Structure of (Alkene)tetracarbonyliron Complexes. Variable-Temperature Circular Dichroism of (5-Substituted 7-oxabicyclo[2.2.1]hept-2-ene)tetracarbonyliron Complexes

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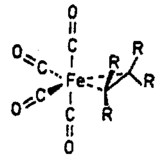
Optically pure (+)-tetracarbonyl[(1*S*,4*R*,5*R*,6*S*)-5,6-η-7-oxabicyclo[2.2.1]hept-5-en-2-one]iron, (+)-tetracarbonyl[(1*R*,2*R*,3*S*,4*S*)-2,3-η-5-methylene-7-oxabicyclo[2.2.1]hept-2-ene]iron, (+)-tetracarbonyl-[(1*R*,2*R*,3*S*,4*S*,5*R*)-2,3-η-5-*endo*-methyl-7-oxabicyclo[2.2.1]hept-2-ene]iron, and (+)-tetracarbonyl-[(1*R*,2*R*,3*S*,4*S*,5*S*)-2,3-η-5-*exo*-methyl-7-oxabicyclo[2.2.1]hept-2-ene]iron have been prepared. Their CD spectra were temperature dependent. This is in accord with the existence of equilibria of conformers which can be interpreted as arising from a rotation about the Fe–alkene bond, thus leading to a distortion of the double bond from the equatorial plane of the trigonal-bipyramidal structure.

Introduction

Gas-phase electron diffraction,[1] single-crystal X-ray diffraction,[2-14] IR spectroscopy,[15] and NMR spectroscopic studies[16] as well as MO calculations[17] are consistent with trigonal-bipyramidal structure for (alkene)tetracarbonyliron complexes. They may be regarded as being derived from $Fe(CO)_5$ by replacing an equatorial CO group by an alkene as in **1**. For C_{2h} olefinic ligands, such as fumaric acid[3] and fumarodiphenone,[6] the C=C double bond makes an angle, α = 11° (R = COOH),[3] and α = 13° and 16° (R = COPh, two independent molecules in the unit cell),[6] respectively, with the equatorial plane (see **2**). The reason for this distortion was attributed to the necessity for a relaxation of intramolecular contact distances between the groups R and the carbonyl ligands.[3]



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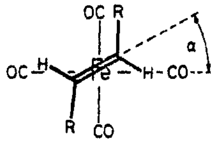

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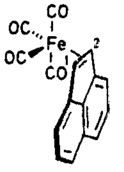
For C_{2v} olefinic ligands,[4,7-10] such a rotation about the Fe–alkene bond would not be expected at first glance.17 In the crystal, **3** possesses virtual C_s symmetry with the axial plane ($Fe(CO)_2$) coinciding with the mirror plane of the acenaphthene ligand.[4] The small displacements measured for carbon atoms C(1) and C(2) from it were not considered to be significant.[4] In the double complex **4**, deviation from the C_s symmetry was more significant.[9] The two olefinic carbon atoms were found not symmetrically bound to the metal atoms, implying also an angle of rotation, $\alpha \neq 0$. Distortions from C_s symmetry were also observed in the crystal structure of **5**.[8] The accuracy of the measurements, however, made them of questionable significance. For the analogous complex **6** a value of α = 8° was observed.[10] Similar distortions were found in the crystal structures of $Fe(CO)_4$ complexes of C_s and C_1 alkenes.[11-14] Because of the absence of virtual symmetry in the latter complexes, α values not equal to 0 cannot be interpreted as being an intrinsic property of (alkene)tetracarbonyliron complexes.



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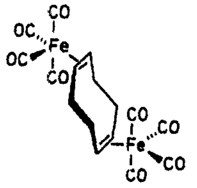

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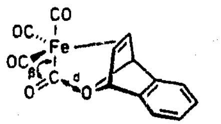

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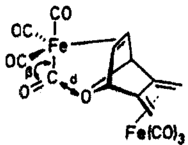
β = 168.8, 170.5°; d = 2.44, 2.47 Å



6

β = 170.1°; d = 2.48 Å[10]

If the distortions α were also real in solution, (alkene)tetracarbonyliron complexes should be involved in equilibria **7** ⇄ **8** where **7** and **8** are two enantiomeric conformers. Such equilibria were not detected by low-temperature ^1H and ^{13}C NMR.[16] For asymmetric olefinic ligands, the equilibrium constant K for equilibrium **7** ⇄ **8** should be different from unity and should vary with temperature. Since the hypothetical pairs **7** and **8** have opposite chirality, variable-temperature circular dichroism (CD) should be a suitable technique to detect such equilibria. We report the preparation of optically pure 7-oxabicyclo[2.2.1]hept-2-ene complexes (+)-**9**–(+)-**12**. Their

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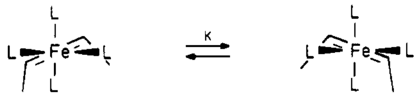
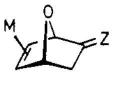
CD spectra were temperature dependent consistently with the existence of equilibria 7 $\rightleftarrows$ 8.

