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Stereocontrolled Preparation of Stereocomplementary Regioisomeric Tricarbonyliron Complexes in Enantiopure Form

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Abstract—The use of ultrasound to form ferralactone complexes from an enantiomerically pure allylic epoxide with an adjacent hydroxymethyl substituent affords a pair of stereocomplementary isomers that offer a regioconvergent route to the same chiral pentadienyliron complex. The enantiomeric purity, CD properties, and absolute configurations of intermediate η^4-diene complexes are reported, and X-ray diffraction analysis of a pair of rearranged ferralactone complexes establishes their relative stereochemistries, and confirms their absolute stereochemistries.

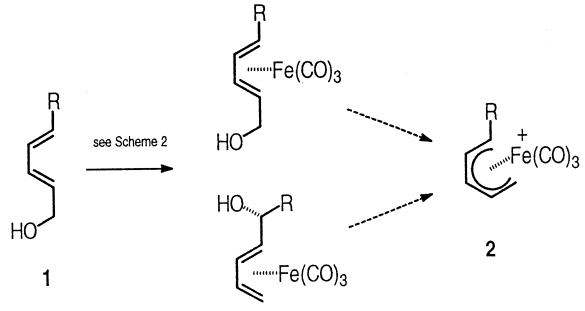
Introduction

The tricarbonyliron control group offers powerful stereodirection and activation effects, but its use in enantioselective organic synthesis requires efficient methods to prepare optically pure diene and dienyl complexes. Originally, classical resolution procedures[1] were employed, and strategies for kinetic resolution of racemic complexes[2] and asymmetric induction during complexation of prochiral ligands[3] have been examined. With acyclic complexes, the use of chiral allylborane[4] and alkylzinc[5] reagents and biological esterification and reduction procedures[6] have proved particularly effective, while in the cyclic (cyclohexadiene) series, asymmetric delivery of $Fe(CO)_3$ from chiral azadiene complexes to prochiral dienes,[7] and an approach based on the biodioxygenation of arenes followed by diastereoselective complexation of the resulting diene ligand, have given good results.[8,9] In this way, a derivative of the simplest of the chiral cyclohexadienyl complex [tricarbonyl(η^5-1-methylcyclohexadienyl)iron(1+) PF_6(1−)] has been obtained in optically pure form.[8] Although this procedure requires a separation of regioisomers, the corresponding preparation[9] of the 1-trifluoromethyl analogue was fully controlled.

In a recent development, ferralactone complexes have been shown[10,11] to be important as intermediates to non-racemic η^4 tricarbonyliron complexes of dienes as well as valuable control groups[12,13] and important as synthetic intermediates[14] in their own right. Access to diene complexes via ferralactones is attractive because the allylic epoxide starting materials are themselves easily obtained by asymmetric induction using the widely applicable Sharpless epoxidation and dihydroxylation methods. Unfortunately, there is a difficulty with the approach as the iron-mediated opening of the epoxide typically lacks diastereoselectivity, so that the chirality of the epoxide is not efficiently relayed to control the planar chirality in the binding of the iron moiety to the ligand. Modification of the complexation procedure to give access, not to mixtures of diastereoisomers, but to mixtures of regioisomers, however, would ultimately allow stereoconvergent utilisation of the products via cationic η^5 intermediates of type **2** (Scheme 1).

Results and Discussion

We report here the results of an initial study of the enantioselective preparation of tricarbonyl(η^5-1-methylpentadienyl)iron(1+) PF_6(1−) **2** (R=Me), the acyclic counterpart to tricarbonyl(η^5-1-methylcyclohexadienyl)-iron(1+) PF_6(1−). Racemic η^4 dienol complexes are easily



Scheme 1.

Keywords: tricarbonyliron; dienyl complexes; ferralactone; enantioselective synthesis; circular dichroism; absolute configuration.

