses **3**⇄**3'** and **4**⇄**4'** could be two different representations of the same equilibrium. In principle, unequal Fe-C(diene) distances are expected for C_1 species such as **3**, **3'**, **4**, and **4'**, a feature that has never been detected yet by X-ray crystallography [2–4]. Interestingly, unequal Ni-C(terminal) dis-

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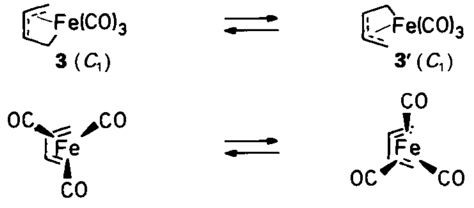
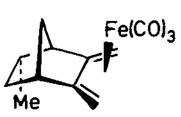
tances have been observed in the crystal structure of a (1,3-diene)nickel complex [8]. Recently, we have reported the variable-temperature circular dichroism (CD) spectra of complexes **5**–**7** [9] which were proposed to be consistent with the existence of equilibria between pairs of rapidly interconverting diastereoisomers according to hypothesis **3**⇄**3′** or **4**⇄**4′**.



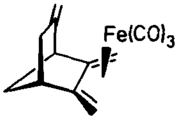
3 (C_1) **3′** (C_1)

4 (C_1) **4′** (C_1)



(+)-**5**

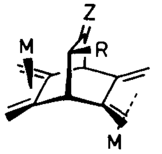
(−)-**6**



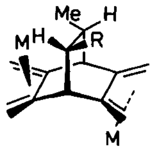
(−)-**7**

We report here the syntheses of optically pure 7-substituted *trans*-μ-(2,3,5,6-tetramethylidenebicyclo[2.2.2]octane)bis(tricarbonyliron) complexes. Their CD spectra were found to be solvent- and concentration-independent, but temperature-dependent. The data were in accord with the existence of equilibria involving rapidly interconverting diastereoisomeric species of similar free enthalpy.

Results and Discussion. – Methylenation (Zn, CH_2Br_2, $TiCl_4$, THF) [10] of the optically pure, doubly complexed ketone (+)-**8** [11] gave the corresponding pentaene (−)-**9** (58% yield) whose chirality arises from the *trans*-configuration of the two $Fe(CO)_3$ moieties. Catalytical hydrogenation (PtO_2, H_2) yielded the methyl derivative (−)-**10** (94%). The reaction was highly stereoselective due to the steric shielding of the $Fe(CO)_3$ moiety near the methylidene function at C(7) which makes only one face at the uncoordinated olefin available for the hydrogenation. The configuration at the methyl-substituted C-atom in (−)-**10** was established by its 360-MHz-^{1}H-NMR spectrum which allowed one to determine the H,H coupling constants between H–C(7) and the vicinal protons at C(8). A *cis*-vicinal coupling constant of 10 Hz was measured, whereas the *trans*-vicinal coupling constant was 6.5 Hz. The assignments of H_{syn} and H_{anti}[2]) at C(8) in (−)-**10** were



(+)-**8** R = H, Z = O
(−)-**9** R = H, Z = CH_2
11 R = D, Z = O
12 R = D, Z = CH_2



(−)-**10** R = H
13 R = D

M = $Fe(CO)_3$

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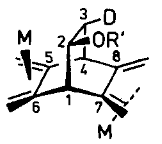
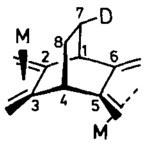
[2]) The terms *syn* and *anti* are used to characterize the H-atoms oriented towards and away from the $Fe(CO)_3$ moiety, respectively.



