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## Absolute Configuration and Circular Dichroism of Methyl Substituted Tricarbonyl(1,3-butadiene)iron(0) Complexes

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**Abstract:** The optically active methyl substituted tricarbonyl(1,3-butadiene)iron(0) complexes (2*S*,3*R*,4*S*)-(-)-**1** and (2*R*,3*S*,4*R*)-(+)-**2** have been synthesized by ionic hydrogenation with Et<sub>3</sub>SiH/BF<sub>3</sub> from the acetate (-)-**5** and from (+)-**10** via (-)-**9** in stereoselective reactions. The regioselectivity of the transformation leading from (-)-**5** to **1** has been checked with deuterium labelled substrates **6**, **7**, and **8**. An X-ray crystal structure of the (1*S*,4*R*)-camphanoate (-)-**4** allowed the assignment of the absolute configurations of (-)-**3**, (-)-**5** and hence of (-)-**1**. The stereoselective reduction of (2*R*,3*R*,4*S*)-**10** via **11** to **9** and the subsequent regioselective isomerization allowed the assignment of absolute configuration to (+)-**2**. The chiroptical properties of (+)-**1** and (+)-**2** were determined and compared with those of (2*S*,3*R*)-(+)-tricarbonyl(isoprene)iron(0) [(+)-**12**]. Copyright © 1996 Elsevier Science Ltd

The use of enantiomeric tricarbonyl(1,3-diene)iron(0) complexes for the synthesis of optically active compounds has developed a great deal recently<sup>1,2</sup>. One of the advantages of the use of these complexes is the strong stereoelectronic effect of the Fe(CO)<sub>3</sub> moiety<sup>3</sup> that allows the prediction of the absolute configuration of newly created stereogenic centers, provided the absolute configuration of the starting complex has been established unambiguously. Therefore we have prepared (-)-tricarbonyl(η<sup>4</sup>-1,3-pentadiene)iron(0) [(-)-**1**] and (+)-tricarbonyl(η<sup>4</sup>-3-methyl-1,3-pentadiene)iron(0) [(+)-**2**] in addition to the (+)-tricarbonyl(η<sup>4</sup>-isoprene)-iron(0) complex<sup>2</sup> described previously. To achieve this goal the known (±)-tricarbonyl(η<sup>4</sup>-2,4-pentadien-1-ol)-iron(0) complex **3** was acylated with (1*S*,4*R*)-(-)-camphanoyl chloride<sup>4</sup> to give the diastereomeric esters **4**. Recrystallization from cyclohexane gave the less soluble camphanoyl derivative (-)-**4** as yellow crystals, mp 120.9–122.3 °C. An X-ray crystal structure<sup>5</sup> of (-)-**4** (Figure 1) shows the (2*S*,3*R*,4*S*)-configuration of the alcohol moiety because the (1*S*,4*R*)-configuration of the camphanoyl part is known<sup>3</sup>. Saponification of (-)-**4** with aqueous KOH provided the pure enantiomer (2*S*,3*R*,4*S*)-(-)-**3**. Acetylation of (-)-**3** gave the acetate (2*S*,3*R*,4*S*)-(-)-**5** which could be converted into (2*S*,3*R*,4*S*)-(-)-**1** by ionic reduction at -78 °C with BF<sub>3</sub>/Et<sub>3</sub>SiH in dichloromethane. This correlation establishes the absolute configuration (2*S*,3*R*,4*S*) for (-)-**1** provided that no 1,5-rearrangement took place in course of the ionic reaction procedure. To exclude this possibility the corresponding deuterated acetate (±)-**7** was prepared via the alcohol (±)-**6**. Ionic reduction<sup>2</sup> of **7** with BF<sub>3</sub>/Et<sub>3</sub>SiH gave pure (±)-**8** with the two deuterium atoms in the methyl group. Optically active (-)-**1** has been

prepared by Franck-Neumann et al.<sup>6</sup> in a different way and its absolute configuration was established by a number of chemical transformations that lead finally to the known (*R*)-2-hydroxy-2-phenylpropanal.