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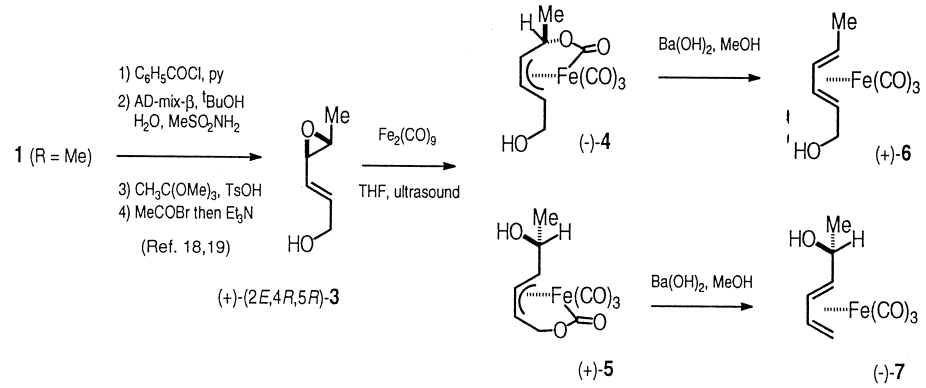
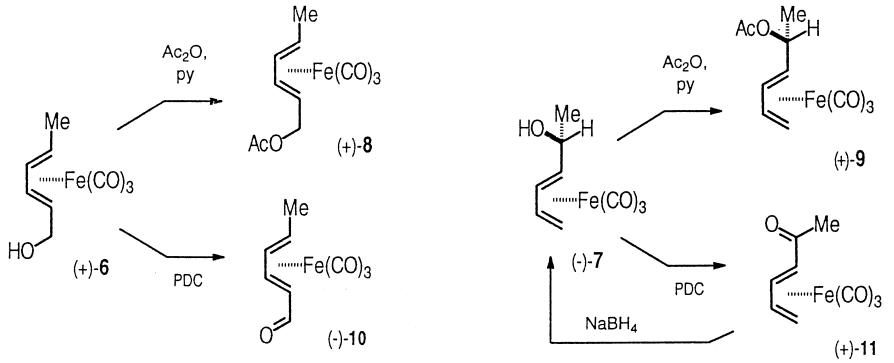


Scheme 2.

made by direct complexation with $Fe(CO)_5$ or $Fe_2(CO)_9$, but an important alternative has been described by Aumann[15] and more recently by Ley, Meek, Metten and Piqué[16] and Böhner, Hampel and Schobert[17] through the opening of alkenylepoxides with $Fe_2(CO)_9$. The required (2*E*,4*R*,5*R*)-epoxide **3** was obtained in enantiopure form as described by Sharpless,[18,19] using asymmetric dihydroxylation of the benzoate of **1** (R=Me) as the starting point (Sharpless asymmetric epoxidation is unsatisfactory with dienols[20]). Following this route (Scheme 2), using AD-mix-β, we can prepare the epoxide starting material in a convenient way. In practice, the optical purity of the product varies slightly from run to run (we have observed $[\alpha]_D$ values in the range 48–53), but a typical large scale preparation of **3** gave a sample with $[\alpha]_D=+53.3$ ($c=2$, $CHCl_3$), which has proved adequate to give access to optically pure metal complexes. Ley, Burkhardt, Cox and Meek,[21] working in the racemic series (obtained by direct epoxidation of ethyl sorbate), have described an important anomalous complexation of **3** which affords a rearranged secondary alcohol as well as the normal pair of *endo* and *exo* primary alcohols. We have found that use of sonication[22] to effect reaction of (+)-**3** with $Fe_2(CO)_9$ affords only two products, the *endo* complex (−)-**4** and the regioisomeric secondary alcohol (+)-**5** in roughly equal amounts (47:53 by nmr). Thus under the ultrasound conditions, the formation of the rearranged product is far more favoured than is the case with the standard conditions[23] (we obtained **4** in 43% yield by ultrasound, compared to 20% reported previously[21]). As described earlier,[21] these ferralactone isomers are difficult to separate, so the mixture was converted directly into the corresponding η^4 diene complexes by the normal procedure[15] by treatment with barium hydroxide. In this way, (+)-**6** and (−)-**7** were obtained in a combined yield of 80% (37 and 43% yields, respectively) in a convenient and straightforward fashion.