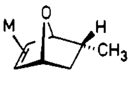


7

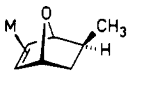
8



(+)-9, Z = O
(+)-10, Z = CH_2



(+)-11

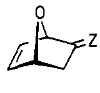


(+)-12

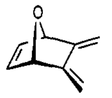
M = $Fe(CO)_4$

Results and Discussion

The choice of 5-substituted 7-oxabicyclo[2.2.1]hept-2-enes was dictated by the necessity to have rigid olefinic ligands with remote substituents that introduce only small deviations from unity for the equilibrium constant K for the equilibrium 7 $\rightleftarrows$ 8. The methylene (10) and methyl (11, 12) substituents at C(5) were retained because they do not introduce further conformational equilibration. Moreover, they are nonpolar groups, thus limiting interferences in the CD spectra attributable to aggregation and solvation effects.[19]



(+)-13, Z = O
(+)-14, Z = CH_2



15

The optically pure (ee > 98%) (+)-(1R)-7-oxabicyclo[2.2.1]hept-5-en-2-one [(+)-13] was derived from the Diels–Alder addition of furan to 1-cyanovinyl camphanate.[20] Wittig methylenation ($Ph_3P^+CH_3Br^-$, t-BuOK, THF, 20 °C, 2 h) of (+)-13 furnished 1,4-diene (+)-14 (31%). Treatment of (+)-13 and (+)-14 with $Fe_2(CO)_9$ in 2-propanol at 30 °C afforded the complexes (+)-9 (44%) and (+)-10 (34%), respectively. No trace of a $Fe(CO)_4$ complex resulting from coordination of the exocyclic double bond of (+)-14 could be detected. This is consistent with the earlier observation[10,18] with triene 15 whose endocyclic double bond always coordinates to a transition-metal carbonyl with greater facility than does the exocyclic diene moiety. These results and others[8] (see, e.g., the structure of 6; Figure 8) suggest that the O(7)···C=O interactions in these complexes corresponds to an attractive rather than to a repulsive effect.[18]

Raney nickel catalyzed hydrogenation of (+)-10 gave a 2:1 mixture of the *endo*- and *exo*-methyl-substituted complexes (+)-11 and (+)-12, respectively, which were separated and purified by chromatography on silica gel. The structures of complexes (+)-9–(+)-12 were established by their spectral data and elemental analyses. The absence of vicinal coupling constant between the olefinic protons and the bridgehead protons H–C(1) and H–C(4) is consistent only with the exo configuration of the $Fe(CO)_4$ moiety.[10,21]

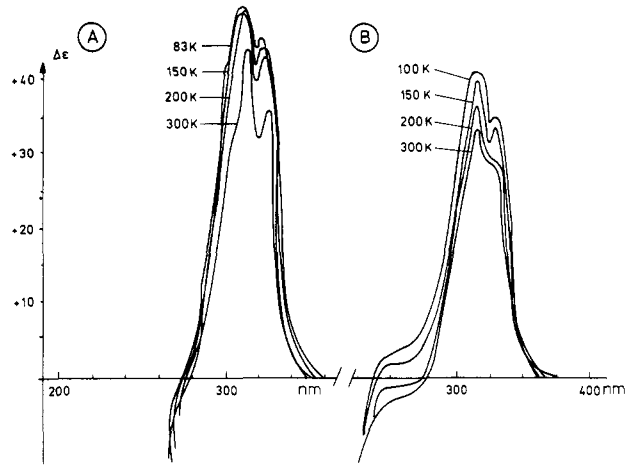


Figure 1. Variable-temperature CD spectra of (+)-9: (A) in isopentane/methylcyclohexane, 3:1 (IPM 31); (B) in ether/isopentane/ethanol, 5:5:2 (EPE 552).