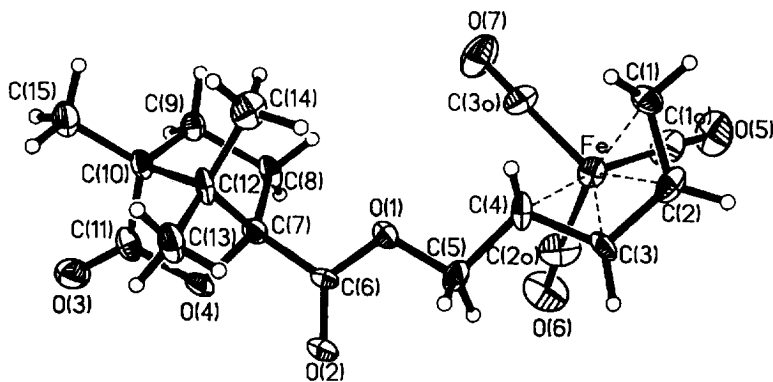
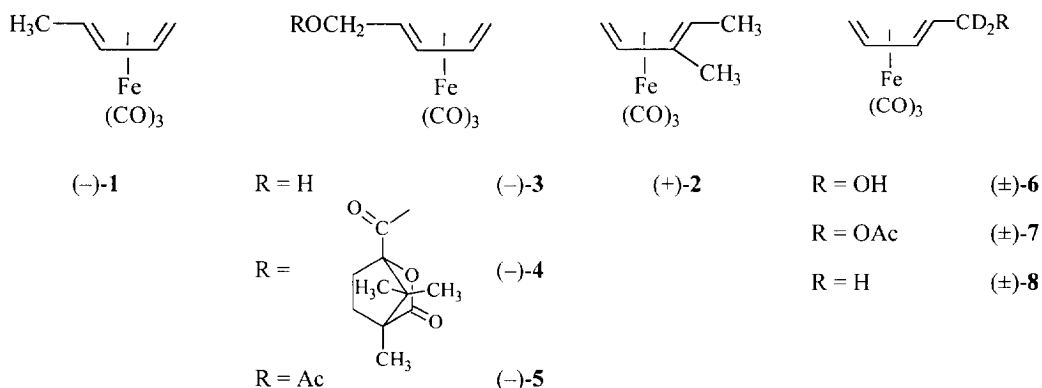
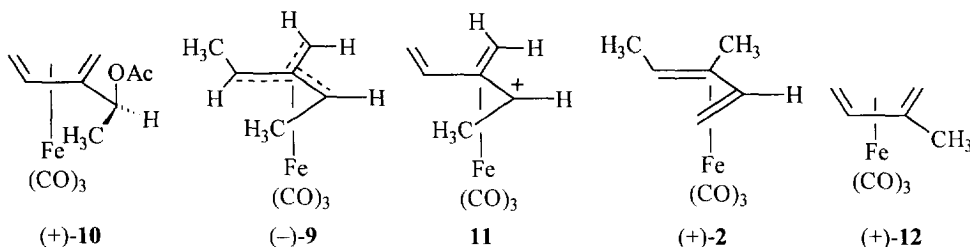


Figure 1

In a previous work<sup>3</sup> we had prepared the optically active dimethyl tricarbonyl[tris(methylene)methane]iron(0) complex (*2S,4S*)-(+)-**9** by stereoselective ionic hydrogenation from (*2R,3R,4S*)-(-)-**10** with known absolute configuration. We repeated this experiment with the enantiomeric compound (*2S,3S,4R*)-(+)-**10** (cp. structural formula). Stereoselective ionic hydrogenation provided (*2R,4R*)-(-)-**9**. During this ionic hydrogenation<sup>3</sup> the carbocation **11** generated from (+)-**10** with  $\text{BF}_3$  is trapped mainly by hydride transfer to C-5. The complex (-)-**9** isomerized completely into (+)-**2** within 5 min in 85%  $\text{H}_2\text{SO}_4$  at 25 °C, probably by a protonation-deprotonation reaction. In an analogous case<sup>3</sup> we had shown that this isomerization is completely stereoselective. Assuming the same stereoselectivity in the present reaction leads to (*2R,3S,4R*)-(+)-**2**.

