Assignment of Absolute Configurations from the Circular Dichroism Spectra of Cyclic η^4-Diene Complexes of $Fe(CO)_3$

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The circular dichroism spectra of a set of 1-substituted tricarbonyl(η^4-cyclohexadiene)iron(0) complexes with comparable absolute configurations reveal a pattern of bands that correlates with the absolute stereochemistry of the complexes; the nature of the substituents attached at C-1 of the diene is important in the interpretation of the CD spectra of these compounds, since the sign of the highest wavelength band can be reversed for a particular absolute configuration, depending on whether electron-donating or electron-withdrawing substituents are present.

Organometallic π-complexes often show circular dichroism (CD) spectra, which contain characteristic bands that can provide a useful indication of their absolute configurations.[1–4] In the case of tricarbonyliron complexes, which are extensively employed in organic synthesis,[5] reliable CD correlations are particularly valuable to assist the development of new applications of homochiral complexes in enantioselective work.[6] Correlations between the forms of CD curves, and the absolute configurations of these complexes, have been discussed by several groups of workers.[2] A relationship between the sign of a high wavelength CD band, and the absolute configuration of the metal π-complex, has been proposed.[3] Recently, a study of the relationship between the CD spectra of acyclic η^4-diene complexes and their absolute configurations has been described.[4] In view of the current interest in this area, we report the results of a related study of cyclic diene complexes in which a similar type of correlation is possible. Our results are of particular significance, since, with the electron-donating substituents used in this investigation, the relationship between the sign of $\Delta\varepsilon$ for the highest wavelength band, and the absolute configuration of the π-complex, is reversed when compared with results obtained by other workers[4] using complexes bearing electron-withdrawing substituents. Our results indicate that the nature of substituents must be taken into account when interpreting CD spectra of complexes of this type.

A selection of related optically active 1-substituted tricarbonyliron cyclohexa-1,3-diene-5,6-diol complexes† (Scheme 1) have been prepared by arene dioxygenation (using the microorganism *Pseudomonas putida*) and complexation with $Fe_2(CO)_9$, following standard procedures described earlier[7] for the preparation of complex **1a**. Corresponding ether and ester derivatives were obtained by derivatisation (MeI, BaO, $BaCO_3$ for **2a,b** or Ac_2O, pyridine for **3a,b**) prior to the complexation step. Chiroptical data from CD spectra obtained from these complexes are listed in Table 1. In view of the similarity between the CD spectra of all the complexes in this series, it is reasonable to propose that all share the same absolute configuration. Indeed, the absolute configurations of the complex **1a** and its methyl ether have been determined unambiguously by chemical correlation.[6,7] The absolute configuration of 1-chlorocyclohexa-1,3-diene-5,6-diol has been inferred from two separate CD investigations of metal-free systems,[8] and has been assigned on this basis to be the

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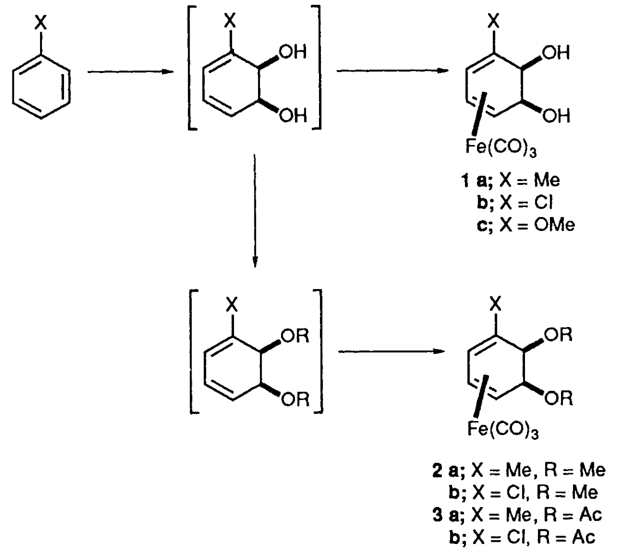
† All new complexes have been characterised by NMR, IR, and mass spectrometry and by microanalysis or high resolution mass spectrometry.