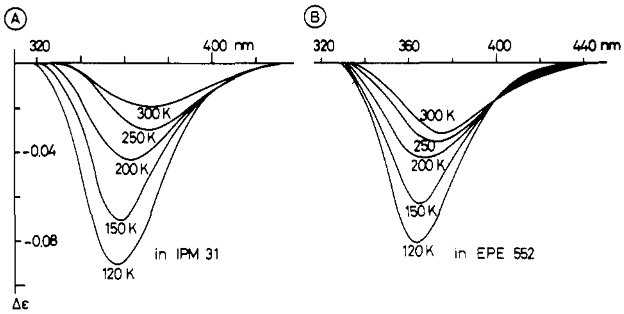


Figure 2. Variable-temperature CD spectra of (+)-10: (A) in isopentane/methylcyclohexane, 3:1 (IPM 31); (B) in ether/isopentane/ethanol, 5:5:2 (EPE 552).

The CD spectra of (+)-9 measured between 83 and 300 K appear in Figure 1. Because of instrumental limitations, they would not be recorded below 280 nm. A relatively strong Cotton effect (CE) was observed between 300 and 320 nm. It is typical of the ketone carbonyl chromophore. Because of the polar nature of the ketone, the relatively small temperature effect detected for these CD spectra cannot be taken as an indication of the existence of an equilibrium between conformers. It is interesting to note, however, that the temperature effect on the spectra measured in the polar solvent ether/isopentane/ethanol, 5:5:2 (EPE 552), is relatively larger on the shoulder at 285 nm, attributed to an (alkene)$Fe(CO)_4$ transition than at the maximum (305 nm) attributed to the ketone n $\rightarrow$ π^*_{CO} transition (see Figure 1B). Fourier transform infrared spectroscopy on (+)-9 showed only four bands for the $Fe(CO)_4$ group. The line width (>7 cm^{-1}; see Experimental Section) was too large and did not allow one to detect the existence of two, or more, conformers.

The CD spectra of (+)-10 measured in a nonpolar [isopentane/methylcyclohexane, 3:1 (IPM 31)] and a polar solvent (EPE 552) are reproduced in Figure 2. Negative CE's were observed in both solvents between 320 and 440 nm. Because of instrumental limitations due to the unfavorable $\Delta\epsilon/\epsilon$ ratio, the spectra could not be recorded in a reproducible fashion below 320 nm. Significant temperature effects were observed in both solvents, the ellipticities increasing on lowering the temperature. A blue-

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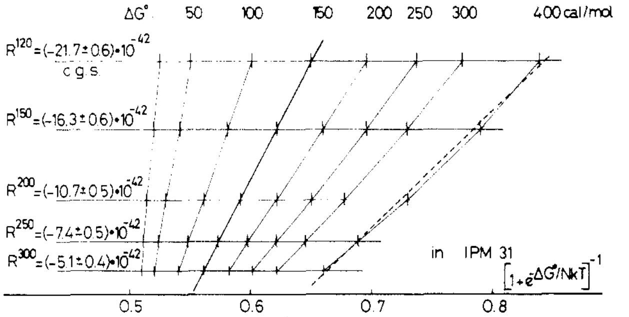

Figure 3. Plot of R^{T} against $[1 + e^{-\Delta G^\circ/NkT}]^{-1}$ for the CD spectra of Figure 2A for various trial values of ΔG° (cal/mol).

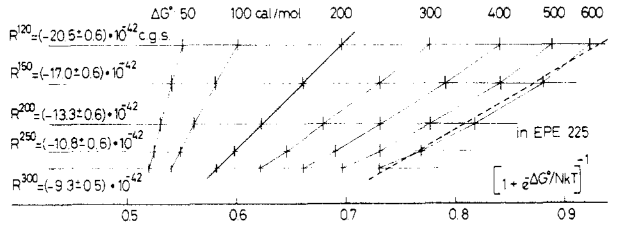

Figure 4. Plot of R^T against $[1 + e^{-\Delta G^\circ/NkT}]^{-1}$ for the CD spectra of Figure 2B for various trial values of ΔG° (cal/mol).

shift of the minimum of the CD spectrum was seen on lowering the temperature (370 nm at 300 K; 355 nm at 120 K). For the spectra measured in EPE 552, an isochroic point was observed near 400 nm (Figure 2B). This suggested the existence of an equilibrium involving two species. The experimental rotational strength R^T at a given temperature T were evaluated by using eq 1[22] between λ_1

$$R^{\mathrm{T}} = 0.696 \times 10^{-42} \int_{\lambda_1}^{\lambda_2} \frac{[\theta]}{\lambda}\, d\lambda \simeq 2296 \times 10^{-42} \sum \frac{\Delta\epsilon(\lambda)}{\lambda} \Delta\lambda \qquad (1)$$

= 320 and λ_2 = 440 nm, with $\Delta\lambda$ = 5 nm. They are reported in Figures 3 and 4. If there are only two species at equilibrium and assuming the entropy change is zero, the observed rotational strength R^T is given by eq 2,[22]

$$R^T = (R_a - R_b)[1 + e^{-\Delta G^\circ/NkT}]^{-1} + R_b \qquad (2)$$

where R_a and R_b are the rotational strengths of the stable conformer and the less stable conformer, respectively.