(+)-**14** R' = H
(+)-**15** R' = O_2SCH_3



(−)-**16**

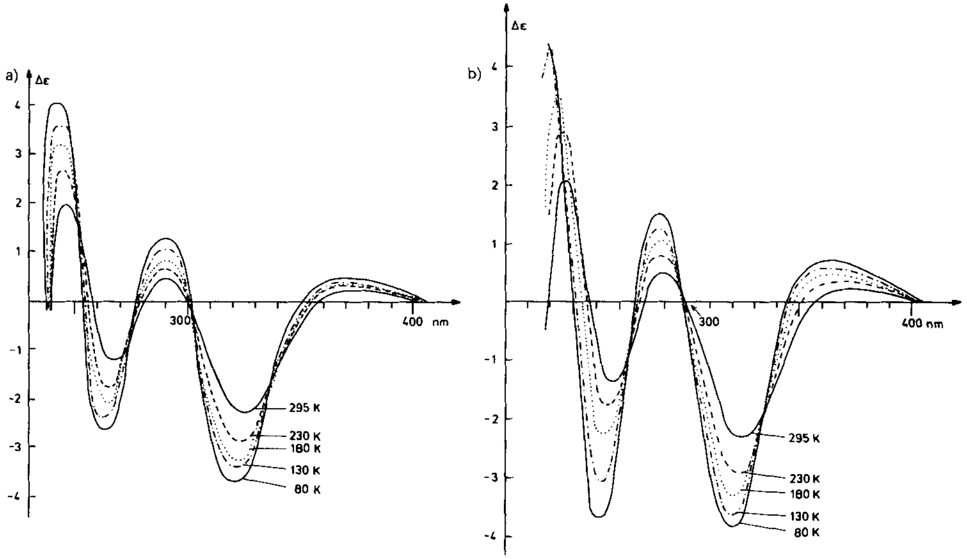


Fig. 1. *Variable-temperature CD spectra of (−)-***9** *in (*a*) IPM 41 and (*b*) EPE 552*

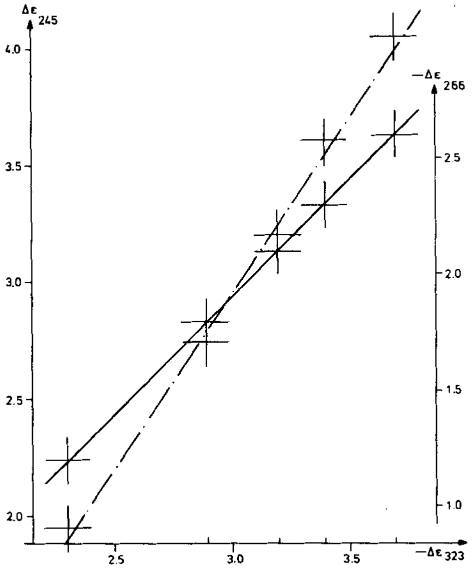


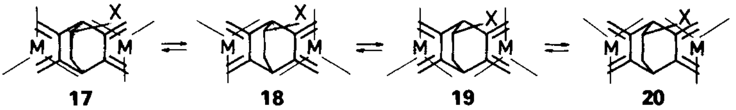
Fig. 2. *Linear plots of $\Delta\varepsilon_{245}$* vs. *$\Delta\varepsilon_{323}$ and of $\Delta\varepsilon_{266}$* vs. *$\Delta\varepsilon_{323}$ for the variable-temperature spectrum of (−)-***9** *in EPE 552*

determined by synthesis of the deuterated derivative **13** which was obtained by methylenation of the known deuterated ketone **11** [11] [12] (→**12**) followed by catalytical hydrogenation (→**13**; see *Exper. Part*).

The synthesis of the optically pure (d.e. > 98%) monodeuterated alcohol (+)-**14** has already been reported [11]. Treatment of (+)-**14** with methanesulfonyl chloride in pyridine yielded the mesylate (+)-**15** (79%) which was reduced to (−)-**16** (36%) with $NaBH_4$ in THF. The absolute configurations of our starting materials (+)-**8** and (+)-**14** have been determined by X-ray crystallography of a derivative [13]. The absolute configurations of (−)-**9**, (−)-**10**, and (−)-**16** are thus established also.

The CD spectrum of the doubly complexed pentaene (−)-**9** is reported in *Fig. 1*. It is nearly the same in both the non-polar (isopentane/methylcyclohexane 4:1; IPM 41) and polar (Et_2O/isopentane/EtOH 5:5:2; EPE 552) solvent. It is also very similar to that observed for the tricarbonyl(diene)iron complex (−)-**7** [9]. Thus, if a through-space interaction between the two diene $Fe(CO)_3$ chromophores [14] in (−)-**9** exists, little evidence for it is obtained from the comparison of the CD spectra of (−)-**7** and (+)-**9** [11]. The CD spectra of (−)-**9** were temperature-dependent. Moreover, the temperature dependence is apparently the same in both solvents. Linear plots were obtained for the maximum and the minimum of the dichroic curves *(e.g. Fig. 2)*. Furthermore, four isochroic points were observed between 80 and 295 K *(Fig. 1)* for the spectra in both solvents.