The alcohols **6** and **7** were converted (Scheme 3) into their acetate derivatives (+)-**8** and (+)-**9** to establish the optical purity of these products. The determination of the enantiomeric excess of the acetate **8** by ^1H NMR in the presence of tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]europium(III) [Eu(hfc)$_3$] has been described by Howell,[24] and in this way, we proved by integration of signals from the acetate methyl group that the enantiomeric excess of the sample of **8** furnished by the asymmetric dihydroxylation/ferralactone route was at least 99%. The use of the chiral shift reagent with the acetate (+)-**9** has not been reported before. Our dihydroxylation-derived sample showed only one singlet for the acetate in the presence of the shift reagent. An authentic racemic sample of **9** was needed to check the validity of the analysis and this was obtained by Freidel–Crafts acetylation of (butadiene)-$Fe(CO)_3$,[25] reduction of the resulting ketone, and acetylation of the alcohol. This complex showed the expected two singlets when the ^1H NMR spectrum was measured under the same conditions with the same quantity of the shift reagent. Furthermore, when a small portion of racemic **9** was added to the nmr sample of (+)-**9** in the presence of Eu(hfc)$_3$, small peaks corresponding to the pair of signals



Scheme 3.

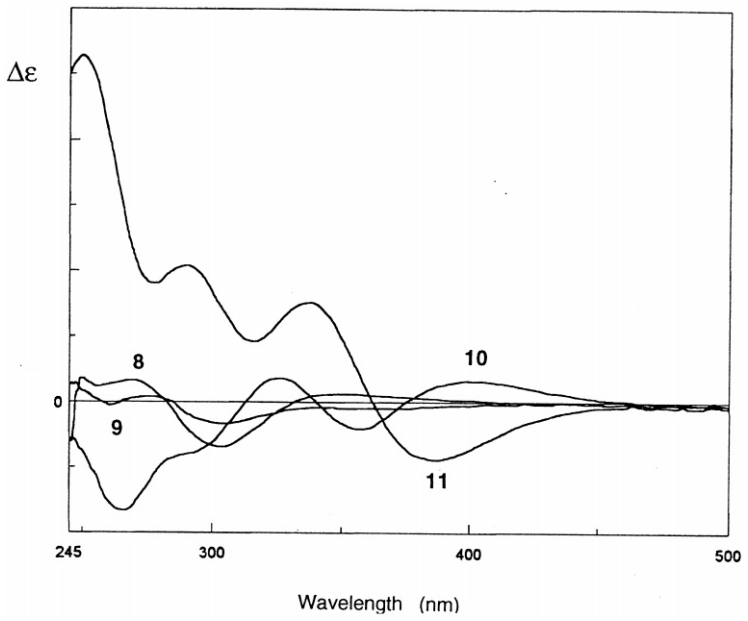


Figure 1. Circular dichroism (CD) curves of tricarbonyliron diene complexes.

from the OAc group of the minor enantiomer were seen to appear. These experiments prove that the epoxide opening, the isomerisation to form **7**, and the rearrangement of the ferralactones to the η^4 products, all proceed with no significant racemisation of the intermediates.