For the R^T values evaluated from the CD spectra of (+)-**10** measured in IPM 31 (Figure 2A), linear relationships between R^T and $[1 + e^{-\Delta G^\circ/NkT}]^{-1}$ were found for $\Delta G^\circ \leq 400$ cal/mol (see Figure 3). The relatively large error limits retained for the measured R^T values are due to the extreme instrumental conditions required for the spectrum recordings. Taking $\Delta G^\circ = 150$ cal/mol, one calculates $R_a = -87 \times 10^{-42}$ cgs and $R_b = 100 \times 10^{-42}$ cgs for the rotational strength of the two equilibrating conformers of (+)-**10** (K = 0.779 at 300 K). For the CD spectra recorded in EPE 552 (Figure 2B), the corresponding rotational strength R^T reported in Figure 4 were evaluated. In this case, linear relationships between R^T and $[1 + e^{-\Delta G^\circ/NkT}]^{-1}$ were obtained for $\Delta G^\circ \leq 600$ cal/mol. Using $\Delta G^\circ = 200$ cal/mol, $R_a = -49 \times 10^{-42}$ cgs and $R_b = 46 \times 10^{-42}$ cgs were calculated (K = 0.716 at 300 K).

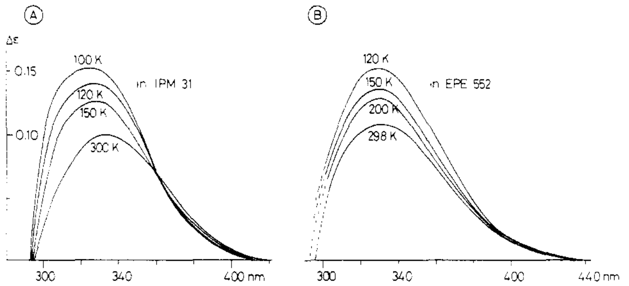

Figure 5. Variable-temperature CD spectra of (+)-**11**: (A) in isopentane/methylcyclohexane, 3:1 (IPM 31); (B) in ether/isopentane/ethanol, 5:5:2 (EPE 552).

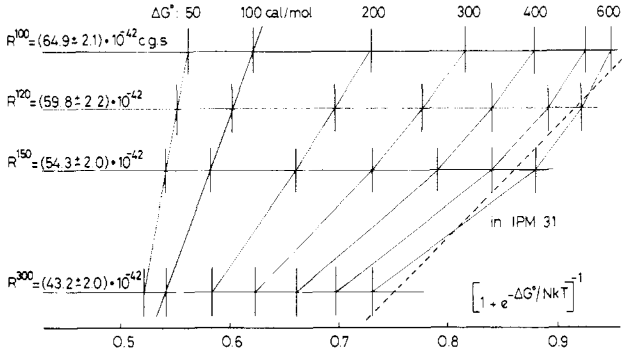

Figure 6. Plot of R^T against $[1 + e^{-\Delta G^\circ/NkT}]^{-1}$ for the CD spectra of Figure 5A for various trial values of ΔG° (cal/mol).

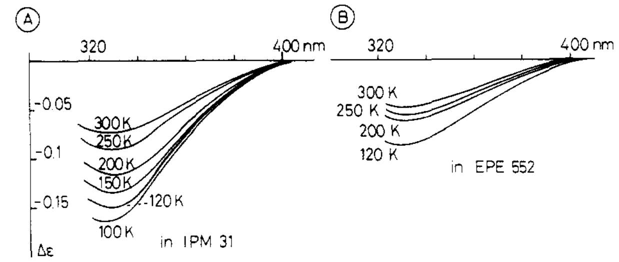

Figure 7. Variable-temperature CD spectra of (+)-**12**: (A) in isopentane/methylcyclohexane, 3:1 (IPM 31); (B) in ether/isopentane/ethanol, 5:5:2 (EPE 552).