These results are consistent with the existence of an equilibrium between pairs of rapidly interconverting diastereoisomers. The question arises now whether there are more than two species of similar stability in the equilibrium. If one considers the diastereoisomers to result from a twist of the $Fe(CO)_3$ tripods with respect to the s-*cis*-butadiene moieties (deviation from local mirror plane of symmetry), one would expect equilibria involving the four species **17**–**20**. As long as the CD spectra of each individual diastereoisomer are not known, one cannot reject that possibility, eventhough isochroic points are observed for the variable-temperature CD spectra. For instance, one can imagine an equilibrium **17**⇄**18** leading to intense CD spectra whereas the pair **19**⇄**20** would contribute to a smaller extent to the $\Delta\varepsilon$ values of the measured CD spectra. The accuracy of our measurements does not yet allow one to eliminate this hypothesis.



17 **18** **19** **20**

The CD spectra of the methyl-substituted doubly complexed tetraene (−)-**10** in IPM 41 and EPE 552 are reported in *Fig. 3*. They present features similar to those observed for (−)-**9**. In this case, only two isochroic points are visible for the temperature-dependent spectra. Linear plots were also obtained for the $\Delta\varepsilon_{min}$ *vs.* $\Delta\varepsilon_{max}$, and this in both the polar and non-polar solvent. These data indicate the existence of equilibria between diastereoisomeric species.

Very interesting also were the CD spectra of the deuterated doubly complexed tetraene (−)-**16** (see *Fig. 4*). As in the case of (−)-**9** and (−)-**10**, they were solvent-independent, but temperature-dependent in accord with the existence of equilibria between diastereoisomeric species. The $\Delta\varepsilon$ values measured for (−)-**16** are about one order of magnitude

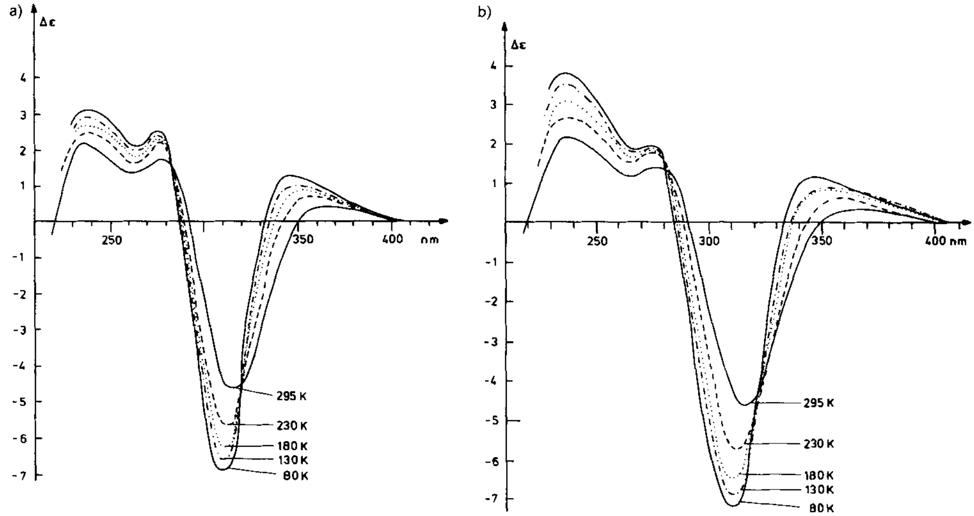


Fig. 3. *Variable-temperature CD spectra of (–)-***10** *in (*a*) IPM 41 and (*b*) EPE 552*