Since the absolute configuration of the acetate **8**[26] is known, the stereochemical course of the route from (+)-**3** can be established with certainty. The configuration of the secondary alcohol **7** is not known. Circular dichroism (CD) spectra (Fig. 1) were measured for the two acetates **8** and **9**, but the forms of these two curves were not sufficiently similar for the absolute configuration of (+)-**9** to be assigned by comparison with (+)-**8**. However, the signs of the highest wavelength bands in the CD curves were opposite, suggesting that the two complexes might have different absolute configurations in the η^4 region. The similarity between the substituents at the two ends of the diene in **8** makes a clear comparison of these two CD spectra difficult. This problem was overcome by oxidation of the alcohols (+)-**6** and (−)-**7** to afford the aldehyde (−)-**10** and the ketone (+)-**11**. The specific rotation for the sample of (−)-**10** $\{[\alpha]_D=-114$ (c=1.5, $CHCl_3$)$\}$ was consistent with the value reported by Howell[27] for a sample $\{[\alpha]_D=-112\}$ with an ee of 99%. Electron withdrawing substituents are known[28,29] to exert a large influence on the chiroptical properties of (η^4-diene)$Fe(CO)_3$ complexes, so in the disubstituted diene complex **10** the effects of the two substituents should be distinguishable. As the aldehyde and ketone functional groups should influence the CD curves in a similar fashion, comparison of these two complexes can be expected to yield a more clear-cut conclusion. The CD curves (Fig. 1) were now much more similar, with the crucially diagnostic[29] high wavelength bands showing a maximum at 398 nm ($\Delta\epsilon$ +1.6, c=0.038 M) for **10** and a minimum at 384 nm ($\Delta\epsilon$ −4.4, c=0.036 M) for **11**. As with the acetates, the two complexes had opposite signs for $\Delta\epsilon$ in the 400 nm region. This band at around 400 nm is typical of tricarbonyl(η^4-1,3-diene)iron(0) complexes with aldehyde and ketone substituents at C1,[28] indicating that the complexes **10** and **11** must have their electron withdrawing substituents at opposite ends of the chiral η^4-diene moiety (see Fig. 2), allowing the absolute configuration of the planar chiral element in (+)-**11** to be assigned as *S*.[30]

The availability of **11** allowed the relative configuration between the secondary alcohol and the metal-bound diene to be examined. Reduction of **11** (Scheme 3) was performed with sodium borohydride in the same manner as described earlier in the preparation of racemic **9**, and afforded a single diastereoisomer in 99% yield. Comparison of the ^1H NMR spectra of the reduction product and that of the sample of **9**

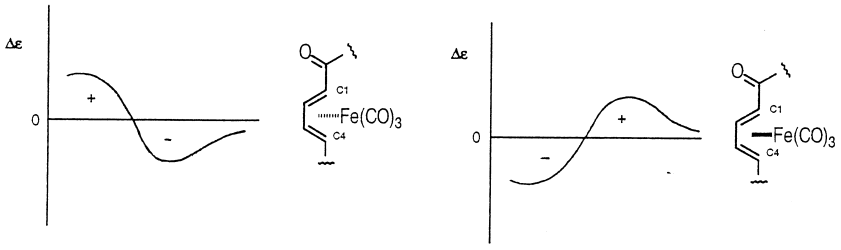


Figure 2. Typical CD curves in the 320–470 nm range for the enantiomers of 1-acylbutadiene complexes of $Fe(CO)_3$ (numbering based on (1-4η)-butadiene not on (2-5-η)-pentadien-1-one structures).