The CD spectrum of (-)-fumaric acid-FeCO)$_4$ complex in MeOH solution has been reported by Musco et al.[23] A rotational strength of ca. 3000 × 10^{-42} cgs could be evaluated for the lowest energy transition between 340 and 440 nm. It is premature to discuss the R_a and R_b values calculated for (+)-**10** with the preliminary data reported for (-)-fumaric acid-Fe(CO)$_4$ complex. Nevertheless, our data with (+)-**10** showing about the same temperature dependence for the CD spectra in both polar and nonpolar solvents are consistent with the existence of an equilibrium between two conformers of similar stability and of type **7** ⇄ **8**. The CD spectra of the uncoordinated ligand (+)-**14** in IPM 31 and EPE 552 were temperature-independent.

The CD spectra of the *endo*-methyl derivative (+)-**11** are reproduced in Figure 5. Positive CE's were observed in both the polar and nonpolar solvents between 300 and 440 nm. Due to instrumental limitations, the spectra could not be recorded with good reproducibility below 290 nm in IPM 31 and below 310 nm in EPE 552. The experimental rotational strengths evaluated from the spectra of Fig. 5 A are reported in Figure 6. Linear relationships between R^T and $[1 + e^{-\Delta G^\circ/NkT}]^{-1}$ were obtained for ΔG°

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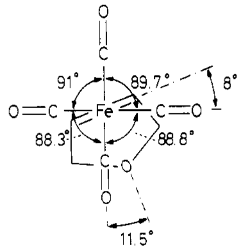
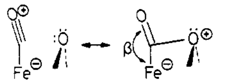


Figure 8. Structural characteristics from the single-crystal X-ray structure of the alkene $Fe(CO)_4$ complex **6**.[10]

≤ 600 cal/mol. If one considers $\Delta G° = 100$ cal/mol, a value for which the best fit straight line is seen in Figure 6, one calculates $R_a = 166 \times 10^{-42}$ cgs and $R_b = -102 \times 10^{-42}$ cgs. These rotational strengths are comparable to those calculated for (+)-**10**. Because the CD spectra of (+)-**11** in EPE 552 could not be measured with good accuracy, we renounced to evaluate the corresponding R^T values. Nevertheless, the data obtained from the spectra of Figure 5A (in the nonpolar solvent, IPM 31) are consistent with the existence of an equilibrium of two conformers of similar stability and of type **7** ⇄ **8**.

The CD spectra of the *exo*-methyl derivative (+)-**12** are reproduced in Figure 7. They could not be measured with good reproducibility below 320 nm. Nevertheless, they showed a significant temperature dependence similar to that observed for the CD spectra of (+)-**10** and (+)-**11**. The comparison of the CD spectra of (+)-**11** and (+)-**12** shows that the inversion of the configuration of the methyl substituted carbon atom C(5) leads to a change of the sign of the CE at ca. 332 nm. This phenomenon cannot be explained at the moment. It should be noticed also that there is a red shift of the minimum of the CE of (+)-**10** (ca. 370 nm) compared with that of (+)-**11** and (+)-**12** (ca. 332 nm). This observation suggests a possible transannular interaction between the exocyclic alkene and the tetracarbonyl(7-oxanorbornene)iron chromophores in (+)-**10**.

The distortion of the alkene in complexes (+)-**10**, (+)-**11**, and (+)-**12** from the equatorial plane of the trigonal-bipyramidal structure may be attributed to the steric interaction between the ethereal bridge of the 7-oxanorbornene moiety and one of the apical CO ligands. X-ray structure of **6**,[10] however, suggests that this interaction is not a destabilizing one, i.e., forcing the olefin rotation, but rather a stabilizing one (see, e.g., X-ray data on donor (oxygen)–acceptor (carbonyl) crystalline complexes[24]) as depicted below.



This hypothesis is confirmed by the observation that the apical CO ligand which interacts with the oxygen bridge in **6** makes the same angles with the two basal CO ligands (Figure 8). Moreover, the bending of this CO ligand ($\beta = 170°$) away from the ethereal bridge is accompanied by a slight lengthening of the C=O bond (1.137 (4) Å) as shown by the comparison with the bond length (1.128 (4) Å) measured for the other apical CO group.[10]

Conclusion

The CD spectra of optically pure tetracarbonyl(5-substituted 7-oxabicyclo[2.2.1]hept-2-ene)iron complexes suggest the existence of equilibria between conformers such as **7** ⇄ **8**. Single-crystal X-ray diffraction data of complexes such as **3** and **4** suggest that such distortion of the alkene from the equatorial plane of the trigonal-bipyramidal structure may also be present in $Fe(CO)_4$ complexes of C_{2v} olefins. The CD test employed in this work should now be applied to such systems in order to determine whether the structural feature discussed here is a general phenomenon or not.[25]