By analogy with other transition metal derivatives it has been suggested<sup>7,8</sup> that the circular dichroism (CD) of optically active substituted tricarbonyl(1,3-butadiene)iron(0) complexes at longer wavelengths is attributable to d-d transitions and its sign could be related to their absolute configurations. The examples described in the literature<sup>7,8</sup> have substituents with carbonyl groups which can act as additional chromophores. Optically active methyl substituted tricarbonyl( $\eta^4$ -1,3-butadiene)iron(0) compounds with known absolute configurations like



(-)-1 and (+)-2 and the (2*S*,3*R*)-(+)-tricarbonyl( $\eta^4$ -isoprene)iron(0) complex (12) described by us previously<sup>2</sup> are unique. Their chiroptical properties will be determined mainly by dissymmetrical perturbations of the d-d transitions of the tricarbonyl( $\eta^4$ -diene)iron(0) chromophore by the methyl substituents. The experimental results are presented in a table. To facilitate the comparison values for the (+)-enantiomer of 1 are given. Strong positive Cotton effects at 296, 298 and 309 nm in the CD spectra and a positive specific rotation at 589 nm are the common feature of the three iron complexes (+)-1, (+)-2 and (+)-12. Additional minor negative maxima show up at ca. 365 nm. The complexes (+)-1 and (+)-2 show positive Cotton effects at 225 and 231 nm, while the isoprene complex (+)-12 has a strong negative one at 202 nm. This contrary behaviour in the CD spectra for transitions that are thought to have d- $\pi^*$  character has yet to be explained theoretically.

Complex	CD: $\Delta\epsilon_{\max}(\lambda[\text{nm}])$						$[\alpha]_D^{20}$
(+)-1	+ 1.31 (225)	- 0.34 (252)	- 0.36 (261)	+ 2.4 (296)	- 0.28 (334)	+ 0.10 (370)	+ 21.4 ( <i>c</i> = 0.37, CHCl <sub>3</sub> )
(+)-2	+ 4.5 (231)			+ 4.2 (298)		- 0.29 (362)	+ 53 ( <i>c</i> = 1.4, pentane)
(+)-12	- 8.0 (202)			+ 1.95 (309)		- 0.37 (365)	+ 63 ( <i>c</i> = 0.9, CHCl <sub>3</sub> )

## EXPERIMENTAL SECTION

<sup>1</sup>H (270.17 MHz) and <sup>13</sup>C (67.94 MHz) NMR spectra were recorded on a Jeol JNM-EX 270 instrument ( $\delta$  in ppm referenced to residual solvent signal, with chemical shifts referred to TMS; *J* in Hz, multiplicities as determined from DEPT spectra). Optical rotations were measured on a Perkin Elmer 241 polarimeter. IR spectra were recorded on a Perkin Elmer 297 instrument. CD spectra were recorded on a JASCO J 600 dichrograph. Melting points were determined on a Büchi 510 melting point apparatus. Kieselgel 60 F<sub>254</sub> glass plates (from Merck) were used for TLC, compounds were visualized by conc. H<sub>2</sub>SO<sub>4</sub>/5 min 160 °C. All solvents were distilled before use. Diethyl ether was filtered through ICN Alumina B prior to use. Elemental analyses were performed by the microanalytical laboratory of Ilse Beetz, D 96317 Kronach.

(2*S*,3*R*,4*S*)-(-)-Tricarbonyl[ $\eta^4$ -2,4-pentadien-1-yl-(1*S*,4*R*)-camphanoate]iron(0) [(-)-4]: Under Ar a solution of ( $\pm$ )-3<sup>9</sup> (2.750 g; 12.28 mmol) in pyridine (5 ml) was added to (1*S*,4*R*)-(-)-camphanoyl chloride<sup>4</sup> (2.954 g; 13.63 mmol) in pyridine (5 ml). After stirring for 2 h at room temp. the solution was dropped slowly into 1 M H<sub>2</sub>SO<sub>4</sub> (150 ml) and the mixture was extracted twice with Et<sub>2</sub>O (100 ml). The extracts were washed twice with 2 M KHCO<sub>3</sub> (100 ml), dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated. The residue (4.860 g) was recrystallized from cyclo-