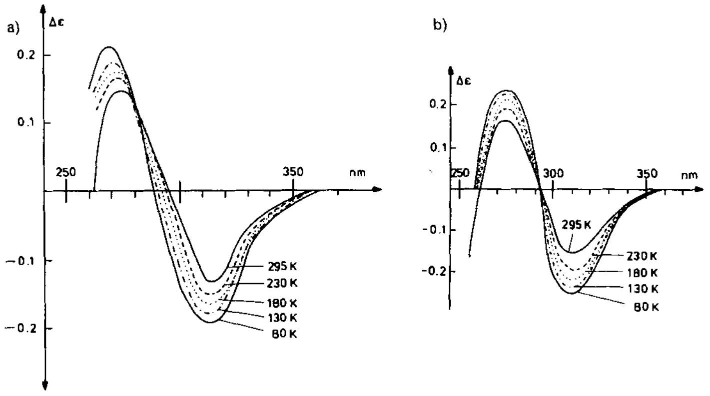
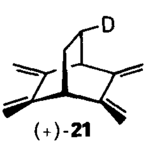
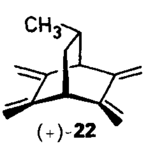


Fig. 4. *Variable-temperature CD spectra of (–)-***16** *in (*a*) IPM 41 and (*b*) EPE 552*

smaller than those found for (–)-**9** and (–)-**10**. This can be interpreted by invoking equilibrium constants for the rapidly interconverting diastereoisomers such that K is closer to unity in the case of (–)-**16** than for (–)-**9** and (–)-**10**. In the former complex, the D-substituent is expected to introduce a smaller perturbation than the methylidene and methyl substituents in the latter derivatives. This hypothesis, however, must be tempered because it is also possible that the methylidene and methyl substituents in (–)-**9** and (–)-**10**, respectively, induce larger rotational strength to the diene-Fe(CO)$_3$ chromophores than the D-substituent, and this already for both enantiomeric pairs **3**$\rightleftarrows$**3'** or **4**$\rightleftarrows$**4'**.



(+)-**21**



(+)-**22**

Conclusion. – Since the CD spectra of the optically pure uncomplexed tetraene (+)-**21** and (+)-**22** were found to be solvent- and temperature-independent (single energy hypersurfaces) [11b], the variable-temperature CD spectra observed for the double complexes (−)-**9**, (−)-**10**, and (−)-**16** indicate, as for the simpler complexes (+)-**5**, (−)-**6**, and (−)-**7** [9], the existence of equilibria of rapidly interconverting C_1 species (multiple minimum energy hypersurfaces) of type (σ,η^3-allyl)Fe(CO)$_3$ (**3**$\rightleftarrows$**3'**) or/and distorted tetragonal pyramidal structures (*e.g.* **4**$\rightleftarrows$**4'**) for (s-*cis*-butadiene)tricarbonyliron complexes.

We thank *F. Hoffmann-La Roche & Co. AG*, Basel, the *Swiss National Science Foundation*, and the *Fonds Herbette*, Lausanne, for generous financial support. We are grateful to Prof. *B. Testa*, Ecole de Pharmacie, Université de Lausanne, for use of his *Roussel-Jouan* dichrograph.

Experimental Part

General. See [11a]. CD: $\lambda(\Delta\varepsilon)$ in nm; in isopentane/methylcyclohexane 4:1 (IPM 41); Et_2O/isopentane/EtOH 5:5:2 (EPE 552). Corrections for solvent contractions were made for low-temperature spectra. No effects of concentration could be detected for the CD spectra of (−)-**9**, (−)-**10**, and (−)-**16**.

