

Circular Dichroism Spectra of Tricarbonyliron  $\pi$ -Complexes

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A number of optically active tricarbonyliron  $\pi$ -complexes with unsymmetrical cyclohexadiene and cyclohexadienyl ligands have been prepared from diols available by the oxidation of arenes by *Pseudomonas putida*. The circular dichroism spectra of the metal complexes provide an empirical guide for the assignment of absolute configuration from chiroptical data for this class of compounds.

Transition metal  $\pi$ -complexes offer complete stereocontrol in alkylations.<sup>1,2</sup> Optically pure complexes of this type can be obtained by the complexation<sup>3,4</sup> of diols available from a wide range of arenes by the action<sup>5</sup> of a mutant strain of *Pseudomonas putida* which has been manipulated to ensure the accumulation of the diol product. We have recently demonstrated diastereoface selectivity in the complexation of this type of diol ligand, and have developed methods for the stereocontrolled elaboration of the diols by means of intermediate organoiron  $\pi$ -complexes.<sup>4</sup> For the application of these methods in enantioselective organic synthesis, it is important to know the absolute configuration of the metal complexes. This paper concerns the empirical correlation of circular dichroism (CD) spectra with absolute configurations in a series of organometallic compounds. We offer a guide for the assignment of absolute configurations of complexes of this type. Part of this work has been the subject of a preliminary communication.<sup>6</sup>

An earlier study<sup>7</sup> examined a set of four cationic  $\eta^5$ -dienyl complexes in which a consistent trend was observed in the sign of the highest wavelength CD band at 350–380 nm. On the basis that this band might involve a contribution from a metal-centred d–d transition, it was proposed that the sign of this CD band should provide a reliable guide to the absolute configuration of planar chirality in the metal complex. Similar arguments could be applied to neutral  $\eta^4$ -cyclohexadiene complexes, but only one pair of 2-OMe substituted complexes was examined in that investigation. Subsequently, correlations have been defined<sup>8</sup> in an extensive series of terminally substituted acyclic  $\eta^4$ -butadiene  $\pi$ -complexes. Attention again focussed on the highest wavelength CD band. This detailed investigation has confirmed earlier proposals<sup>9</sup> for the interpretation of CD spectra of acyclic  $\eta^4$ -tricarbonyliron complexes. Our own work has addressed the question of assignment of the absolute configurations of chiral  $\eta^4$ -cyclohexadiene complexes of  $\text{Fe}(\text{CO})_3$  by the examination of a series of optically active 1-substituted\* complexes of type 3 (X = Me, Cl and OMe). Preparatory work<sup>2</sup> with two 1-methyl substituted complexes in this series had already demonstrated that very similar CD curves were observed in regions of the spectra dominated by the metal complex. It is now clear that this similarity appears consistently throughout the much more extensive series of cyclic diene complexes examined in our present investigation.

## Results

Measurements of the CD spectra of a number of readily available toluene-derived *cis*-diol complexes (prepared<sup>4</sup> by

\* In the interests of clarity in the comparison of different ligand substitution patterns, a self-consistent numbering system (that of the simple tricarbonyl complexes) has been employed in this paper; the correct IUPAC naming for a diol obtained by bio-oxygenation is 3-substituted cyclohexa-4,5-diene-1,2-diol.

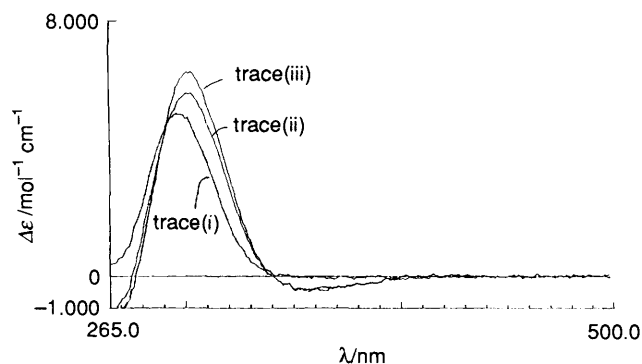
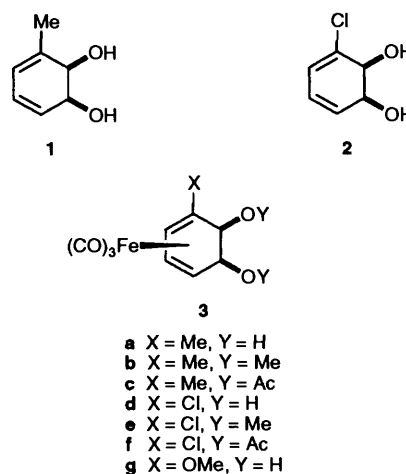


Fig. 1 Circular dichroism curves for 1-methyl substituted complexes: (i) complex 3a, (ii) complex 3b and (iii) complex 3c

direct complexation of 1, its methyl ether, or acetyl ester) quickly established that, despite different substitution on the ring, very similar CD spectra were obtained (Fig. 1). In general, the 1-methyl substituted complexes exhibited two CD bands (350–360 and 295–305 nm), though in the case of the diol complex 3a, the highest band at 350–360 nm was absent or too small to observe. Complexes bearing other C-1 substituents were examined next. The 1-chloro diol 2 is available by the microbial dioxygenation of chlorobenzene.<sup>10</sup> Direct complex-



ation by the method used to form 3a, afforded the diol complex 3d in 45% yield. Unlike the case of the diol 3a, the CD spectrum of the diol 3d showed a clear high-wavelength minimum at 350 nm, as was seen for 3b and 3c. The methyl ether and acetate derivatives were also prepared. Methylation or acetylation of the diol 2 was followed by disappointingly inefficient complexation with  $\text{Fe}_2(\text{CO})_9$  to afford small amounts of the

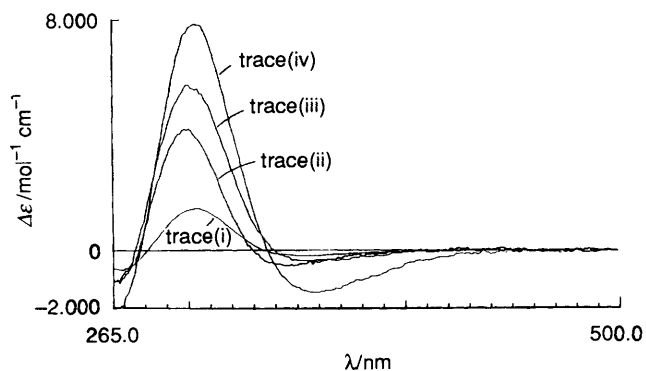


Fig. 2 Circular dichroism curves for 1-chloro- and 1-methoxy substituted complexes: (i) complex **3e**, (ii) complex **3d**, (iii) complex **3f** and (iv) complex **3g**

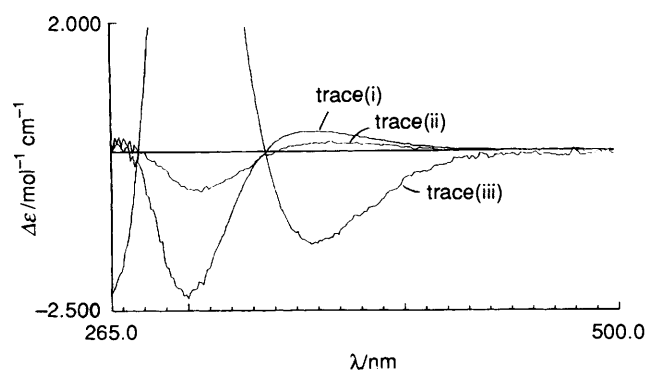
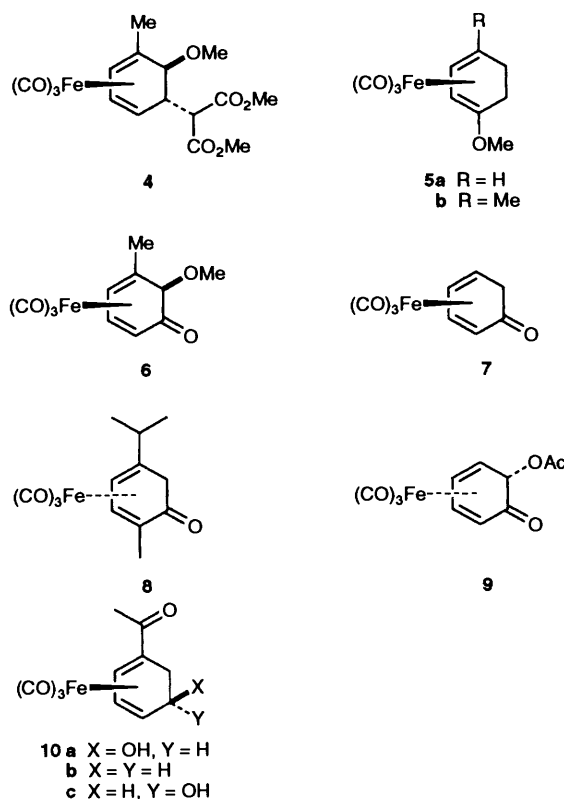