hexane (100 ml). The crystals obtained (1551 mg) were again recrystallized from 40 ml (1504 mg) and then from 35 ml of cyclohexane affording 1225 mg (22 %) of (-)-4 as pale yellow crystals, mp 120.9—122.3 °C (dec.),  $R_f = 0.53$  (cyclohexane/AcOEt, 2 : 1),  $[\alpha]_D^{20} = -35.4$  ( $c = 1.03$ , benzene). —  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = -0.13$  (dd,  $J = 8.9, 2.0$ , 1 H, 5- $\text{H}_{\text{syn}}$ ), 0.61 (ddd,  $J = 8.2, 7.9, 2.1$ , 1 H, 2-H), 0.68 (s, 3 H, 7'- $\text{Me}_{\text{syn}}$ ), 0.848, 0.852 (2 s, 6 H, 4'-Me, 7'- $\text{Me}_{\text{anti}}$ ), 1.19—1.25 (3 H, 5'-H, 5- $\text{H}_{\text{anti}}$ ), 1.70—1.80 (m, 1 H, 6'- $\text{H}_{\text{n}}$ ), 2.07—2.17 (m, 1 H, 6'- $\text{H}_{\text{x}}$ ), 3.87 (dd,  $J = 12.0, 2.1$ , 1 H, 1- $\text{H}_{\text{A}}$ ), 4.01 (dd,  $J = 12.0, 7.9$ , 1 H, 1- $\text{H}_{\text{B}}$ ), 4.40 (m, 1 H, 4-H), 4.68 (dd,  $J = 8.2, 5.0$ , 1 H, 3-H). —  $^{13}\text{C NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = 9.8$  (q, 7'- $\text{Me}_{\text{anti}}$ ), 16.5 (q, 7'- $\text{Me}_{\text{syn}}$ ), 16.8 (q, 4'-Me), 28.8 (t, C-5'), 30.9 (t, C-6'), 40.7 (t, C-5), 54.0 (s, C-7'), 54.59 (s, C-4'), 54.63 (d, C-2), 66.9 (t, C-1), 83.3 (d, C-4), 87.4 (d, C-3), 90.6 (s, C-1'), 167.5 (s, 1'- $\text{CO}_2$ ), 177.2 (s, C-3'), 211.0 [s,  $\text{Fe}(\text{CO})_3$ ].

(2*S*,3*R*,4*S*)-(-)-Tricarbonyl( $\eta^4$ -2,4-pentadien-1-ol)iron(0) [(-)-3]: A mixture of (-)-4 (989 mg; 2.45 mmol) in MeOH (20 ml) and 2 M KOH (50 ml) was boiled for 1 h. After cooling the mixture was extracted twice with cyclohexane (50 ml). The extracts were washed with water (50 ml), dried ( $\text{Na}_2\text{SO}_4$ ) and evaporated affording 268 mg (49 %) of (-)-3 as a yellow oil which crystallized spontaneously, mp 39.9—41.4 °C, bp 75 °C/0.02 Torr (ref.<sup>9</sup> 91—93 °C/0.3 Torr for ( $\pm$ )-3),  $R_f = 0.39$  (cyclohexane/AcOEt, 2 : 1),  $[\alpha]_D^{20} = -23.0$  ( $c = 1.17$ , cyclohexane). — IR ( $\text{CCl}_4$ ):  $\tilde{\nu} = 3620$  (OH), 2050, 1985, 1975 ( $\text{C}\equiv\text{O}$ ), 630. —  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = -0.08$  (dd,  $J = 9.3, 2.4$ , 1 H, 5- $\text{H}_{\text{syn}}$ ), 0.61—0.68 (2 H, 2-H, OH), 1.26 (ddd,  $J = 7.0, 2.3, 1.3$ , 1 H, 5- $\text{H}_{\text{anti}}$ ), 3.11—3.29 (2 H, 1-H), 4.48 (m, 1 H, 4-H), 4.64 (dd,  $J = 8.2, 4.6$ , 1 H, 3-H). —  $^{13}\text{C NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = 40.0$  (t, C-5), 62.7 (d, C-2), 64.0 (t, C-1), 82.0 (d, C-4), 86.5 (d, C-3), 211.8 (s, CO). The IR spectrum is in good accordance with that given in ref.<sup>9</sup> for ( $\pm$ )-3.