Experimental Section

General remarks, see ref 26. Rotation angles were measured with thermostated Perkin-Elmer Hitachi 340 polarimeter. The circular dichroism (CD) spectra were taken on a Roussel-Jouan (Jobin-Yvon) dichrograph III instrument, equipped with a Oxford-instruments DN 704 cryostat and Oxford-Instruments DTC2 temperature controller. CD solvents: isopentane/methylcyclohexane, 3:1 (IPM31); ether/isopentane/ethanol, 5:5:2 (EPE 552). Corrections for solvent contractions were made for low-temperature spectra: for IPM 31, the observed $\Delta\epsilon$ values were multiplied by 0.95 at 250 K, 0.905 at 200 K, 0.86 at 150 K, 0.83 at 120 K, and 0.815 at 100 K; for EPE 552, the observed $\Delta\epsilon$ values were multiplied by 0.953 at 250 K, 0.905 at 200 K, 0.856 at 150 K, and 0.833 at 120 K. We have ignored any corrections due to changes in the index of refraction with temperature.[22c]

(+)-(4*R*)-5-Methylene-7-oxabicyclo[2.2.1]hept-2-ene [(+)-(14)]. Methyltriphenylphosphonium bromide (3.92 g, 11 mmol) was added to a stirred solution of *t*-BuOK (1.46 g) and (+)-(1*R*)-7-oxabicyclo[2.2.1]hept-5-en-2-one[27] ((+)-**13**, 1.2 g, 10 mmol) at 20 °C. After being stirred at 20 °C for 2 h under N_2 atmosphere, the mixture was poured into ice cold saturated aqueous solution of NH_4Cl (100 mL). The mixture was extracted with Et_2O (50 mL, four times). After drying (Na_2SO_4), the extract was concentrated by distillation under reflux and purified by filtration through silica gel (pentane/AcOEt, 50:1). Solvent evaporation and distillation of the residue afforded 336 mg (31%) of a colorless oil. UV (isooctane): λ_{max} 200 nm (ϵ 7500). UV (EtOH): λ_{max} 203 (ϵ 7900). IR (CCl_4): 3095, 3030, 3005, 2980, 2950, 2850, 1675, 1315, 1085, 1020, 895 cm^{-1}. ^1H NMR (360 MHz, $CDCl_3$): δ 6.35 (br s, H—C(2), H—C(3)), 5.0 (m, H_2C=C(5), H—C(1), H—C(4)), 2.44 (dm, $J_{gem} = 16$, J(H—C(1), H-C(6-exo)) = 4 Hz, H-C(6-exo)), 1.84 (dm, $J_{gem} = 16$ Hz, H-C(6-endo)). ^{13}C NMR (90 MHz, $CDCl_3$): δ 144.4 (s), 135.3 (d, 176), 133.7 (d, 178), 104.5 (t, 158), 82.0 (d, 166), 78.9 (d, 166), 31.9 (t, 137). MS (70 eV): m/e (relative intensity) 108 (19, M^+), 91 (7), 80 (100), 78 (70), 69 (86), 51 (24). Optical rotations: $[\alpha]^{25}_{589}$ +484°, $[\alpha]^{25}_{578}$ +506°, $[\alpha]^{25}_{546}$ +588°, $[\alpha]^{25}_{436}$ +1107°, $[\alpha]^{25}_{365}$ +1995° (c 6.64 mg/mL, CH_2Cl_2). CD (isooctane): $\Delta\epsilon_{210} = 28.6$. CD (EtOH, 95%): $\Delta\epsilon_{209} = +26.9$. Anal. Calcd for C_7H_8O (108.14): C, 77.75; H, 7.46. Found: C, 77.70; H, 7.52.

(+)-Tetracarbonyl[(1*S*,4*R*,5*R*,6*S*)-5,6-η-7-oxabicyclo[2.2.1]hept-5-en-2-one]iron [(+)-9]. A mixture of $Fe_2(CO)_9$ (970 mg, 2.6 mmol) and (+)-**13** (220 mg, 2 mmol) in 2-propanol (10 mL) was stirred under Ar for 2 days at 30 °C. After filtration and solvent evaporation, the residue was purified by column chromatography on Florisil (AcOEt/hexane, 1:3), yielding 248 mg (44%) of a yellow oil. UV (isooctane): λ_{max} 206 (ϵ 68700), 270 (13800). UV (EtOH, 95%): λ_{max} 206 (ϵ 49000), 270 (13800). IR ($CHCl_3$): 3010, 2097, 2030, 2017, 1995, 1767, 1060 cm^{-1}. IR (3% in CCl_4, FT-IR, Bruker, resolution 0.5 cm^{-1}): 2091.7 (bandwidth = 7 cm^{-1}), 2025.6, 2015.5, 1990.7 cm^{-1} (bandwidth = 19 cm^{-1}). ^1H NMR (360 MHz, $CDCl_3$) δ 4.76 (d, 5, H-C(4)), 4.0 (br s, H—C(1)), 3.28 (d, 6, H—C(5)), 3.06 (d, 6, H—C(6)), 2.37 (dd, 17, 5, H—C(3-exo)), 1.99 (d, 17, H-C(3-endo)). ^{13}C NMR (90 MHz, $CDCl_3$): 208.98