Fig. 3 Comparison of circular dichroism curves of 1-methoxy substituted complexes: (i) complex **5a**, (ii) complex **5b** and (iii) complex **3g** enlarged to same scale (see Fig. 2); complexes **5a**, **5b** are known to be of low optical purity

required products **3e** and **3f** in only 6 and 2% overall yield, respectively. Even so, this was sufficient for the spectroscopic investigation. Once again, very similar CD spectra were obtained from these materials (Fig. 2). Thus, for  $Y = \text{Me}$  and  $\text{Ac}$ , similar CD characteristics were observed in the methyl- and chloro-diene series of complexes; only for diols  $Y = \text{H}$  was the position uncertain, although in this case too there was a pronounced similarity between the CD curves around 300 nm. A methoxy diene *cis*-diol complex **3g** ( $Y = \text{H}$ ) was examined to probe further the form of the high wavelength band of the CD spectra of the diol series of complexes. The free ligand was obtained by microbial dioxygenation of anisole, and was complexed as before, affording **3g** in 52% yield. Complexation of the diols in these cases is more efficient than the reactions of the *O*-protected species. This product possessed the expected CD band at 360 nm (Figs. 2 and 3), showing that diol complexes can be expected to exhibit CD spectra similar to those of the methyl and acetyl derivatives. Indeed, all the cyclohexadiene complexes so far examined possess analogous CD properties in both the first two bands, with a minimum (or zero, in the case of **3a**)  $\Delta\epsilon$  around 350–360 nm and a maximum at around 295–305 nm.

Comparison with the CD curve<sup>2</sup> obtained from **4** indicated that the stereochemistry of attachment of substituents at the methylene positions C-5 and C-6 is not crucial in determining the form of the CD spectrum in this region. Despite the *exo* attachment of the malonate ester substituent, a similar spectrum was produced. This point was further explored by examination of a partially resolved sample<sup>11,12</sup> of **5a** which lacks substituents at both C-5 and C-6. In this case, too, the same properties were observed (Fig. 3). The *1R* isomer of **5a** (the opposite absolute configuration to **3g**) exhibited the expected



CD properties with a maximum at 354 nm, the reverse of the form shown in Fig. 2.

In contrast to the above results, the CD spectrum of the dienone complex **6** took a quite different form. This complex contained in its ligand the 1-methylcyclohexadiene moiety that had the same absolute configuration of the metal complex as that present in **3b**. Nonetheless, the minimum at 357 nm for **3b** was replaced by a much larger maximum at 366 nm. The second band was also inverted to show a minimum at 309 nm. Clearly, the replacement of CHOMe with C=O had a far more marked effect than the other changes to the substitution at C-5, a result that seems reasonable since the chromophore in **6** is extended by bringing the  $\pi$ -system into conjugation with the ketone. The proposition that this feature was dominating the CD properties of **6** was supported by examination of a partially resolved sample<sup>11</sup> of the simple dienone complex **7**. Compared to the dienone unit in **6**, the metal centre is present in **7** in the same absolute configuration. The CD spectrum showed the same form, with a maximum at 353 nm and a minimum at 305 nm. Other dienone complexes have also been examined. The dienone **8**<sup>13</sup> is derived from complexation of (*R*)-(-)-carvone and contains a metal centre in the opposite configuration to those examined in **6** and **7**. As expected, the CD curve took the reverse form with a minimum at 357 nm and a maximum at 311 nm. Finally, the circular dichroism spectrum of a 6-acetoxy substituted dienone complex **9** was recorded. This complex was obtained from the diol **3g** by reaction with  $\text{HPF}_6$  in acetic anhydride followed by hydrolysis with water. Like **8**, this dienone complex has the *2S* configuration for the metal complex. The CD curve also took the same form as seen for **8**. From these comparisons (Fig. 4), it is clear that all four dienone complexes **6**, **7**, **8** and **9** demonstrate the same relationship between the CD curves and absolute configurations of the metal complexes, and that the dienone complexes are distinct from the simple cyclohexadiene complexes of type **3** described above.

Other electron-withdrawing substituents can also have a profound effect on the form of CD curves. Preliminary results<sup>14</sup> with trifluoromethyl and fluorine groups indicate a different

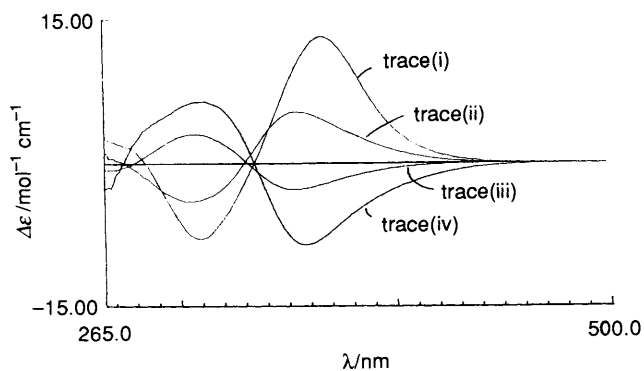


Fig. 4 Circular dichroism curves of dienone complexes: (i) complex 6, (ii) complex 7, (iii) complex 9 and (iv) complex 8. Complex 7 is known to be of low optical purity.

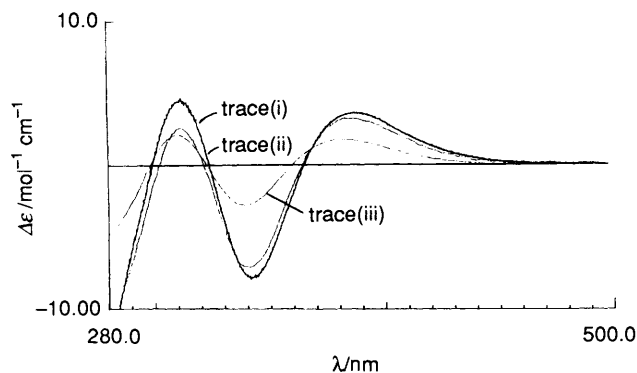


Fig. 5 Circular dichroism spectra of 1-acyl substituted complexes: (i) complex 10a, (ii) complex 10b and (iii) complex 10c

pattern of CD bands, a situation also encountered in recent correlations of absolute configurations of acyclic complexes in which the electron-withdrawing substituents are formyl or ester groups.<sup>8</sup> In order to reconcile our findings with these new results, we examined the easily accessible 1-acetyl complexes **10a** and **10b** to explore the effect of the acetyl substituent in the cyclic system. Microbial oxidation of acetophenone,<sup>15</sup> and complexation by  $\text{Fe}_2(\text{CO})_9$  afforded **10a**. This was treated with acid and reduced to form **10b**. In contrast to the diol complexes examined earlier, the CD spectra of both **10a** and **10b** exhibited an additional band at 383 nm, showing a similar CD profile to the acetyl-substituted diene complexes in the acyclic cases.<sup>6</sup> This suggests that it is the presence of the electron-withdrawing acetyl substituent in **10a** and **10b**, not the constraint of the diene within the 6-membered ring, that accounts for observed differences in CD curves. Hydroxide addition to the dienyl complex derived from **10a** gave **10c** which is the C-5 epimer of **10a**. Again a similar CD curve was observed (Fig. 5).