(2*S*,3*R*,4*S*)-(-)-Tricarbonyl( $\eta^4$ -2,4-pentadien-1-yl-acetate)iron(0) [(-)-5]: A solution of (-)-3 (185 mg; 0.83 mmol) and  $\text{Ac}_2\text{O}$  (4.0 ml; 4.3 g, 42 mmol; Merck) in dry pyridine (5 ml) was stirred at room temp. for 16 h. Then the solution was poured into 50 ml of 1 M  $\text{H}_2\text{SO}_4$  and the mixture was extracted twice with diethyl ether (50 ml). The extracts were washed with 2 M  $\text{KHCO}_3$  (100 ml), dried ( $\text{Na}_2\text{SO}_4$ ) and evaporated to give 209 mg (95 %) of (-)-5 as a yellow oil, bp 55—60 °C/0.002 Torr,  $R_f = 0.67$  (cyclohexane/AcOEt, 2 : 1),  $[\alpha]_D^{20} = -42.0$  ( $c = 1.06$ , cyclohexane). — IR ( $\text{CCl}_4$ ):  $\tilde{\nu} = 2045, 1985, 1975$  ( $\text{C}\equiv\text{O}$ ), 1740 ( $\text{C}=\text{O}$ ), 1225 ( $\text{C}-\text{O}$ ), 635. —  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = -0.12$  (ddd,  $J = 9.2, 2.6, 1.0$ , 1 H, 5- $\text{H}_{\text{syn}}$ ), 0.67 (dddd,  $J = 8.3, 7.3, 6.3, 1.0$ , 1 H, 2-H), 1.22 (ddd,  $J = 7.0, 2.6, 1.0$ , 1 H, 5- $\text{H}_{\text{anti}}$ ), 1.68 (s, 3 H, Me), 3.77 (dd,  $J = 11.9, 6.3$ , 1 H, 1- $\text{H}_{\text{A}}$ ), 3.99 (dd,  $J = 11.9, 7.3$ , 1 H, 1- $\text{H}_{\text{B}}$ ), 4.41 (dddd,  $J = 9.3, 7.0, 4.7, 1.0$ , 1 H, 4-H), 4.67 (dd,  $J = 8.4, 4.8$ , 1 H, 3-H). —  $^{13}\text{C NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = 20.3$  (q, Me), 40.3 (t, C-5), 56.5 (d, C-2), 65.5 (t, C-1), 82.6 (d, C-4), 87.3 (d, C-3), 169.7 (s,  $\text{CO}_2$ ), 211.3 [s,  $\text{Fe}(\text{CO})_3$ ]. — Anal. calcd. for  $\text{C}_{10}\text{H}_{10}\text{FeO}_5$  (266.03): C, 45.15; H, 3.79. Found: C, 45.19; H, 3.69.

(2*S*,3*R*,4*S*)-(-)-Tricarbonyl( $\eta^4$ -1,3-pentadiene)iron(0) [(-)-1]: Under an atmosphere of  $\text{N}_2$  at  $-78$  °C  $\text{BF}_3$  gas was bubbled through a solution of (-)-5 (536 mg; 2.01 mmol) and  $\text{Et}_3\text{SiH}$  (1.00 ml; 0.73 g; 6.3 mmol; Fluka) in dry  $\text{CH}_2\text{Cl}_2$  (30 ml) for 3 min. After stirring for an additional 20 min 2 M  $\text{KHCO}_3$  (20 ml) was added and the mixture was warmed to room temp. The organic layer was washed twice with 2 M  $\text{KHCO}_3$  (50 ml) and evaporated. The residue (0.78 g) was filtered through silica gel (15 g) and was eluted with pentane to give 256 mg (61 %) of (-)-1 as a brown oil, bp 71—75 °C/7 Torr,  $R_f = 0.71$  (pentane),  $[\alpha]_D^{20} = -21.4$  ( $c = 0.37$ ,  $\text{CHCl}_3$ ) [ref.<sup>5</sup>  $[\alpha]_D^{20} = -26$  ( $c = 0.7$ ,  $\text{CHCl}_3$ )], CD ( $\text{CH}_3\text{CN}$ ):  $\Delta\epsilon_{\text{max}}(\lambda[\text{nm}]) = -0.10$  (370), +0.28 (333), -2.39 (295), +0.36 (261), +0.34 (252), -1.31 (225). — IR ( $\text{CCl}_4$ ):  $\tilde{\nu} = 3010, 2970, 2920$  (CH), 2050, 1980, 1970 ( $\text{C}\equiv\text{O}$ ), 1385, 680, 630, 620. —  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = -0.14$  (dd,  $J = 8.9, 2.3$ , 1 H, 1- $\text{H}_{\text{syn}}$ ), 0.59 (dq,  $J = 7.9, 6.3$ , 1 H, 4-

H), 1.01 (d,  $J = 6.3$ , 3 H, 5-H), 1.24 (ddd,  $J = 6.6, 2.3, 1.0$ , 1 H, 1-H<sub>anti</sub>), 4.42—4.53 (2 H, 2-H, 3-H). — <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 18.9$  (q, C-5), 39.5 (t, C-1), 58.3 (d, C-4), 80.9 (d, C-3), 89.1 (d, C-2), 212.6 (s, CO).