*(−)-*trans*-μ-[(1*R*,2*R*,3*S*,4*S*,5*S*,6*R*)-C,2,3,C-η:C,5,6,C-η-(2,3,5,6,7-Pentamethylidenebicyclo[2.2.2]octane)]bis(tricarbonyliron)* ((−)-**9**). Under N_2, 660 mg of Zn powder were dried by heating with a hot gun. After cooling to 20°, CH_2Br_2 (234 μl) and anh. THF, (3 ml) were added. The flask was sealed with a septum. Under stirring and at 20°, $TiCl_4$, (270 μl) in anh. CH_2Cl_2 (2.5 ml) were added dropwise within *ca.* 15 min. Then, a soln. of (+)-**8** [11a] (100 mg, 0.22 mmol) in anh. THF (1.8 ml) was added (syringe). After stirring at 20° for 40 min, CH_2Cl_2 (20 ml) was added. The mixture was poured onto a vigorously stirred sat. aq. $NaHCO_3$ soln. (10 ml). After filtration over silica gel (10 g), the org. layer was washed with sat. aq. $NaHCO_3$ soln. (15 ml), then with H_2O (20 ml, twice). After drying ($MgSO_4$), the solvent was evaporated *in vacuo* and the residue purified by filtration on silica gel (3 g, CH_2Cl_2/hexane 1:1) yielding 58 mg (58%), yellow crystals; m.p. 127–128° (for the racemic mixture (±)-**9**: m.p. 133–134°). $[\alpha]_D^{25} = -57°$ ($c = 2$, $CHCl_3$), $[\alpha]_{578}^{25} = -60°$, $[\alpha]_{546}^{25} = -70°$, $[\alpha]_{365}^{25} = 12°$. UV (isooctane): 285 (sh, 5000). CD (IPM 41, 25°, c = 0.015 to 0.13 mg/ml): 405 (0), 372 (+0.24), 357 (0), 324 (−2.29), 300 (0), 288 (+0.55), 279 (0), 266 (−1.12), 257 (0), 246 (+2.01), 240 (0). CD (EPE 552, 25°, c = 0.012 to 0.1 mg/ml): 400 (0), 374 (+0.21), 356 (0), 323 (−2.31), 298 (0), 288 (+0.50), 280 (0), 265 (−1.35), 256 (0), 246 (+2.10), 237 (0; see *Fig. 1*). IR (KBr): 3000, 2960, 2940, 2040, 1985, 1960, 1475, 1450, 1150, 900, 890. ^{1}H-NMR ($CDCl_3$): 5.23, 4.93 (2 *m*, CH_2=C(7)); 2.88 (*s*, H–C(1)); 3.46 (*t*, $J = 3$, H–C(4)); 2.84 (*m*, CH_2(8)); 2.11, 2.10, 1.93, 1.89, 0.56, 0.52, 0.35, 0.30 (8 *d*, $J = 3$, CH_2=C). ^{13}C-NMR ($CDCl_3$): 145.5, 111.8, 111.6 (3 *s*); 108.3 (*t*, $J = 158$, CH_2=C(7)); 108.1, 105.7, (2 *s*); 53.3, 41.9 (2 *d*, $J = 144$, C(1), C(4)); 38.7, 38.6, 38.3, 36.4, 35.8 (5 *t*, $J = 160$, C(8), 4 CH_2=C). CI-MS: 451 (7), 449 (6), 423 (14), 422 (12), 395 (100), 384 (5), 367 (8), 343 (4), 339 (1), 333 (3), 315 (5), 311 (2), 283 (4), 255 (2), 254 (3). Anal. calc. for $C_{19}H_{14}Fe_2O_6$ (450.01): C 50.71, H 3.13; found: C 50.73, H 3.18.