Further information has also been obtained to confirm the properties of the cationic  $\eta^5$ -dienyl complexes examined earlier. Our work with optically active complexes prepared from arene-derived *cis*-diols had made available<sup>2</sup> a 2-methyl substituted cationic cyclohexadienyl complex **11** bearing an additional substituent at C-6. Comparison of the CD spectrum of **11** with that of tricarbonyl( $\eta^5$ -2-methylcyclohexadienyl)iron(1+)  $\text{PF}_6(1-)$  **12**<sup>7</sup> further supports the earlier conclusions that the CD spectra in cationic dienyl  $\eta^5$ -complexes are dominated by the metal complex. As with the neutral complexes described above, the additional malonate ester substituent in **11** had no significant effect on the form of the CD curve.

## Discussion

When transition-metal  $\pi$ -complexes contain planar chirality in the organometallic portion, an unsymmetrical pattern of

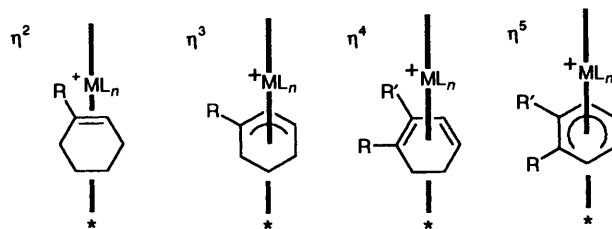
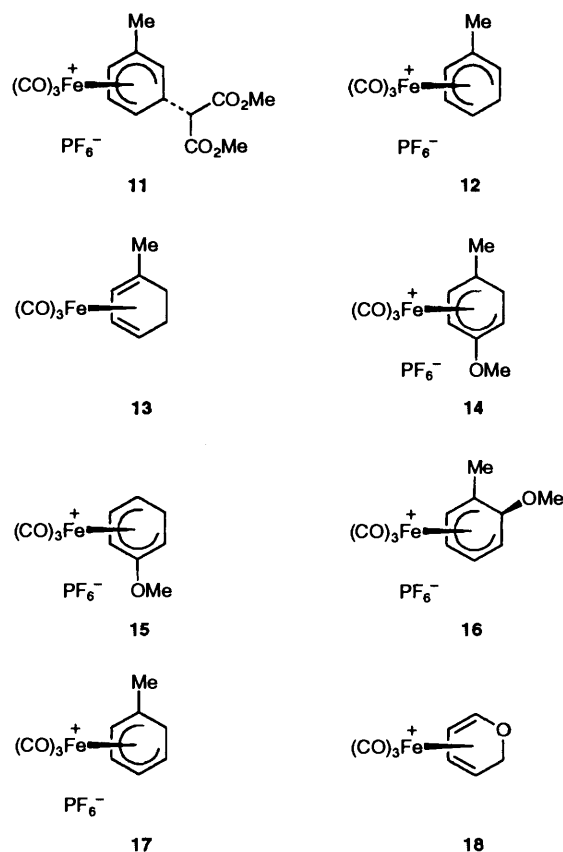
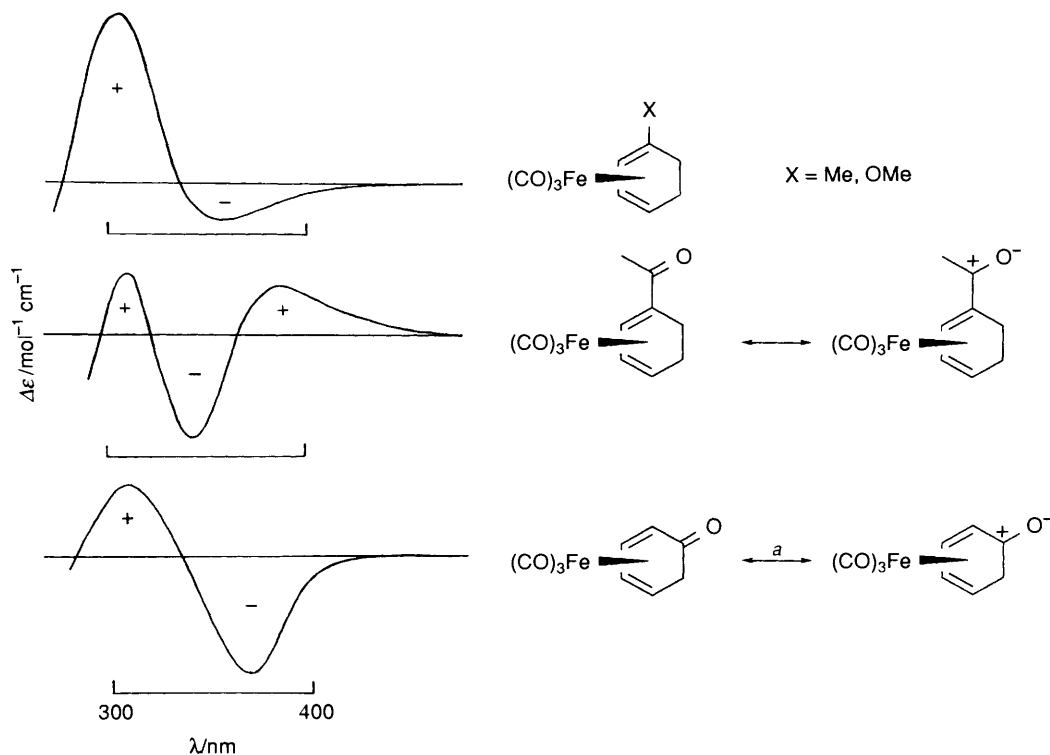


Fig. 6 Location of potential symmetry planes in  $\eta^{2-5}$  complexes [ $R = R' = H$ ; \* = symmetry plane]



substituents is present on the ligand bound to the metal. The effect of this unsymmetrical substitution is manifest in the regiocontrol of alkylations,<sup>16</sup> an important consideration in synthetic studies, and also in the contribution of the metal-bound  $\pi$ -system to the circular dichroism spectrum of the compound. Studies of substituent effects on CD spectra of organometallics suggest that clear trends will emerge that correlate the sign of particular CD bands with the absolute stereochemistry of attachment of the metal to the  $\pi$ -system of the ligand.<sup>7,8,17</sup> In our investigations, for example, we have observed a consistent empirical relationship (Figs. 1–3) between CD and absolute stereochemistry in a series of eight 1-substituted  $\eta^4$ -cyclohexadiene complexes (**3a–f**, **4** and **5a**), of known absolute configuration bearing three different C-1 substituents. In addition, the complex **3g** showed the same form of CD curve.

The unsaturated ligands in  $\pi$ -complexes possess potential symmetry planes lying through the centre of the  $\eta^n$  region of the ligand, perpendicular to the plane of the ligand itself. These are illustrated for a series of metal complexes in Fig. 6. The attachment of the metal distinguishes the two faces of the ligand, and, in chiral complexes, the substituents ( $R, R' \neq H$ ; Fig. 6) distinguish the two sides of the potential symmetry plane, and break the symmetry of the complex. These substituents, lying off the central plane, are important in influencing the form of the



**Fig. 7** Archetypal CD curves for 1-alkyl, 1-alkoxy, 1-acyl and dienone tricarbonyl( $\eta^4$ -cyclohexadiene)iron complexes (*a* canonical form resembles a  $\eta^5$ -cyclohexadienyl complex in this case)

CD spectrum of a complex. In this paper, we have presented data for the  $\eta^4$  and  $\eta^5$  members of this series, but the principles of interpretation revealed should be generally applicable across the whole series.