(±)-Tricarbonyl( $\eta^4$ -1,1-dideutero-2,4-pentadien-1-ol)iron(0) [(±)-6]: A suspension of 90 % LiAlD<sub>4</sub> (1.94 g; 42 mmol; Merck; > 98 % D) in Et<sub>2</sub>O (80 ml) was added dropwise under N<sub>2</sub> within 2½ h to a solution of 2,4-pentadienoic acid<sup>10</sup> (4.755 g; 48.5 mmol) in Et<sub>2</sub>O (50 ml) at 0 °C. After 30 min at 0 °C the reaction was quenched with satd. K<sub>2</sub>CO<sub>3</sub> (10 ml) and the mixture was warmed to room temp. The ethereal layer was removed and the residue was washed three times with 50 ml of Et<sub>2</sub>O. The extracts were dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated to give 1.116 g (26.4 %) of (*E*)-1,1-dideutero-2,4-pentadien-1-ol as a pale yellow liquid [<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 5.09$  (d,  $J = 9.6$ , 1 H, 5-H<sub>E</sub>), 5.21 (d,  $J = 15.8$ , 1 H, 5-H<sub>Z</sub>), 5.83 (d,  $J = 13.5$ , 1 H, 2-H), 6.20—6.41 (2 H, 3-H, 4-H)], which was used immediately for the next step without further purification.

Under an Ar atmosphere a mixture of the deuterated alcohol (1.023 g; 11.7 mmol) and Fe<sub>2</sub>(CO)<sub>9</sub> (7.70 g; 21.2 mmol) in Et<sub>2</sub>O (50 ml) was boiled for 20 h. After cooling to room temp. the solution was filtered through 10 g of silica gel, eluted with Et<sub>2</sub>O and evaporated. The residue (2.03 g) was chromatographed on 300 g of silica gel (cyclohexane/AcOEt, 2 : 1) to yield 1.525 g (57 %) of (±)-6 as an orange oil,  $R_f = 0.42$ . — <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = -0.08$  (dd,  $J = 9.3, 1.6$ , 1 H, 5-H<sub>syn</sub>), 0.64 (s, br, 1 H, OH), 0.65 (m, 1 H, 2-H), 1.27 (ddd,  $J = 7.0, 2.3, 1.3$ , 1 H, 5-H<sub>anti</sub>), 4.48 (m, 1 H, 4-H), 4.65 (dd,  $J = 8.2, 4.6$ , 1 H, 3-H). The signal of 1-H at 3.11—3.29 in (–)-3 cannot be detected.

(±)-Tricarbonyl( $\eta^4$ -1,1-dideutero-2,4-pentadien-1-yl-acetate)iron(0) [(±)-7]: A mixture of dry pyridine (5 ml), (±)-6 (1067 mg; 4.72 mmol) and Ac<sub>2</sub>O (2.0 ml; 2.2 g, 21 mmol; Merck) was stirred at room temp. for 16 h. Then the solution was poured into 100 ml of 1 M H<sub>2</sub>SO<sub>4</sub> and the mixture was extracted twice with Et<sub>2</sub>O (50 ml). The extracts were washed twice with 2 M KHCO<sub>3</sub> (50 ml), dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated to afford 1.22 g (96 %) of (±)-7 as an orange oil. — <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = -0.11$  (ddd,  $J = 9.2, 2.6, 1.0$ , 1 H, 5-H<sub>syn</sub>), 0.66 (d,  $J = 8.6, 1$  H, 2-H), 1.22 (ddd,  $J = 7.0, 2.6, 1.0$ , 1 H, 5-H<sub>anti</sub>), 1.68 (s, 3 H, Me), 4.41 (dddd,  $J = 9.3, 7.0, 4.7, 1.0$ , 1 H, 4-H), 4.68 (dd,  $J = 8.4, 5.0$ , 1 H, 3-H). — <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 20.3$  (q, Me), 40.4 (t, C-5), 56.3 (d, C-2), 64.9 [quint, <sup>1</sup>J(<sup>13</sup>C, <sup>2</sup>H) = 21, C-1], 82.7 (d, C-4), 87.3 (d, C-3), 169.8 (s, CO<sub>2</sub>), 211.3 [s, Fe(CO)<sub>3</sub>].