Table 1 Chiroptical properties of cyclohexadiene complexes

Complex			Circular dichroism data[a]					Polarimetry data[b]	
	X	R	λ_1/ nm	$\Delta\varepsilon_1$/ cm^2 mol^{-1}	λ_2/ nm	$\Delta\varepsilon_2$/ cm^2 mol^{-1}	Conc./ mg dm^{-3}	$[\alpha]_D$ (°)	Conc./ mg dm^{-3}
1a	Me	—	—	—	296	+5.12	50	+72.0	5
1b	Cl	—	350	−0.54	300	+4.20	50	+14.4	5
1c	OMe	—	360	−1.46	305	+7.87	50	−7.4	10
2a	Me	Me[c]	357	−0.38	300	+5.80	10	+142.9	10
2b	Cl	Me	355	−0.19	305	+1.30	30	−15.4	10
3a	Me	Ac	352	−0.53	298	+6.69	50	+94.4	10
3b	Cl	Ac	350	−0.19	300	+1.15	30	+28.0	10

[a] Recorded in $CHCl_3$ at 22 °C. [b] Recorded in $CHCl_3$ at 25 °C. [c] See ref. 6.



1 a; X = Me
b; X = Cl
c; X = OMe

2 a; X = Me, R = Me
b; X = Cl, R = Me
3 a; X = Me, R = Ac
b; X = Cl, R = Ac

Scheme 1

same in the chlorodiene complex **1b**. For the 1-methoxy substitution pattern in **1c**, CD comparison with a simple 1-methoxydiene complex of known absolute configuration,[9] also supports the assignment of absolute configurations made in Scheme 1. Furthermore, in general, *P. putida* effects arene dioxygenation with consistent enantioface selectivity,[10] and, since complexation by $Fe(CO)_3$ is known to occur on the face of the diene bearing the two OH groups,[6,11] the series of complexes (**1a–c**, **2a,b** and **3a,b**) is well suited for use to establish the relationship between CD spectra and the absolute configuration of the (cyclohexadiene)$Fe(CO)_3$ moiety. These complexes constitute an internally consistent set of compounds.

Analysis of the CD bands indicated in Table 1 shows that the highest wavelength band (λ_1) at around 350–360 nm had a negative $\Delta\varepsilon$ in all cases except **1a** for which the CD signal was too small to measure in this region. With all the complexes, a CD maximum was observed in the region 295–305 nm (λ_2). The CD profiles in general took the form shown for curve *A* in Fig. 1. In the case of **1c** a further comparison is possible, since the absolute configuration is known[9] for the parent 1-OMe substituted complex **4**, which lacks the diol substituents. We have measured the CD spectrum of the (1*R*) isomer of this complex for comparison with **1c**. In **4**, the metal is attached to the opposite face of the diene; **4** and **1c** contain epimeric regions of planar chirality. As expected, the CD spectrum for **4** (see Fig. 1, curve *B*) took the opposite form to that found for complexes of type (**1**, **2** and **3**). This comparison supports our proposal that the pattern of two bands at λ_1 and λ_2, illustrated by curve *A* in Fig. 1, correlates with the (1*S*) planar chirality of the 1-substituted diene complexes shown in Scheme 1.

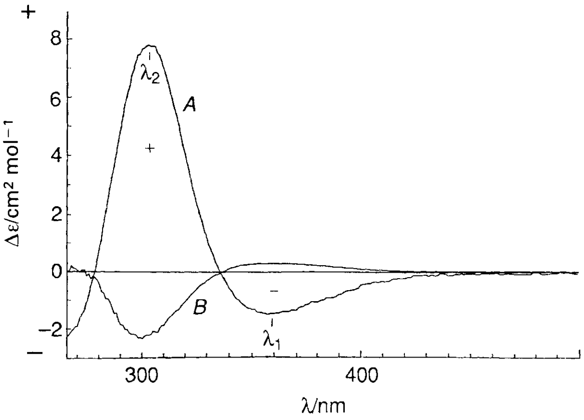
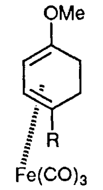
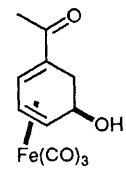