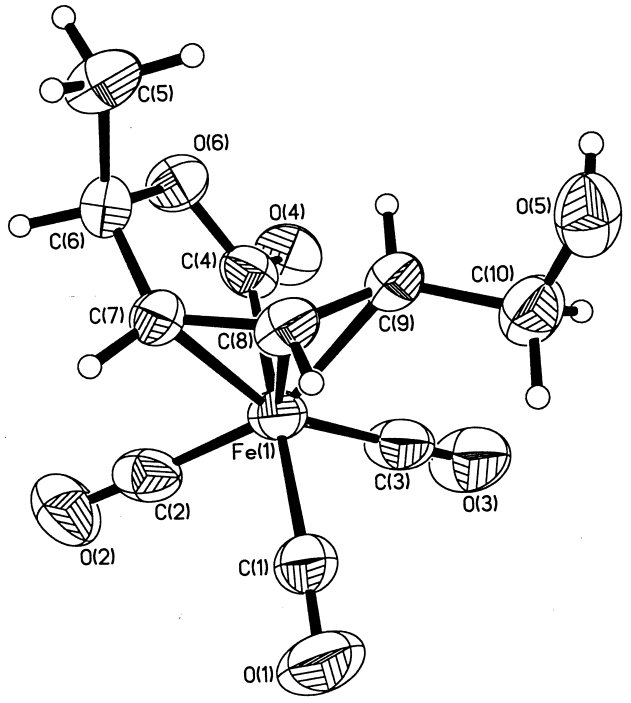


Figure 3. Molecular structure of ferralactone (−)-**4** [Fe(1)-C(4)=1.986 (4), Fe(1)-C(7)=2.100 (5), Fe(1)-C(8)=2.057(5), Fe(1)-C(9)=2.194(5), C(7)-C(8)=1.412(7), C(8)-C(9)=1.385(6) Å; C(7)-C(8)-C(9)=124.2 (4)°].

formed by the $Ba(OH)_2$ reaction, showed the two complexes to be identical. Unlike aldehydes,[31] ketones adjacent to tricarbonyl(η^4-diene)iron complexes react with nucleophiles in a stereochemically controlled fashion. The stereodirecting influence of the metal is known from results reported[32] for a selection of nucleophiles, with attack occurring from the face opposite to the tricarbonyliron group when the ketone is in the *cissoid* conformation drawn in Scheme 3. Since hydride should thus be delivered *trans* to the metal, the stereochemistry of (−)-**7** can be assigned as 2*R*,3*S*, as drawn in Scheme 2. The configuration of the C2 centre was shown in this way to be identical to that at the corresponding position in the ferralactone complex (+)-**5** (determined by X-ray crystallography, see below). As expected, the $Ba(OH)_2$ step has not influenced the stereochemistry at this position. These results are consistent with the generally accepted mechanisms for the formation of ferralactone complexes[21] and the stereochemical course of their conversion into η^4 diene complexes by the action of barium hydroxide,[15] which proceeds with a *syn*, *anti* isomerisation of terminal substituents at the metal complex. The definition of the stereochemical course of these reactions was confirmed by separation of a small portion of the mixture of ferralactone complexes. The faster eluting isomer (−)-**4** (Fig. 3)[33] {$[\alpha]_D$=−173 (*c*=1, $CHCl_3$)} showed the expected doublet for the C6 methyl group in the ^{1}H NMR spectrum and was identified as one of the stereoisomers initially reported[34] in racemic form by Ley and Meek. As a final check, **4** was oxidised with PDC to obtain the corresponding aldehyde {$[\alpha]_D$=+356}, which had identical nmr properties to those reported.[21,34] The secondary alcohol (+)-**5** was recrystallised from hexane as orthorhombic colourless crystals (mp 130–133°C; $[\alpha]_D$=+55, *c* 1, $CHCl_3$), and X-ray diffraction analysis proved the relative stereochemisty (Fig. 4) which had not been established in the earlier investigations[21] of the racemate. The absolute configuration was also confirmed through this procedure. Working on a small scale, the conversion of **4** into **6**, and **5** into **7**, respectively, was checked using pure samples of each complex.

Finally, a preliminary investigation of the formation of η^5-dienyl complexes was performed. Because of the position of the OH groups in each case, the same configuration of the dienyl product would be expected, starting from either