*(−)-*trans*-μ-[(1*R*,2*R*,3*S*,4*S*,5*S*,6*R*,7*S*)-C,2,3,C-η:C,5,6,C-η-(7-Methyl-2,3,5,6-tetramethylidenebicyclo[2.2.2]octane)]bis(tricarbonyliron)* ((−)-**10**). (−)-**9** (50 mg, 0.11 mmol), PtO_2 (15 mg), and AcOEt (5 ml) were stirred at 20° for 20 h under 4 atm of H_2. After filtration through *Celite*, the solvent was evaporated, and the residue was recrystallized from hexane yielding 47 mg (94%), yellow crystals, m.p. 54–55°. $[\alpha]_D^{25} = -35°$ ($c = 1$, $CHCl_3$), $[\alpha]_{578}^{25} = -36°$, $[\alpha]_{546}^{25} = -43°$, $[\alpha]_{365}^{25} = -65°$. UV (isooctane). 295 (sh, 6000), 215 (sh, 51000). CD (IPM 41, 25°, c = 0.01 − 0.18 mg/ml): 410 (0), 366 (+0.48), 350 (0), 317 (−4.49), 294 (0), 278 (+1.83), 264 (+1.45), 235 (2.24), 220 (0). CD (EPE 552, 25°, c = 0.01 − 0.15 mg/ml): 410 (0), 365 (+0.44), 350 (0), 315 (−4.45), 292 (0), 277 (+1.69), 264 (+1.38), 235 (+2.33), 220 (0; see *Fig. 3*). IR (KBr): 3070, 3010, 2980, 2940, 2920, 2880, 2050, 2040, 1995, 1970, 1965, 1945, 1460, 1450, 1370, 1300, 1270, 1230, 1190, 1165, 1100, 1040, 985, 945, 770. ^{1}H-NMR ($CDCl_3$, 360 MHz): 3.31 (*t*, $J = 3$, H–C(4)); 3.15 (*d*, $J = 3$, H–C(1)); 2.45 (*m*, H_{syn}–C(7)); 2.28 (*m*, H_{anti}–C(7); this signal was not visible in the ^{1}H-NMR spectrum of **13**; see below); 2.05, 1.98, 1.88 (3 *d*, $J = 3$); 1.78 (*m*); 1.60 (*d*, $J = 3$); 1.43 (*d*, $J = 7$, CH_3); 0.48, 0.43, 0.28, 0.18 (4*d*, $J = 3$). ^{13}C-NMR ($CDCl_3$): 117.4, 111.3, 106.0, 105.3 (4 *s*, C(5),C(6),C(7),C(8)); 49.1 (*d*, $J = 142$, C(1)); 42.9 (*d*, $J = 144$, C(4)); 38.8 (*t*, $J = 160$); 37.0 (*t*, $J = 132$, C(3)); 36.6 (*t*, $J = 160$); 36.2 (*d*, $J = 138$); 36.0 (*t*, $J = 160$); 34.1 (*t*, $J = 160$); 19.8 (*q*, $J = 128$). CI-MS (CH_4): 453 (55), 425 (34), 397 (100), 386 (10), 317 (7), 313 (15), 285 (10), 259 (13), 258 (12), 257 (9). Anal. calc. for $C_{19}H_{16}Fe_2O_6$ (452.02): C 50.49, H 3.56; found: C 50.60, H 3.49.

(±)-trans-μ-[(1RS,2RS,3SR,4SR,5SR,6RS,8RS)-C,2,3,C-η:C,5,6,C-η-(2,3,5,6,7-Pentamethylidene(8-D)-bicyclo[2.2.2]octane)]bis(tricarbonyliron) (**12**). Same procedure as for the preparation of (–)-**9** starting with the deuterated ketone **11** [11a]. Yellow crystals, m.p. 125–126°. ^{1}H-NMR ($CDCl_3$): same as for (–)-**9**, except: 3.46 (*d*, *J* = 3, H–C(4)); 2.84 (*m*, H–C(8)). CI–MS (CH_4): 452 (11), 450 (9), 424 (22), 423 (19), 396 (100), 385 (9), 368 (14), 344 (7), 340 (2), 334 (3), 316 (10), 312 (4), 284 (7), 256 (5), 255 (7).

(±)-trans-μ-[(1RS,2RS,3SR,4SR,5SR,6RS,7SR,8RS)-C,2,3,C-η:C,5,6,C-η-(7-Methyl-2,3,5,6-tetramethylidene(8-D)bicyclo[2.2.2]octane)]bis(tricarbonyliron) (**13**). Same procedure as for the preparation of (–)-**10** starting with **12**. Yellow crystals, m.p. 79–80°. IR (KBr): 3060, 3000, 2985, 2975, 2900, 2050, 2040, 2000, 1980, 1965, 1950, 1920, 1445, 1275, 1250, 1225, 1180, 1095, 740, 720. ^{1}H-NMR ($CDCl_3$, 360 MHz): 3.31 (*d*, *J* = 3, H–C(4)); 3.15 (*d*, *J* = 3, H–C(1)); 2.45 (*m*, *J*(H,H) = 7, 6.5, 3.0, *J*(H,D) ≈ 1.5, H_{syn}–C(7)); 2.05, 1.98, 1.88 (3*d*, *J* = 3); 1.78 (*m*, *J*(H,H) = 6.5, 3.0, *J*(H,D) ≈ 2, H–C(8)); 1.60 (*d*, *J* = 3.0); 1.43 (*d*, *J* = 7,0, CH_3); 0.48, 0.43, 0.28, 0.18 (4*d*, *J* = 3.0). MS (70 eV): 453 (1), 425 (37), 397 (78), 395 (16), 369 (37), 341 (13), 313 (69), 285 (100), 283 (24), 257 (10), 229 (28). Anal. calc. for $C_{19}H_{15}DFe_2O_6$ (453.02): C 50.37, H 3.78; found: C 50.38, H 3.71.