(±)-Tricarbonyl( $\eta^4$ -5,5-dideutero-1,3-pentadiene)iron(0) [(±)-8]: Under N<sub>2</sub> atmosphere BF<sub>3</sub> gas was bubbled through a solution of (±)-7 (609 mg; 2.27 mmol) and Et<sub>3</sub>SiH (1.00 ml; 0.73 g; 6.3 mmol; Fluka) in dry CH<sub>2</sub>Cl<sub>2</sub> (30 ml) at –78 °C for 3 min. After stirring for an additional 20 min 2 M KHCO<sub>3</sub> (20 ml) was added and the mixture was warmed to room temp. The organic layer was washed twice with 2 M KHCO<sub>3</sub> (50 ml) and evaporated. The residue (0.55 g) was filtered through silica gel (15 g) and was eluted with pentane to give 124 mg (26 %) of (±)-8 as a brown oil, bp 70 °C/9 Torr,  $R_f = 0.71$  (pentane). — <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = -0.14$  (dd,  $J = 8.9, 2.3$ , 1 H, 1-H<sub>syn</sub>), 0.58 (dd,  $J = 8.0, 6.3$ , 1 H, 4-H), 0.98 [dt,  $J = 6.3, {}^2J(^1H, {}^2H) = 2.2$ , 1 H, 5-H], 1.25 (dd,  $J = 6.6, 2.3$ , 1 H, 1-H<sub>anti</sub>), 4.42—4.54 (2 H, 2-H, 3-H). — <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 18.3$  [dq, <sup>1</sup>J(<sup>13</sup>C, <sup>2</sup>H) = 19, C-5], 39.5 (t, C-1), 58.1 (d, C-4), 81.0 (d, C-3), 89.1 (d, C-2), 212.6 (s, CO).

(2*R*,4*R*)-(–)-Tricarbonyl( $\eta^4$ -3-methylidene-2,4-pentadienyl)iron(0) [(–)-9]: Under N<sub>2</sub> atmosphere at –78 °C BF<sub>3</sub> gas was bubbled through a solution of (+)-10<sup>3</sup> (500 mg; 1.79 mmol) and Et<sub>3</sub>SiH (1.00 ml; 0.73 g; 6.3 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 ml) for 5 min. After stirring for 20 min at –78 °C 2 M KHCO<sub>3</sub> (20 ml) was added and the mixture was warmed to room temp. The organic layer was separated, the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (50 ml) and the combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated. The residue (0.46 g)

was chromatographed on 70 g of silica gel (pentane); 198 mg (50 %) of (-)-**9** as a yellow oil,  $R_f = 0.91$ ,  $[\alpha]_D^{20} = -42$  ( $c = 1.0$ , pentane) [ref.<sup>3</sup>  $[\alpha]_D^{20} = +56$  ( $c = 0.84$ ,  $\text{CHCl}_3$ ) for (+)-**9**]. The IR and NMR spectra are according to those reported for (+)-**9** in ref.<sup>3</sup>.

(2*R*,3*S*,4*R*)-(+)-Tricarbonyl( $\eta^4$ -3-methyl-1,3-pentadiene)iron(0) [(+)-**2**]: A solution of 184 mg (0.83 mmol) of (-)-**9** in 5 ml of 85 %  $\text{H}_2\text{SO}_4$  was stirred at room temp. for 10 min. Then water (100 ml) was added and the dark orange mixture was extracted five times with 50 ml of pentane; 141 mg (77 %) of (+)-**2** as a yellow oil,  $R_f = 0.72$  (pentane), bp 80 °C/12 Torr,  $[\alpha]_D^{20} = +53$  ( $c = 1.4$ , pentane), CD ( $\text{CH}_3\text{CN}$ ):  $\Delta\epsilon_{\text{max}}(\lambda[\text{nm}]) = -0.29$  (362), +4.16 (298), +4.48 (231). The IR and NMR spectra are according to those reported for ( $\pm$ )-**2** in ref.<sup>3</sup>.

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### References and Notes

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