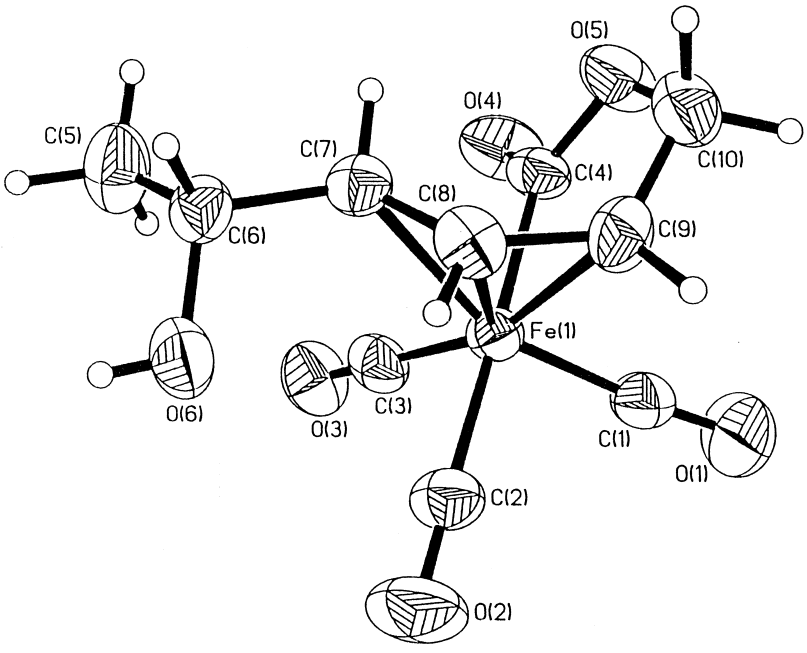


Figure 4. Molecular structure of ferralactone (+)-**5** [Fe(1)-C(4)=1.985(4), Fe(1)-C(7)=2.201(5), Fe(1)-C(8)=2.077(5), Fe(1)-C(9)=2.098(5), C(7)-C(8)=1.392(7), C(8)-C(9)=1.416(7) Å; C(7)-C(8)-C(9)=122.4(4)°].

6 or **7**. This opens the way for straightforward stereoselective access to enantiopure dienyl complexes without the need to separate isomers[35] by a reaction sequence utilising sharpless dihydroxylation, ferralactone regioisomer formation by the ultrasound procedure, conversion into η^4-diene complexes, and acid mediated $\eta 4-\eta^5$ interconversion by dehydroxylation. Simple conversion of either **6** or **7** into (η^5-hexadienyl)$Fe(CO)_3$ (**2**, R=Me) by reaction with HPF_6 gave the expected product but in racemic form. Reaction of **6** with the minimum quantity of HPF_6 following Howell's procedure,[36] however, afforded a sample of the salt with an $[\alpha]_D$ of approximately −19 (c=1, CH_3CN) (this decreased gradually during the measurement). Reaction starting with **7** was slower but afforded the same enantiomer of the product, $[\alpha]_D=-24$ (c=1, CH_3CN).

Conclusions

Starting from a readily available enantiopure hydroxymethyl-substituted allylic epoxide, we have shown that by the use of ultrasound to effect ferralactone formation, pairs of stereocomplementary regioisomers can be obtained and converted into the corresponding tricarbonyliron diene complexes without loss of optical purity. The route onwards to the synthetically important cationic η^5 complexes is less straightforward but we have demonstrated that a single stereoisomer (5*S*) is formed from each of the two products from the 4*R*,5*R* epoxide. We have shown in this study that diverting the normally non-diastereoselective epoxide opening to give regioisomeric products, provides a suitable strategy for a regioconvergent approach to non-racemic hexadienyl complexes, which does not rely on the need for separation of isomers, and we have fully defined the stereochemical processes in these reaction sequences and determined the absolute configurations of the intermediate complexes. Because of their completely stereoselective reactions with nucleophiles, organometallic complexes of this class in both the cyclic and acyclic series are valuable in enaniopure form for the asymmetric synthesis of chiral target structures. Our work in this area aims to make such complexes more readily available.

Experimental

All experiments were carried out in flame or oven dried glassware, under an environment of dry, oxygen-free nitrogen or argon. Ether and THF were dried by distillation from sodium metal and benzophenone, and CH_2Cl_2 by distillation from calcium hydride. The dried solvents were stored over activated 4A molecular sieves. Pyridine was distilled from potassium hydroxide. Column chromatography was performed using silica gel (Silica Matrex 60, 70–200 microns, Fisons) and analytical thin-layer chromatography was performed on aluminium backed silica plates, Merck 5554. IR spectra were recorded as thin films or in solution, using a Perkin–Elmer 1720X FTIR spectrometer. NMR spectra were recorded on JEOL EX270 FT NMR. Mass spectra were determined on a Kratos MS 25 spectrometer and microanalyses were carried out using Carlo Erba EA1108 by Mr A. W. R. Saunders of the University of East Anglia. High resolution mass spectra were measured at the Engineering and Physical Sciences Research Council (EPSRC) National Mass Spectrometry Service Centre at the University of Wales, Swansea. CD spectra were recorded using Jasco J-600 spectrometer, and $[\alpha]_D$ measurements were performed on a Jasco DIP/360 polarimeter. X-ray data was collected on Rigaku AFC7R diffractometer.