(+)-trans-μ-[(1S,2S,3S,4R,5R,6S,7S,8R)-C,5,6,C-η:C,7,8,C-η-(5,6,7,8-Tetramethylidene(3-D)-bicyclo[2.2.2]oct-2-yl) methanesulfonate]bis(tricarbonyliron) ((+)-**15**). A soln. of (+)-**14** [11a] (228 mg, 0.5 mmol) in anh. pyridine (1 ml) was cooled to 0°, methanesulfonyl chloride (74 mg, 0.6 mmol) added, and the mixture stirred for 30 min at 20° under N_2. CH_2Cl_2 (15 ml) was added and the soln. washed with 1N HCl (10 ml, 4 times). The solvent was evaporated and the residue recrystallized from CH_2Cl_2/hexane yielding 210 mg (79%), yellow crystals, m.p. 123–124°. $[\alpha]_D^{25}$ = +38° (*c* = 2, $CHCl_3$), $[\alpha]_{578}^{25}$ = +39°, $[\alpha]_{546}^{25}$ = +45°, $[\alpha]_{436}^{25}$ = +6°. CD (isooctane, 25°): 365 (0), 328 (+0.75), 306 (0), 300 (–0.15), 292 (0), 270 (+0.53), 248 (0). CD (95% EtOH, 25°): 370 (0), 323 (+0.52), 303 (+0.17), 278 (+0.73), 246 (0). IR (KBr): 3030, 3000, 2940, 2040, 1990, 1970, 1470, 1450, 1360, 1340, 1300, 1250, 1225, 1180, 1140, 1010, 970, 890, 850, 830, 790, 750. ^{1}H-NMR ($CDCl_3$): 5.41 (*m*, H–C(2)); 3.90 (*d*, *J* = 3, H–C(1)); 3.51 (*d*, *J* = 3, H–C(4)); 3.07 (*s*, CH_3); 2.74 (*m*, H–C(3)); 2.18, 2.10, 1.94, 1.88 (4*d*, *J* = 3); 0.67, 0.63, 0.41, 0.33 (4*d*, *J* = 3). MS (70 eV): 533 (9), 505 (15), 477 (407), 449 (11), 439 (41), 421 (12), 409 (20), 397 (7), 381 (100), 365 (17). Anal. calc. for $C_{19}H_{15}DFe_2O_9S$ (533.10): C 42.80, H 3.21; found: C 42.95, H 3.08.

(–)-trans-μ-[(1R,2R,3S,4S,5S,6R,7R)-C,2,3,C-η:C,5,6,C-η-(2,3,5,6-tetramethylidene (7-D) bicyclo-[2.2.2]octane)]bis(tricarbonyliron) ((–)-**16**). A mixture of $NaBH_4$ (55 mg, 1.4 mmol) and (+)-**15** (20 mg, 0.04 mmol) in anh. THF (2 ml) was stirred at 20° for 20 min. After filtration through silica gel (1 g, THF), the solvent was evaporated and the residue purified by column chromatography on silica gel (1 g, CH_2Cl_2) yielding 6 mg (36%), yellow crystals, m.p. 98–99°. $[\alpha]_D^{25}$ = –2.5° (*c* = 2, $CDCl_3$), $[\alpha]_{578}^{25}$ = –2.5°, $[\alpha]_{546}^{25}$ = –3.0°, $[\alpha]_{436}^{25}$ = –16.8°. CD (IPM 41, 25°, *c* = 0.05 – 0.3 mg/ml): 355 (0), 312 (–0.14), 294 (0), 275 (+0.14), 263 (0). CD (EPE 552, 25°, *c* = 0.04 – 0.3 mg/ml): 255 (0), 312 (–0.16), 293 (0), 276 (+0.17), 260 (0; see *Fig. 4*). IR (KBr): 3000, 2975, 2960, 2890, 2040, 1985, 1975, 1465, 1450, 1420, 1300, 1220, 1140, 950. ^{1}H-NMR ($CDCl_3$): 3.43 (*s*, H–C(1), H–C(4)); 2.13 (*m*, H–C(2), H–C(3)); 2.09, 1.89, 0.50, 0.29 (4 *d*, *J* = 3). Anal. calc. for $C_{18}H_{13}DFe_2O_6$ (439.01): C 49.25, H 3.44; found: C 49.38, H 3.56.