Reliable interpretation of substituent effects depends on an assessment of the contribution to the CD spectrum of any unsymmetrically placed groups that may be present in the molecule. It is important to identify the correct parent chromophore on which to base the assignment. A clear example is found in the data in Table 1. The 1-methyl complexes **3a–c** and **4**, form series based on a parent organometallic moiety **13**. Despite its methyl substitution, the dienone complex **6** does not fit this series, but correlates well with the dienone parent chromophore itself (complex **7**). So large is the effect of the dienone on the CD curve, that the effect of the methyl substituent in **6** is incidental to the overall form of the CD spectrum. The 1,4-disubstituted complex **5b** provides a further example in which two parent chromophores, **13** and **5a**, are in opposition in terms of their effect on the CD curve.

Attachment of powerfully electron-withdrawing substituents on the diene also has a large effect on the CD properties of the complexes. Fluorine, trifluoromethyl and acetyl substituents, introduce different changes in the form of the CD curves. While the properties of the formyl, acetyl, and ester substituents have been identified, an investigation of a larger range of the fluoro complexes is needed before a general interpretation of CD spectra of complexes bearing electron-withdrawing substituents can be proposed. This will be the subject of further study as a wider selection of substituted complexes becomes available.

Based on the data available at this stage, it is clear that the similarity between the CD spectra of methyl-, chloro- and methoxy-cyclohexadienes strongly suggests a common absolute configuration for all complexes **3**. In view of the well established<sup>3,18</sup> *cis* addition of the  $\text{Fe}(\text{CO})_3$  group, this points to a common absolute configuration at the  $\text{CH}(\text{OH})$  sites in the microbial dioxygenation products. On this basis, the absolute

configuration drawn for structures **1** and **2** is also proposed for the diol obtained from anisole (*i.e.*  $\text{X} = \text{OMe}$ ), and the absolute configurations drawn for structures **3** can be extended to include **3g** with reasonable confidence. While the absolute configuration of **1** was determined<sup>19</sup> by chemical correlation, that of **2** has itself been deduced<sup>20</sup> from the CD spectra of a series of free dienes. Since this assignment for **2** is based on two independent methods of interpretation of the CD curve, it is reasonably secure but, nonetheless, is further strengthened by the data reported here for the derived metal complexes. Study of the organoiron derivatives offers a useful tool for the assignment of the absolute configurations in diol structures of this type.

**Conclusions.**—Archetypal CD curve profiles for tricarbonyl( $\eta^4$ -cyclohexadiene)iron(0) complexes bearing electron-donating and electron-withdrawing (organic carbonyl) substituents are illustrated in Fig. 7 for 1-substituted ligands with the metal attached to the upper face of the diene (**3g** = 1*S*-isomer, **10b** = 1*R*-isomer, **7** = 2*S*-isomer). Each has its own CD signature. The CD spectra reported here, and literature spectra,<sup>2,7</sup> suggest a provisional ranking order (see also ref. 7) of substituents [ $\text{Me} < \text{OMe} \ll \text{C}=\text{O}$  (which exerts a large influence through effects of polarised canonical forms shown in Fig. 7)] in terms of power to influence the sign of CD bands relating to the metal complex.

## Experimental

All reactions were performed under a nitrogen atmosphere. CD spectra were recorded using Jasco J-600 spectrometer, and  $[\alpha]_D$  measurements were performed on a Jasco DIP/360 polarimeter; the latter are recorded in units of  $10^{-1} \text{ deg cm}^2 \text{ g}^{-1}$ . IR spectra were recorded using Perkin-Elmer 257 and 1720-X spectrometers. NMR spectra were recorded using a JEOL PMX60, EX-90Q and GX400 spectrometers. Low resolution mass spectra were measured using a Kratos MS 25 spectrometer.

**Table 1** Chiroptical data from tricarbonyliron complexes. Circular dichroism and specific rotation data for complexes **3c-g**, **9** and **10a-c** are compared with data from a representative selection of related tricarbonyliron complexes to indicate the possibility of empirical correlations

Complex <sup>a</sup>	Figure (trace)	$\lambda_1^b$	$\Delta\epsilon_1^c$	$\lambda_2$	$\Delta\epsilon_2$	$\lambda_3$	$\Delta\epsilon_3$	$[\alpha]_D^d$	<i>c</i>	Solvent	Ref.
(1S)- <b>3a</b>	1 (i)	—	—	296	+5.12	—	—	+72.0	0.5	CHCl <sub>3</sub>	4
(1S)- <b>3b</b>	1 (ii)	357	-0.38	300	+5.80	—	—	+142.9	1	C <sub>6</sub> H <sub>12</sub>	4
(1S)- <b>3c</b>	1 (iii)	352	-0.53	298	+6.69	—	—	+94.4	0.5	CHCl <sub>3</sub>	4
(1S)- <b>3d</b>	2 (ii)	350	-0.54	300	+4.20	—	—	+14.4	1	CHCl <sub>3</sub>	—
(1S)- <b>3e</b>	2 (i)	355	-0.19	305	+1.37	—	—	-15.4	1	CHCl <sub>3</sub>	—
(1S)- <b>3f</b>	2 (iii)	350	-0.19	300	+1.15	—	—	+28.0	1	CHCl <sub>3</sub>	—
(1S)- <b>3g</b>	2 (iv)	360	-1.46	305	+7.87	—	—	-7.4	1	CHCl <sub>3</sub>	—
(1S)- <b>4</b>	See ref. 2	353	-0.92	301	+5.25	—	—	-47.1	1	C <sub>6</sub> H <sub>12</sub>	2,4
(1R)- <b>5a</b> <sup>e</sup>	3 (i)	354	+0.30	300	-2.31	—	—	(-)	—	CHCl <sub>3</sub>	11 <sup>f</sup>
(1R)- <b>5b</b> <sup>e</sup>	3 (ii)	360	+0.15	303	-0.42	—	—	(-)	—	CHCl <sub>3</sub>	11
(4S)- <b>6</b>	4 (i)	366	+13.20	309	-7.30	—	—	+546.4	0.5	C <sub>6</sub> H <sub>12</sub>	4
(2R)- <b>7</b> <sup>e</sup>	4 (ii)	353	+5.44	305	-4.10	—	—	(+)	—	CHCl <sub>3</sub>	11 <sup>f</sup>
(2S)- <b>8</b>	4 (iv)	357	-8.55	311	+6.55	—	—	(-)	—	CHCl <sub>3</sub>	13
(2S)- <b>9</b>	4 (iii)	354	-8.40	307	+9.10	—	—	-327.0	0.3	CHCl <sub>3</sub>	—
(1R)- <b>10a</b>	5 (i)	383	+3.00	341	-7.04	312	+2.62	-47.2	0.9	CHCl <sub>3</sub>	—
(1R)- <b>10b</b>	5 (ii)	383	+3.81	341	-7.98	298	+4.87	-201.5	0.6	CHCl <sub>3</sub>	—
(1R)- <b>10c</b>	5 (iii)	384	+1.76	339	-2.84	310	+2.10	-243.0	1	CHCl <sub>3</sub>	—

<sup>a</sup> For typical UV spectra of these complexes, see ref. 6. <sup>b</sup>  $\lambda$  nm. <sup>c</sup>  $\Delta\epsilon$  in mol<sup>-1</sup> cm<sup>-1</sup>. <sup>d</sup>  $[\alpha]_D$  in 10<sup>-1</sup> deg cm<sup>2</sup> g<sup>-1</sup>. <sup>e</sup> Known to be of low optical purity. <sup>f</sup> Both enantiomers in this series are available (ref. 12), but (-)-(1R)-**5a** is formed in higher optical purity; for this reason compounds **5** and **7** were used in the *R* configuration for this investigation.