(+)-(2*E*,4*R*,5*R*)-4,5-Epoxyhex-2-en-l-ol (3). Starting from the dienol **1** (R=Me), Schotten–Baumann benzoylation[37] followed by the standard AD-mix asymmetric dihydroxylation procedure and a version of the representative procedure for the conversion of unactivated diols into epoxides as described by Kolb and Sharpless[19] affords (**3**). (2*E*,4*E*)-hexa-2,4-dien-l-ol (**1**, R=Me) (4.9 g, 50 mmol) was dissolved in pyridine (75 ml). Benzoyl chloride (25 ml) was added gradually while the temperature of the reaction mixture was maintained below 50°C. The mixture was then stirred at rt for 15 h. Hexane (300 ml) was added and the mixture was quenched with 5% aqueous sodium hydrogen carbonate (2×300 ml). The hexane layer was dried with anhydrous $MgSO_4$ and the solvent removed under reduced pressure. The residue was a colourless oil which was purified either by distillation under reduced pressure (bp 130°C/1 mmHg) or by flash chromatography (30 to 70% ethyl acetate in hexane, gradient). (2*E*,4*E*)-2,4-Hexadienyl benzoate (9.7 g, 96%) solidified on cooling. mp 16°C, (Found: C, 77.07; H, 6.72; $C_{13}H_{14}O_2$ requires C, 77.20; H, 6.98%); ν_{max}(film)/cm^{-1} 1717 (C=O), 1662 and 1600 (diene), 1451, 1271, 1115, 990 (*trans* CH=CH), 711 (Ph); $\delta_H(CDC1_3)$ 1.76 (3 H, d, J=6 Hz, Me), 4.8 (2 H, d, J=6 Hz, CH_2), 5.8 (2 H, m, outer-CH), 6.1 (1 H, m, inner-CH), 6.3 (1 H, dd, J=11 Hz, 15, inner-CH) 7.42–8.04 (5 H, m, Ph). $\delta_C(CDC1_3)$ 18 (CH_3), 65 (CH_2), 124–135 (9×CH), 166 (C=O); *m/z* 202 (M^+, 19%), 105 (PhCO, 100), 77 (Ph, 16). This product (0.808 g, 4 mmol) was added to a solution of AD-mix-β (5.6 g) and methyl sulfonamide (0.380 g, 4 mmol) in 1:1 v/v t-butyl alcohol:water (40 ml) at 0°C. The mixture was stirred at 0°C for 2 h and then the temperature was allowed to increase to 15°C. The progress of the reaction was monitored by TLC (silica gel, 7:3 ethyl acetate: hexane, R_f 0.25 for the diol) and continued until the starting material had disappeared (2 h). The colour of the reaction mixture had changed from orange to lemon yellow at the end of the reaction. The mixture was cooled to 5°C and anhydrous sodium sulfite (6.0 g, 48 mmol) was added with vigorous stirring. The suspension was warmed to rt. After 45 min, the product was extracted with ethyl acetate (4×20 ml), the combined extracts were dried with $MgSO_4$ and concentrated. Flash chromatography (silica gel, 40:60 ethyl acetate: hexane) gave two isomeric diols (0.821 g, 88% total yield) [lit.[18] 91%]. The isomer ratio was 75:13 (lit.[18] 83:7). The faster eluting diol, a white solid, mp 54–56°C, $[\alpha]_D^{25}=+12.7$ (c=2, $CHCl_3$) was discarded. Continued elution afforded (+)-(2*E*,4*R*,5*R*)-2,3-dihydroxyhex-2-enyl benzoate, $[\alpha]_D^{25}=+7.7$ (c=2, $CHC1_3$) [lit.[18], +2.2 (c 2, $CHCl_3$)]. Found: C, 65.50; H, 6.95; $C_{13}H_{16}O_4$ requires C, 66.09; H, 6.83%; ν_{max}(film)/cm^{-1} 3399 (OH, br), 3063 (Ph), 2974–2883 (CH) 1717 (CO), 1601 and 1585 (Ph), 1451, 1274, 1113, 978 (CH=CH), 711 (Ph); [lit.[18] (neat) ν_{max}/cm^{-1} 3402 (br. s) 2968–2876, 1702, 1602, 1443, 1254, 1111, 969, 711]; $\delta_H(CDCl_3)$ 1.16 (3 H, d, J=6 Hz, Me), 2.70–3.20 (2 H, br, OH, variable), 3.65