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(s), 207.97 (s), 80.6 (d), 79.4 (d), 56.3 (d), 47.57 (d), 37.9 (t). MS (70 eV): *m/e* (relative intensity) 278 (10, M^+), 250 (52), 222 (8), 194 (61), 166 (45), 152 (25), 138 (71), 124 (50), 110 (57), 84 (52), 68 (39), 56 (100). Optical rotations: $[\alpha]^{20}_{589}$ +711°, $[\alpha]^{20}_{578}$ +753°, $[\alpha]^{20}_{546}$ +910° (*c* 16.8 mg/mL, CH_2Cl_2). CD (IPM31): $\Delta\epsilon_{312}$ = +31.8 (*c* 0.795 mg/mL). CD (EPE 552): $\Delta\epsilon_{312}$ = +33.4 (*c* 0.13 mg/mL; see Figure 1). When racemic (±)-**13** was used for the complexation, the corresponding (±)-**9** was a crystalline compound, mp 83–84 °C dec, recrystallized from hexane/AcOEt. Anal. Calcd for $C_{10}H_6O_6Fe$ (278.0): C, 43.20; H, 2.17; Fe, 20.09. Found: C, 43.17; H, 2.25; Fe, 20.08.

(+)-Tetracarbonyl[(1*S*,2*R*,3*S*,4*S*)-2,3-η-5-methylene-7-oxabicyclo[2.2.1]hept-2-ene]iron [(+)-10]. A mixture of (+)-**14** (252 mg, 2.3 mmol) and $Fe_2(CO)_9$ (1.565 mg, 4.3 mmol) in 2-propanol was stirred under Ar for 3.5 h at 30 °C. After filtration, the solent was evaporated and the residue purified by chromatography on silica gel (petroleum ether/AcOEt, 9:1), yielding 215 mg (34%) of a yellow oil. UV (EtOH, 95%): λ_{max} 200 (ε 39 000), 254 (12 000). IR ($CHCl_3$): 3020, 2090, 2020, 2005, 1990, 1750, 1710, 1065 cm^{-1}. ^1H NMR (80 MHz, $CDCl_3$): δ 4.78 (m, H–C(1), H–C(4), H_2C), 3.1 (br s, H–C(2), H–C(3)), 2.45 (dm, ^2J = 17 Hz, H–C(6-exo)), 2.01 (dm, 17, H–C(6-endo). ^{13}C NMR (90 HZ, $CDCl_3$): δ 210.6 (s), 147.4 (s), 105.4 (t), 82.1 and 79.8 (2d), 56.5 and 55.5 (2d), 35.3 (t). MS (70 eV): *m/e* (relative intensity) 276 (8, M^+), 248 (35), 220 (6), 192 (66), 164 (82), 146 (16), 134 (61), 121 (41), 112 (20), 91 (100), 84 (46), 56 (95). Optical rotations: $[\alpha]^{20}_{589}$ +13.4°, $[\alpha]^{20}_{578}$ +26.7°, $[\alpha]^{20}_{546}$ +27.7°, $[\alpha]^{20}_{436}$ +29.7°, $[\alpha]^{20}_{365}$ +37.6° (*c* 20.2 mg/mL, CH_2Cl_2). CD (IPM31): $\Delta\epsilon_{370}$ = –0.02 (300 K). CD (EPE 552): $\Delta\epsilon_{370}$ = –0.03 (300 K; *c* = 0.16–0.31 mg/mL; see Figure 2). Anal. Calcd for $C_{11}H_8O_5Fe$ (276.03): C, 47.86; H, 2.92; Fe, 20.23. Found: C, 47.94; H, 3.02; Fe, 20.07.