Dichloromethane and acetonitrile were distilled over calcium hydride under nitrogen. Light petroleum refers to the fraction boiling in the range 40–60 °C and ether refers to diethyl ether. 1-Chloro-5,6-dihydroxycyclohexa-1,3-diene **2** ( $[\alpha]_D$  +38.4 *c* 5, CHCl<sub>3</sub>) was provided by ICI Biological Products Ltd., and was used without purification. Complexes **3a-c**, **4**, **6** and **9** were obtained as described earlier.<sup>4</sup>

**Circular Dichroism Measurements.**—Volumetric and spectroscopic measurements were performed in air without special precautions. Accurately weighed samples of the complexes (*ca.* 10–20 mg) were dissolved in chloroform (neutral complexes\*) or acetonitrile (cationic complexes) in 2 cm<sup>3</sup> volumetric flasks. CD spectra were recorded at 22 °C. The same sample was used for  $[\alpha]_D$  determinations. Plots of  $\Delta\epsilon$  against  $\lambda$  are shown in Figs. 1–5. Chiroptical properties for the complexes are shown in Table 1.

**Dioxygenation of Anisole by Pseudomonas putida.**—A fermenter was filled with tap-water (4 dm<sup>3</sup>) and buffer solutions of KH<sub>2</sub>PO<sub>4</sub> (66 g dm<sup>-3</sup> solution; 40 cm<sup>3</sup>) and aqueous K<sub>2</sub>HPO<sub>4</sub> (66 g dm<sup>-3</sup> solution; 80 cm<sup>3</sup>) were added to it. The temperature of the mixture was raised to 27.5 °C and a cell suspension of *Pseudomonas putida*, strain UV-4, (200 cm<sup>3</sup>) was added to it to give a turbidity reading in the range 12–20 OD units measured at 600 nm; after this, ethanol (20 cm<sup>3</sup>) was added to the mixture. Anisole (6 cm<sup>3</sup>, 55 mmol) was then added slowly by syringe pump (6 cm<sup>3</sup> h<sup>-1</sup>) to the mixture and the progression of the transformation was monitored at 30 min intervals by UV spectroscopy. When the concentration of the diol reached steady-state, the transformation was terminated by raising the pH of the broth to 10.

The broth was centrifuged to remove cellular debris. The aqueous supernatant was concentrated to 200–250 cm<sup>3</sup> by rotary evaporation at oil pump pressures and 50 °C. The products were extracted overnight with dichloromethane (2 dm<sup>3</sup>) on a continuous-flow extractor. Removal of dichloro-

methane under reduced pressure afforded a white crystalline solid (1.6 g) which was identified by NMR spectroscopy as crude 1-methoxycyclohexa-1,3-diene-5,6-diol  $\delta_H$ (CDCl<sub>3</sub>) 5.80, (3 H, m, 2,3,4-H), 4.20 (2 H, m, 5,5-H), 3.60 (4 H, br s, 1-OMe and 6-OH) and 3.40 (1 H, br s, 5-H) obtained as a 4:3 mixture with aromatic by-products. This mixture was used in the complexation step without purification, following the procedure described below.

#### Preparation of Neutral Diene Complexes

(-)-(1S)-Tricarbonyl( $\eta^4$ -5R,6S-dihydroxy-1-methoxycyclohexa-1,3-diene)iron(0) **3g**.—The crude mixture of 5,6-dihydroxy-1-methoxycyclohexa-1,3-diene and phenolic materials (0.75 g; 0.42 g, 3.0 mmol of diene), prepared from anisole as described above, was stirred with nonacarbonyldiiron (3.83 g, 10.6 mmol) under a nitrogen atmosphere at room temperature for 16 h to induce complex formation. The reaction mixture was then filtered through Kieselguhr and the filtrate evaporated to afford a crude product, which was purified by chromatography on silica. A green band containing metal carbonyl by-products was eluted with dichloromethane. Eluting with ether then afforded **3g** as a yellow crystalline product (0.43 g, 52%), m.p. 103.8–105.8 °C;  $[\alpha]_D$  -7.4 (*c* 1.0, CHCl<sub>3</sub>);  $\nu_{\max}$ (CHCl<sub>3</sub>)/cm<sup>-1</sup> 2053 and 1984;  $\delta_H$ (400 MHz; CDCl<sub>3</sub>) 5.33 (1 H, d, *J* 4.9, 2-H), 4.98 (1 H, dd, *J* 6.7 and 4.9, 2-H), 4.03 (1 H, d, *J* 6.1, 6-H), 3.90 (1 H, d, *J* 5.2, 5-H), 3.59 (3 H, s, 1-OMe), 3.19 and 3.04 (2 H, 2 br s, 5,6-OH) and 2.93 (1 H, dt, *J* 6.7, 2.0, 4-H); *m/z* 254 (M<sup>+</sup> - CO, 4), 226 (M<sup>+</sup> - 2CO, 8), 198 (M<sup>+</sup> - 3CO, 2) and 108 (C<sub>7</sub>H<sub>8</sub>O<sup>+</sup>, 100%) (Found: C, 42.6; H, 3.5. Calc. for C<sub>10</sub>H<sub>10</sub>FeO<sub>6</sub>: C, 42.6; H, 3.6%);  $\Delta\epsilon$ /mol<sup>-1</sup> cm<sup>-1</sup> -1.46 (360 nm, min.), +7.87 (305 nm, max.) (Fig. 2, trace iv).

(+)-(1S)-Tricarbonyl( $\eta^4$ -1-chloro-5R,6S-dihydroxycyclohexa-1,3-diene)iron(0) **3d**.—Solid 1-chloro-5,6-dihydroxycyclohexa-1,3-diene **2** (1 g, 6.8 mmol) was added, in one portion to a suspension of nonacarbonyldiiron (7.5 g, 20.7 mmol) in dry THF (40 cm<sup>3</sup>) under a nitrogen atmosphere, and the reaction mixture was stirred at room temperature. After 16 h, the reaction mixture was filtered through Kieselguhr and evaporated to afford a crude product, which was purified by chromatography on silica. A green band containing metal

\* Some CD spectra cited for comparison in Table 1 were recorded in solution in cyclohexane. The forms of these CD curves were very similar to those illustrated in Fig. 2, suggesting errors due to differential solvent effects are minimal in these cases.

carbonyl by-products was eluted with dichloromethane. Eluting with ether then afforded the *product 3d* as a yellow crystalline solid (0.27 g, 45%), m.p. 102.6–108.4 °C;  $[\alpha]_D +14.4$  (*c* 1.0 CHCl<sub>3</sub>);  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  2067 and 2004;  $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3)$  5.54 (1 H, dd, *J* 4.3, 1.8, 2-H), 5.13 (1 H, dd, *J* 4.6 and 6.7, 3-H), 3.89 (2 H, m, 5,6-H), 3.24 (1 H, m, 6-OH), 3.10 (1 H, d, *J* 4.3, 4-H) and 3.09 (1 H, br s, 5-OH); *m/z* 258 ( $\text{M}^+ - \text{CO}$ , 9), 230 ( $\text{M}^+ - 2\text{CO}$ , 17), 202 ( $\text{M}^+ - 3\text{CO}$ , 9) and 112 ( $\text{C}_6\text{H}_5\text{Cl}^+$ , 100%) (Found: C, 37.9; H, 2.3. Calc. for  $\text{C}_9\text{H}_7\text{ClFeO}_5$ : C, 37.7; H, 2.5%;  $\Delta\epsilon/\text{mol}^{-1} \text{ cm}^{-1}$  –0.54 (350 nm, min.) and +4.20 (300 nm, max.) (Fig. 2, trace ii).