(+)-(1S,4R,7R)-2,3,5,6-Tetramethylidene(7-D)bicyclo[2.2.2]octane ((+)-**21**). A mixture of freshly sublimed Me_3NO (0.5 g, 6.6 mmol) and (–)-**16** (70 mg, 0.16 mmol) in anh. acetone (40 ml) was stirred at 20° for 20 h. After filtration, H_2O (80 ml) was added to the soln. which was then extracted with hexane (50 ml, 3 times). After drying ($MgSO_4$), the solvent was evaporated and the residue purified by column chromatography on silica gel (3 g, hexane), then by HPLC (silica gel, hexane) yielding 17 mg (67%), colourless crystals, m.p. 99–99.5°. $[\alpha]_D^{25}$ = +6.5° (*c* = 1, hexane), $[\alpha]_{578}^{25}$ = +6.6°, $[\alpha]_{546}^{25}$ = +7.8°, $[\alpha]_{436}^{25}$ = +14.7°, $[\alpha]_{365}^{25}$ = 29.0°. IR (CH_2Cl_2): 3050, 2980, 2830, 2690, 2520, 2410, 2305, 1600, 1550, 1420, 1260, 1155, 985, 900. ^{1}H-NMR ($CDCl_3$): 5.26 (*s*, 4 H); 4.83 (*s*, 4 H); 3.08 (*m*, H–C(1), H–C(4)); 1.74 (H–C(7),H–C(8)). MS (70 eV). 159 (33), 157 (28), 85 (59), 71 (8), 69 (7), 59 (84).

(+)-(1R,4S,7S)-7-Methyl-2,3,5,6-tetramethylidenebicyclo[2.2.2]octane ((+)-**22**). Same procedure as for the preparation of (+)-**21** starting with (–)-**10** (80 mg, 0.18 mmol). Yield: 15 mg (49%), colourless oil. $[\alpha]_D^{25}$ = +7° (*c* = 1, hexane), $[\alpha]_{578}^{25}$ = +7°, $[\alpha]_{546}^{25}$ = 7°, $[\alpha]_{436}^{25}$ = +2.1°. UV (isooctane): 231 (11800), 238 (10900), 251 (9500), 268 (sh, 5300). UV (95% EtOH): 232 (11900), 237 (sh, 11300), 250 (9600). IR (CH_2Cl_2): 3080, 2960, 2930, 2870, 1785, 1755, 1715, 1675, 1615, 1450, 1375, 1340, 1220, 1195, 1155, 1100, 1030, 995, 895, 880. ^{1}H-NMR ($CDCl_3$, 360 MHz): 5.41, 5.30, 5.29, 5.27 (4*d*, *J* = 0.9); 4.86, 4.84, 4.83, 4.82 (4*s*); 3.04 (*t*, *J* = 3, H–C(4)); 2.80 (*d*, *J* = 3, H–C(1)); 2.01, 2.00, 1.18 (3*m*); 0.96 (*d*, *J* = 7, CH_3). ^{13}C-NMR ($CDCl_3$, 90 MHz): 147.6, 147.2, 146.5, 143.5 (4*s*); 106.7, 104.2, 103.9, 103.5 (4*t*, *J* = 158); 55.0, 48.7 (2*d*, *J* = 140, C(1), C(4)); 36.2 (*t*, *J* = 133, C(8)); 31.3 (*d*, *J* = 134, C(7)); 21.1 (*q*, *J* = 126, CH_3). MS (70 eV): 173 (9), 172 (62), 157 (5), 143 (6), 142 (8), 141 (8), 131 (14), 130 (100), 129 (49), 128 (33), 127 (14), 116 (6), 115 (47), 103 (4), 91 (9), 78 (5), 77 (9), 65 (6). Anal. calc. for $C_{13}H_{16}$ (172.27): C 90.64, H 9.36; found: C 90.32, H 9.17.

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