(+)-Tetracarbonyl[(1*R*,2*R*,3*S*,4*S*,5*R*)-2,3-η-5-*endo*-methyl-7-oxabicyclo[2.2.1]hept-5-ene]iron [(+)-11] and (+)-Tetracarbonyl[(1*R*,2*R*,3*S*,4*S*,5*S*)-2,3-η-5-*exo*-methyl-7-oxabicyclo[2.2.1]hept-2-ene]iron [(+)-12]. Raney nickel as a suspension in H_2O (Fluka, Buchs, Switzerland) was washed with EtOH, then with ether, and finally with petroleum ether. This catalyst (94 mg) and a solution of (+)-**10** (472 mg, 1.7 mmol) in petroleum ether (100 mL) containing a trace of MeOH were introduced in a Parr hydrogenation apparatus and carefully degassed. A pressure of 3 atm of hydrogen was established, and the mixture was shaken at 20 °C for 5 days. After filtration, the solvent was evaporated yielding a 2:1 mixture of (+)-**11** and (+)-**12** (315 mg, 66.3%) which was separated by column chromatography on silica gel (hexane/$CHCl_3$, 6:1). Yield: 188 mg of (+)-**11** as a yellow oil and 85 mg of (+)-**12** as a yellow oil.

Data of (+)-**11**. UV (EtOH, 95%): λ_{max} 210 (ε 21 500). UV (isooctane): λ_{max} 210 (ε 26 000). IR (CH_2Cl_2): 2970, 2940, 2880, 2080, 2010, 2000, 1980 cm^{-1}. ^1H NMR (360 MHz, $CDCl_3$): δ 4.38 (d, ^3J = 5 Hz, H–C(1)), 4.25 (d, 4, H–C(4)), 3.33 (d, 5, H–C(2)), 3.18 (d, 5, H–C(3)), 2.13 (m, H–C(5)), 1.95 (dm, 5, H–C(6-exo)), 1.03 (d, $CH_3C(5)$), 0.90 (m, H–C(6-endo)). ^{13}C NMR (90 MHz, $CDCl_3$): δ 211.2 (s), 81.5 and 78.0 (2d, C(1), C(4)), 58.9 and 53.7 (2d, C(2), C(3)), 36.4 (t, C(6)), 34.6 (d, C(5)), 15.8 (q, CH_3). Optical rotations: $[\alpha]^{25}_{589}$ +4.9°, $[\alpha]^{25}_{578}$ +26.2°, $[\alpha]^{20}_{546}$ +76.7°, $[\alpha]^{25}_{436}$ +91.1°, $[\alpha]^{25}_{365}$ +107.9° (*c* 20.2 mg/mL, CH_2Cl_2). CD (IPM31): $\Delta\epsilon_{334}$ = + 0.1 (300 K). CD (EPE 552): $\Delta\epsilon_{332}$ = +0.11 (300 K, see Figure 5). Anal. Calcd for $C_{11}H_{10}O_5Fe$ (278.05): C, 47.48; H, 3.62. Found: C, 47.40; H, 3.71.

Data of (+)-**12**. UV (EtOH, 95%): λ_{max} 210 (ε 24 500). UV (isooctane): λ_{max} 210 (ε 27 100). IR (CH_2Cl_2): 2980, 2950, 2880, 2085, 2015, 2000, 1980 cm^{-1}. ^1H NMR (360 MHz, $CDCl_3$): δ 4.46 (d, 5, H–C(1)), 4.03 (br s, H–C(4)), 3.1 (br s, H–C(2), H–C(3)), 1.78 (m, H–C(5)), 1.6 (m, H–C(6-exo)), 1.25 (m, H–C(6-endo), 1.03 (d, CH_3-C(5)). ^{13}C NMR ($CDCl_3$): δ 211.0 (s, CO), 84.4 and 79.1 (2d, C(1), C(4)), 58.05 and 57.97 (2d, C(2), C(3)), 37.3 (t, C(6)), 35.9 (d, C(5)), 20.04 (q). MS (70 eV): *m/e* (relative intensity) 278 (3, M^+), 250 (19), 222 (36), 194 (46), 166 (88), 151 (100), 134 (14), 124 (8), 112 (5). Optical rotations: $[\alpha]^{25}_{589}$ +37°, $[\alpha]^{25}_{578}$ +53°, $[\alpha]^{25}_{546}$ +55°, $[\alpha]^{25}_{436}$ +88°, $[\alpha]^{25}_{365}$ +96° (*c* 12.1 mg/mL, CH_2Cl_2). CD (IPM31): $\Delta\epsilon_{332}$ = –0.07. CD (EPE 552): $\Delta\epsilon_{332}$ = –0.05 (300 K; see Figure 7). Anal. Calcd for $C_{11}H_{10}O_5Fe$ (278.05): C, 47.48; H, 3.62. Found: C 47.64; H, 3.61.

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