(–)-(1*S*)-Tricarbonyl( $\eta^4$ -1-chloro-5*R*,6*S*-dimethoxycyclohexa-1,3-diene)iron(0) **3e**.—Iodomethane (1.9 cm<sup>3</sup>, 30.1 mmol) was added at room temperature to a stirred solution of 1-chloro-5,6-dihydroxycyclohexa-1,3-diene **2** (2 g, 13.7 mmol) in DMF (10 cm<sup>3</sup>) over barium oxide/barium hydroxide (4 g, 26.1 mmol, and 5 g, 3.1 mmol, respectively). After 20 min, the reaction was quenched with distilled water (50 cm<sup>3</sup>) and the reaction mixture vacuum filtered through Kieselguhr. The filtrate was extracted with ethyl acetate (3 × 25 cm<sup>3</sup>) and the combined extracts were washed with water (3 × 25 cm<sup>3</sup>), dried with saturated brine (50 cm<sup>3</sup>) and MgSO<sub>4</sub> and evaporated to afford the crude dimethyl diether as a yellow–brown oil (0.35 g, 26%);  $\delta_{\text{H}}(\text{CDCl}_3)$  6.24 (1 H, m, 2-H), 5.96 (2 H, m, 3,4-H), 4.28 (1 H, d, 6-H), 3.96 (1 H, d, 5-H) and 3.52 (6 H, br s, 5,6-OMe) together with aromatic by-products. This reaction was repeated and the combined crude products were used in the complexation step without further purification.

A solution of crude 1-chloro-5,6-dimethoxy diene (0.72 g, 4.1 mmol) in ether (40 cm<sup>3</sup>) was refluxed with nonacarbonyldiiron (7.3 g, 20.2 mmol) for 72 h after which it was filtered through alumina and evaporated. Chromatography (silica, 5% ether–95% light petroleum) of the residue afforded the *product 3e* as a yellow crystalline solid (0.31 g, 24%), m.p. 126.1–129.7 °C;  $[\alpha]_D -15.4$  (*c* 1.0, CHCl<sub>3</sub>);  $\nu_{\max}(\text{C}_6\text{H}_{12})/\text{cm}^{-1}$  2071, 2015 and 1989;  $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3)$  5.47 (1 H, dd, *J* 4.6 and 2.1, 2-H), 5.08 (1 H, dd, *J* 6.7, 4.6, 3-H), 3.57 (4 H, br s, 6-H and 6-OMe), 3.43 (1 H, s, 5-H), 3.42 (3 H, s, 5-OMe) and 3.03 (1 H, dt, *J* 6.7 and 2.1, 4-H);  $\delta_{\text{C}}(100 \text{ Mz})$  209.2 (CO), 87.0 (C-2), 85.6 (C-3), 82.9 (C-1), 79.1 (C-6), 78.5 (C-5), 61.5 (C-4), 60.9 (6-OMe) and 58.3 (5-OMe); *m/z* 314 ( $\text{M}^+$ , 0.8), 286 ( $\text{M}^+ - \text{CO}$ , 29), 260 ( $\text{M}^+ - 2\text{CO}$ ; <sup>37</sup>Cl, 33), 258 ( $\text{M}^+ - 2\text{CO}$ ; <sup>35</sup>Cl, 100), 230 ( $\text{M}^+ - 3\text{CO}$ , 3), 168 ( $\text{C}_6\text{H}_5\text{ClFe}^+$ , 47) and 134 ( $\text{C}_6\text{H}_6\text{Cl}^+$ , 77%) (Found: C, 42.0; H, 3.4. Calc. for  $\text{C}_{11}\text{H}_{11}\text{ClFeO}_5$ : C, 42.0; H, 3.5%;  $\Delta\epsilon/\text{mol}^{-1} \text{ cm}^{-1}$  –0.19 (355 nm, min.) and +1.37 (305 nm, max.) (Fig. 2, trace i).

Further elution with 10% ether–90% light petroleum afforded a second complex as a yellow oil (0.27 g). This was tentatively identified as tricarbonyl( $\eta^4$ -1-chloro-5-hydroxy-6-methoxycyclohexa-1,3-diene)iron(0) from its spectroscopic properties;  $\nu_{\max}(\text{C}_6\text{H}_{12})/\text{cm}^{-1}$  2048, 1990 and 1976;  $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3)$  5.40 (1 H, dd, *J* 4.6 and 2.1, 2-H), 5.04 (1 H, dd, *J* 6.7 and 4.6, 3-H), 3.84 (1 H, m, 5-H), 3.52 (4 H, s, 6-H, 6-OMe), 3.30 (1 H, s, 5-OH) and 3.04 (1 H, m, 4-H); *m/z* 300 ( $\text{M}^+$ ).

(+)-(1*S*)-Tricarbonyl( $\eta^4$ -5*R*,6*S*-diacetoxycyclohexa-1,3-diene)iron(0) **3f**.—Acetic anhydride (2.13 cm<sup>3</sup>, 22.6 mmol) was added to a solution of 1-chloro-5,6-dihydroxycyclohexa-1,3-diene **2** (1.5 g, 10.3 mmol) in pyridine (10 cm<sup>3</sup>) at –15 °C and the reaction mixture was kept at 12 °C overnight. Excess of pyridine was then removed by rotary evaporation and the residue dissolved in ether (25 cm<sup>3</sup>). The solution was washed with aqueous sodium hydrogen carbonate (10% solution; 4 × 25 cm<sup>3</sup>) and dried with saturated brine (50 cm<sup>3</sup>) and MgSO<sub>4</sub>, to afford the crude diacetate (0.89 g, 38%). This was identified by its <sup>1</sup>H NMR spectrum [ $\delta(\text{CDCl}_3)$  6.24 (1 H, m, 2-H), 5.84 (2 H, m, 3,4-H), 5.72 (1 H, br s, 6-H), 5.68 (1 H, br s, 5-H), 2.12 (3 H, s, 6-OAc) and 2.08 (3 H, s, 5-OAc)]. This

material was used without purification in the complexation step. A solution of the crude diene (0.9 g, 6.1 mmol) in toluene (30 cm<sup>3</sup>) was sonicated with nonacarbonyldiiron (11 g, 30.5 mmol) for 22 h. Filtration and evaporation of the reaction mixture followed by chromatography (silica, 50:50 ether–light petroleum) of the residue afforded the *product 3f* as a dull yellow crystalline solid (0.16 g, 6.3%); decomp. 130 °C;  $[\alpha]_D +28.0$  (*c* 1.0, CHCl<sub>3</sub>);  $\nu_{\max}(\text{C}_6\text{H}_{12})/\text{cm}^{-1}$  2070, 2012, 1997 and 1746;  $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3)$  5.63 (1 H, m, 2-H), 5.21 (1 H, m, 3-H), 5.10 (1 H, d, *J* 5.8, 6-H), 4.91 (1 H, d, 5-H), 2.94 (1 H, d, *J* 6.1, 4-H), 2.14 (3 H, s, 6-OAc) and 2.08 (3 H, s, 5-OAc);  $\delta_{\text{C}}(100 \text{ MHz}; \text{CDCl}_3)$  208 (s, CO), 169.7 (s, 6-OAc), 169.3 (s, 5-OAc), 85.6 (d, C-2), 82.9 (s, C-1), 79.9 (d, C-3), 72.9 (d, C-4), 69.9 (d, C-6), 60.2 (d, C-5), 20.5 (q, 6-OAc) and 20.3 (q, 5-5-OAc); *m/z* 314 ( $\text{M}^+ - 2\text{CO}$ , 1) and 112 ( $\text{C}_6\text{H}_5\text{Cl}^+$ , 100%) (Found: C, 42.1; H, 3.0. Calc. for  $\text{C}_{13}\text{H}_{11}\text{ClFeO}_7$ : C, 42.1; H, 2.9%;  $\Delta\epsilon/\text{mol}^{-1} \text{ cm}^{-1}$  –0.19 (350 nm, min.) and +1.15 (300 nm, max.) (Fig. 2, trace iii).