Fig. 1 CD spectra (*A*: compound **1c**; *B*: compound **4**)



4 R = H
5 R = Me



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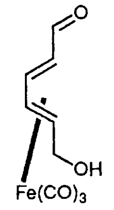

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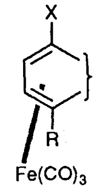

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The UV spectra of three of the complexes (**1a**: ε 3200, 280 nm, 12500, 227 nm; **1b**: ε 5000, 280 nm, 17000, 233 nm; **2a**: ε 5700, 280 nm, 19700, 228 nm) were also recorded and found to be very similar in form. The diether **2a** showed the largest extinction coefficients; this spectrum is shown in Fig. 2. The region corresponding to λ_1 and λ_2 in the CD spectrum has the form of a simple curve descending from ε_{max} at 280 nm in the UV spectrum. No discrete UV bands were resolved in this region.

In complexes with a more extensive chromophore, for example **6**, we have observed[12] an additional CD band with λ_{max} at 385 nm. This same high wavelength band appears in the chiroptical data reported[4] for acyclic complexes, where a positive $\Delta\varepsilon$ in this region correlates with, for example, the absolute configuration indicated for complex **7**. The second and third CD bands, however, appearing in the regions 340–360 nm and 280–300 nm for the acyclic complexes, show a similar form to the CD profile observed in our present study. These two sets of results can be reconciled if C-1 substituents, which can interact directly with the π-system (X = Cl, OMe, COMe and CO_2Me, for example) are regarded as dominating the CD spectrum for tricarbonyliron complexes of type (**8**, R

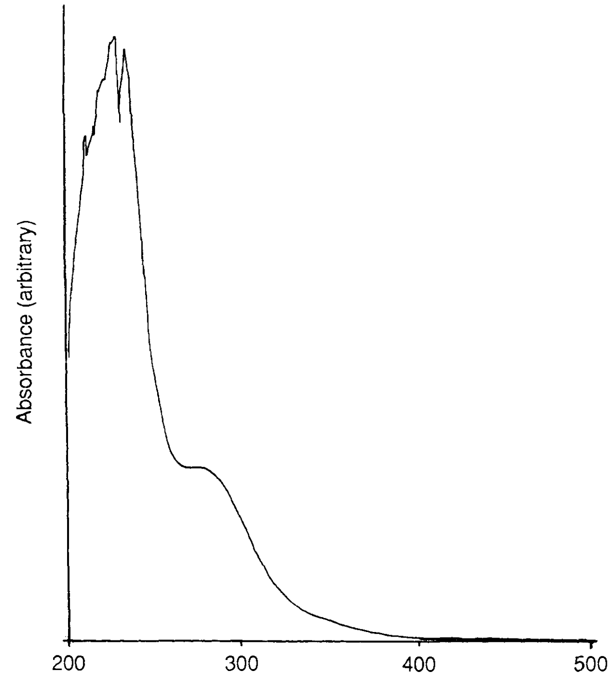

Fig. 2 UV spectrum of compound **2a**

= alkyl).‡ Maxima at *ca.* 290 nm and minima at *ca.* 350 nm correlate with the (1*S*) configuration of **8**. Because of the alternating pattern of bands, it is a maximum that is observed at *ca.* 400 nm in cases with X = COMe or CO_2Me where the additional high wavelength band is present.

These results indicate that patterns of bands in the CD spectra of tricarbonyl(η^4-cyclohexa-1,3-diene)iron(0) complexes show a consistent form that correlates with the absolute configurations of the complexes examined. In the empirical interpretation of CD spectra of complexes of this type, the nature of substituents on the complex must be taken into account, since this determines the number of bands appearing in the alternating sequence, and hence the sign of the highest wavelength band that correlates with a particular absolute configuration.

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‡ Support for this proposal, in the cases with cyclic complexes, can be gained by examination of examples bearing both electron-donating and alkyl substituents. For this purpose, we have examined the disubstituted complex **5**, in which both OMe and Me substituents are present at opposing ends of the π-system. The CD curve for this material corresponds to that measured for **4**, indicating in this case the negligible influence of the Me substituent.