(–)-(2*S*)-Tricarbonyl( $\eta^4$ -6*R*-acetoxycyclohexa-2,4-dienone)iron(0) **9**.—Aqueous hexafluorophosphoric acid (52% solution; 0.5 cm<sup>3</sup>, 1.78 mmol) was added to a stirred solution of **3g** (0.16 g, 0.55 mmol) in acetic anhydride (2 cm<sup>3</sup>). After 3 h, dilution of the reaction mixture with diethyl ether (10 cm<sup>3</sup>) precipitated a mixture of salts (0.13 g, 51%) (Found: C, 31.7; H, 2.3. Calc. for  $\text{C}_{12}\text{H}_{11}\text{F}_6\text{FeO}_6\text{P}$ : C, 31.9; H, 2.5%;  $\nu_{\max}(\text{MeCN})/\text{cm}^{-1}$  2117, 2107 and 2058. This mixture of salts is provisionally assigned as tricarbonyl( $\eta^5$ -6-endo-acetoxy-1-methoxycyclohexadienyl)iron(1+) hexafluorophosphate(1–) [ $\delta_{\text{H}}(400 \text{ MHz}; \text{MeCN})$  6.72 (1 H, t, *J* 6.1, 3-H), 6.00 (1 H, t, 6.1, 4-H), 5.53 (1 H, s, 6-H), 4.62 (1 H, d, *J* 6.1, 2-H), 3.83 (1 H, d, *J* 6.1, 5-H), 3.70 (3 H, s, 1-OMe) and 2.16 (3 H, s, 6-endo-OAc)] and tricarbonyl( $\eta^5$ -6-endo-acetoxy-2-methoxycyclohexadienyl)iron(1+) hexafluorophosphate(1–) [ $\delta_{\text{H}}(400 \text{ MHz}; \text{MeCN})$  6.88 (1 H, d, *J* 5.8, 3-H), 5.95 (1 H, t, *J* 5.8, 4-H), 4.93 (1 H, s, 6-H), 3.98 (1 H, d, *J* 5.8, 5-H), 3.74 (3 H, s, 2-OMe), 3.72 (1 H, s, 1-H) and 1.92 (3 H, s, 6-endo-OAc)] on the basis of the NMR data presented and its conversion into product **9**. The reaction was repeated, and the samples of salts were combined. The mixture of salts was taken on to the next step without separation or further characterisation. A portion (0.182 g; 0.126 g, 0.28 mmol, of the 1-methoxy isomer) was dissolved in acetonitrile (5 cm<sup>3</sup>) and dilute aqueous hydrochloric acid (5 cm<sup>3</sup>) was added to the solution, which was then stirred at room temperature for 30 min. The reaction mixture was then extracted with diethyl ether (3 × 15 cm<sup>3</sup>) and the combined extracts were washed with water (2 × 20 cm<sup>3</sup>) and dried with saturated brine (25 cm<sup>3</sup>) and MgSO<sub>4</sub>. Removal of excess of solvent afforded the *product (–)9* as a yellow crystalline solid (0.037 g, 45%), m.p. 108–111 °C;  $[\alpha]_D -327.0$  (*c* 0.3, CHCl<sub>3</sub>);  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  2072, 2015, 1998, 1762 and 1703;  $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3)$  5.88 (1 H, ddd, *J* 6.10, 4.6 and 1.8, 3-H), 5.66 (1 H, dd, *J* 6.7 and 4.6, 4-H), 4.99 (1 H, br s, 6-H), 3.32 (1 H, dd, *J* 6.1 and 1.5, 2-H), 3.21 (1 H, dt, *J* 6.7 and 1.8, 5-H) and 2.18 (3 H, s, 6-OAc); *m/z* 264 ( $\text{M}^+ - \text{CO}$ , 3), 236 ( $\text{M}^+ - 2\text{CO}$ , 15) and 208 ( $\text{M}^+ - 3\text{CO}$ , 100%) (Found: C, 45.2, H, 2.6. Calc. for  $\text{C}_{11}\text{H}_8\text{FeO}_6$ : C, 45.2; H, 2.8%;  $\Delta\epsilon/\text{mol}^{-1} \text{ cm}^{-1}$  –8.40 (354 nm, min.) and +9.10 (307 nm, max.) (Fig. 4, trace iii).

(–)-(1*R*)-Tricarbonyl[ $\eta^4$ -5*R*-hydroxy-1-(1'-oxoethyl)cyclohexa-1,3-diene]iron(0) **10a**.—Microbial dioxygenation of acetophenone (36 g, 0.3 mol) was performed as described for anisole to afford a crude biotransformation product, which was isolated by continuous extraction of the aqueous phase using chloroform. Nonacarbonyldiiron (6.87 g, 18.9 mmol) was added to a stirred solution of the crude dienes (2.86 g) in THF (65 cm<sup>3</sup>) and the reaction mixture was stirred for 65 h under a nitrogen atmosphere. The reaction mixture was filtered through Kieselguhr and the excess of solvent and pentacarbonyliron was removed under reduced pressure to afford a dark brown oil.

Column chromatography (silica gel, light petroleum–diethyl ether, gradient elution) afforded a golden oil (1.72 g) which was found to consist of an 11:2 mixture of two complexes. Further chromatography (40% diethyl ether in light petroleum) afforded the product **10a** (1.4 g, 2%). This product was converted without delay into the  $\eta^5$  cation which was reduced to form **10b**.

(–)(1R)-Tricarbonyl[ $\eta^4$ -5R-hydroxy-1-(1'-oxoethyl)cyclohexa-1,3-diene]iron(0) **10a**. [ $\alpha$ ]<sub>D</sub> –47.2 (*c* 0.9 CHCl<sub>3</sub>);  $\nu_{\max}$ (CHCl<sub>3</sub>)/cm<sup>–1</sup> 2062, 2000 and 1666;  $\delta_{\text{H}}$ (400 MHz; CDCl<sub>3</sub>) 6.02 (1 H, d, *J* 4.6, 2-H), 5.33 (1 H, m, *J* 6.9, 3-H), 4.01 (1 H, m, 5-*exo*-H), 3.36 (1 H, d, *J* 6.8, 4-H), 2.19 (3 H, s, 1-COCH<sub>3</sub>), 2.13 (1 H, br s, 5-*endo*-OH), 1.93 (1 H, dd, *J* 16.0 and 4.6, 6-*endo*-H) and 1.84 (1 H, dd, *J* 16.0 and 2.3, 6-*exo*-H); *m/z* 250 (M<sup>+</sup> – CO, 10), 222 (M<sup>+</sup> – 2CO, 26), 194 (M<sup>+</sup> – 3CO, 17), 176 (C<sub>8</sub>H<sub>8</sub>FeO<sup>+</sup>, 82), 120 (C<sub>8</sub>H<sub>8</sub>O<sup>+</sup>, 42) and 105 (C<sub>7</sub>H<sub>5</sub>O<sup>+</sup>, 100%) [Found: *m/z* 278.9956 (M<sup>+</sup> + H). C<sub>11</sub>H<sub>11</sub>FeO<sub>5</sub> requires 278.9956;  $\Delta\epsilon$ /mol<sup>–1</sup> cm<sup>–1</sup> +3.00 (383 nm, max.), –7.04 (341 nm, min.), and +2.62 (312 nm, max.) (Fig. 5, trace i). The minor product was tentatively identified as tricarbonyl[ $\eta^4$ -5,6-di-*endo*-dihydroxy-1-(1'-oxoethyl)cyclohexa-1,3-diene]iron(0) on the basis of NMR spectroscopic results;  $\delta_{\text{H}}$ (400 MHz; CDCl<sub>3</sub>) 5.82 (1 H, dd, *J* 4.57 and 1.71, 2-H), 5.40 (1 H, dd, *J* 6.86 and 4.57, 3-H), 3.92 and 3.78 (2 H, 2 br s, 5,6-H) and 3.42 (1 H, dt, *J* 6.86 and 1.71, 4-H).

(–)(1R)-Tricarbonyl[ $\eta^5$ -1-(1'-oxoethyl)cyclohexadienyl]iron(1+) Hexafluorophosphate(1–).—A solution of the 5-*endo*-hydroxy complex **10a** (1.44 g, 5.2 mmol) in acetic anhydride (5 cm<sup>3</sup>) was treated with hexafluorophosphoric acid (75% aqueous solution; 2.9 cm<sup>3</sup>, 14.8 mmol) at low temperature (–15 °C). The reaction mixture was allowed to reach room temperature when a yellow suspension was formed. After 3 h, IR spectroscopy revealed the complete consumption of starting material. The product (1.81 g, 86%), precipitated by the addition of diethyl ether (20 cm<sup>3</sup>) to the reaction mixture, was collected as a yellow precipitate by vacuum filtration; [ $\alpha$ ]<sub>D</sub> –74.0 (*c* 0.4, MeCN);  $\nu_{\max}$ (MeCN)/cm<sup>–1</sup> 2121, 2075 and 1713;  $\delta_{\text{H}}$ (400 MHz, (CD<sub>3</sub>)<sub>2</sub>CO) 7.68 (1 H, t, *J* 6.3, 3-H), 6.84 (1 H, d, *J* 6.3, 2-H), 6.41 (1 H, t, *J* 6.3, 4-H), 5.05 (1 H, t, *J* 6.3, 5-H), 3.65 (1 H, dt, *J* 16.0 and 6.3, 6-*endo*-H), 2.20 (1 H, d, *J* 16.0, 6-*exo*-H) and 2.05 (3 H, s, 1-COCH<sub>3</sub>) (Found: C, 32.0; H, 2.2. Calc. for C<sub>11</sub>H<sub>6</sub>F<sub>6</sub>FeO<sub>4</sub>P: C, 32.5; H, 2.2%).

In an alternative procedure, a solution of triphenylcarbenium hexafluorophosphate (0.198 g) in dry dichloromethane (3 cm<sup>3</sup>) was added to a solution of the 1-acyl complex **10a** (0.089 g, 0.34 mmol) also in dry dichloromethane (2 cm<sup>3</sup>). After 20 h the product was precipitated by the addition of moist diethyl ether (20 cm<sup>3</sup>) to the reaction mixture. The product (0.063 g, 46%) was collected by vacuum filtration, washed with diethyl ether (2 × 5 cm<sup>3</sup>) and water (5 cm<sup>3</sup>), and dried *in vacuo*.

(–)(1R)-Tricarbonyl[ $\eta^4$ -1-(1'-oxoethyl)cyclohexa-1,3-diene]iron(0) **10b**.—A solution of (–)(1R)-tricarbonyl[ $\eta^5$ -1-(1'-oxoethyl)cyclohexadienyl]iron(1+) hexafluorophosphate(1–) (0.28 g, 0.69 mmol) in dry acetonitrile (6 cm<sup>3</sup>) was treated with sodium borohydride (0.019 g, 0.5 mmol) at 0 °C. After being stirred for 10 min the reaction mixture was treated with distilled water (25 cm<sup>3</sup>) and the product extracted with diethyl ether (3 × 25 cm<sup>3</sup>). The combined ethereal layers were washed with water (3 × 25 cm<sup>3</sup>) and dried with saturated brine and MgSO<sub>4</sub>. Removal of the excess of solvent afforded a brown oil which was subjected to column chromatography (silica gel, 40% diethyl ether in light petroleum) to afford the title compound as a yellow oil (0.134 g, 0.51 mmol, 74%); [ $\alpha$ ]<sub>D</sub> –201.5 (*c* 0.6, CHCl<sub>3</sub>);  $\nu_{\max}$ (C<sub>6</sub>H<sub>12</sub>)/cm<sup>–1</sup> 2057, 1996 and 1678;  $\delta_{\text{H}}$ (400 MHz; CDCl<sub>3</sub>) 6.07 (1 H, d, *J* 4.3, 2-H), 5.41 (1 H, m, 3-H), 3.42 (1 H, m, 4-H), 2.22 (3 H, s, 1-COCH<sub>3</sub>) and 2.1–1.4 (4 H, m, 5,6-*endo*-H and 5,6-*exo*-H);  $\delta_{\text{C}}$ (100 MHz, CDCl<sub>3</sub>) 210 (s, 1-COCH<sub>3</sub>), 203 (s, CO), 87.1 (s, C-2), 85.6 (s, C-3), 73.4 (s, C-1),

63.2 (s, C-4), 27.0 and 25.8 (2 s, C-5 and C-6) and 23.6 (s, 1-COCH<sub>3</sub>);  $\Delta\epsilon$ /mol<sup>–1</sup> cm<sup>–1</sup> +3.81 (383 nm, max.), –7.98 (341 nm, min.) and +4.87 (298 nm, max.) (Fig. 5, trace ii) [lit.,<sup>21</sup>  $\nu_{\max}$ (thin film)/cm<sup>–1</sup> 2055, 1990 and 1680;  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 6.06 (1 H, d, *J* 4.5, 2-H), 5.40 (1 H, m, *J* 6, 3-H), 3.42 (1 H, m, *J* 6, 4-H) and 2.5–1.4 (7 H m, 1-COCH<sub>3</sub>, 5,6-*endo*-H and 5,6-*endo*-H); racemate].

(–)(1R)-Tricarbonyl[ $\eta^4$ -5S-hydroxy-1-(1'-oxoethyl)cyclohexa-1,3-diene]iron(0) **10c**.—A solution of (–)(1R)-tricarbonyl[ $\eta^5$ -1-(1'-oxoethyl)cyclohexadienyl]iron(1+) hexafluorophosphate(1–) (0.2 g, 0.50 mmol) in acetonitrile (3 cm<sup>3</sup>) was treated with saturated aqueous sodium hydrogen carbonate (2 cm<sup>3</sup>) and the reaction mixture stirred at room temperature for 10 min until gas evolution ceased. The reaction mixture was diluted with water (10 cm<sup>3</sup>) and extracted with diethyl ether (3 × 25 cm<sup>3</sup>). The combined extracts were washed with water and dried with saturated brine and MgSO<sub>4</sub>. Removal of diethyl ether afforded the crude product which was purified by column chromatography (silica gel, diethyl ether). The excess of diethyl ether was removed under reduced pressure to afford the product as a yellow crystalline solid (0.071 g, 51%). An analytically pure sample was obtained by recrystallisation from chloroform; m.p. 102–105 °C; [ $\alpha$ ]<sub>D</sub> –243.0 (*c* 1.0 CHCl<sub>3</sub>);  $\nu_{\max}$ (CHCl<sub>3</sub>)/cm<sup>–1</sup> 2063, 2001, 1987 and 1666;  $\delta_{\text{H}}$ (400 MHz; CDCl<sub>3</sub>) 6.26 (1 H, d, *J* 4.9, 2-H), 5.51 (1 H, dd, *J* 6.1 and 4.9, 3-H), 4.48 (1 H, m, *J* 10.0, 5-H), 3.22 (1 H, m, 4-H), 2.77 (1 H, dd, *J* 15.0 and 10.0, 6-*endo*-H), 2.16 (3 H, s, 1-COCH<sub>3</sub>), 1.70 (1 H, d, *J* 5.8 Hz, 5-*endo*-OH) and 1.43 (1 H, dd, *J* 15.1 and 2.9, 6-*exo*-H); *m/z* 250 (M<sup>+</sup> – CO, 0.2), 222 (M<sup>+</sup> – 2CO, 0.3), 176 (C<sub>8</sub>H<sub>8</sub>FeO<sup>+</sup> 0.9), 120 (C<sub>8</sub>H<sub>8</sub>O<sup>+</sup> 41) and 105 (C<sub>7</sub>H<sub>5</sub>O<sup>+</sup>, 100%) (Found: C, 47.8; H, 3.5. Calc. for C<sub>11</sub>H<sub>10</sub>FeO<sub>5</sub>: C, 47.5; H, 3.6%);  $\Delta\epsilon$ /mol<sup>–1</sup> cm<sup>–1</sup> +1.76 (384 nm, max.), –2.84 (339 nm, min.) and +2.10 (310 nm, max.) (Fig. 5, trace iii).

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Paper 4/01237B

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