(1 H, m, CHOH), 3.90 (1 H, t, J=6 Hz, CHOH), 4.81 (2 H, d, J=6 Hz, CH_2), 5.83 (1 H, dd, J=6 Hz, 15.5, CH), 5.96 (1 H, m, CH), 7.7–8.1 (5 H, m, Ph); [lit.[18] δ_H (400 MHz, $CDCl_3$) 1.16 (3 H, d, J=6.4 Hz), 2.72 (1 H, s), 2.85 (1 H, s), 3.64 (1 H, t, J=6.4 Hz), 3.90 (1 H, m), 4.81 (2 H, d, J=6 Hz), 5.97 (1 H, m), 7.42–8.02 (5 H, m, Ph)]; δ_C & DEPT ($CDCl_3$) 18.9 (Me), 64 (CH_2), 70, 76, 126, 128, 129, 130, 133, 133 (Ph), 166 (CO); m/z 219 (M^+-17, 0.4%), 123 (PhCOOH, 37), 105 (PhCO, 100) 77 (Ph, 23), 70 (C_5H_{10}, 70). To a mixture of this product (1.050 g, 4.45 mmol), pyridinium p-toluene sulfonate (10.5 mg, 0.045 mmol) and dry CH_2Cl_2 (6 ml) at rt, was added trimethyl orthoacetate (0.67 ml, 5.4 mmol) by microsyringe. The mixture was stirred for 15 min, then evaporated and residual methanol removed under vacuum (0.1 mmHg) for 2 min. The residue was taken up in dry CH_2Cl_2 (6 ml) triethylamine (12 μl, 0.09 mmol) was added followed by acetyl bromide (0.4 ml, 5.37 mmol) over 4 min during which the solution was cooled occasionally to maintain temperature below 40°C. After 30 min, when all the diol had been consumed, (TLC, silica gel, 2:1 ethyl acetate: hexane) the solvent was removed, the residue was dissolved in methanol (18 ml) and K_2CO_3 (1.07 g, 7.7 mmol) was added to vigorously stirred solution. After 70 min, saturated NH_4Cl solution (35 ml) was added and the product extracted with CH_2Cl_2 (3×30 ml). The combined organic layers were dried with $MgSO_4$, filtered and evaporated. The residue was purified by filtration through a pad of silica gel and the pad was washed with 20% ethyl acetate in hexane. Evaporation of the filtrate under vacuum gave the crude epoxide (0.792 g, 82%) which was purified by chromatography (0–70% ethyl acetate in hexane gradient). (+)-(2*E*,4*R*,5*R*)-4,5-epoxyhex-2-en-l-ol (**3**): $[\alpha]_D^{25}$=+53.3 (c=2, $CHCl_3$) ν_{max}(film)/cm^{-1} 3402 (OH, br. s), 1740 (C=O), 1447, 1379, 1092, 1009, 969 (CH=CH), 854; δ_H($CDCl_3$) 1.34 (3 H, d, J=5 Hz, Me), 2.54 (1 H, s, OH), 2.93 (1 H, m, epoxy-CH), 3.1 0 (1 H, dd, J=2 Hz, 8, epoxy-CH), 4.14 (2 H, d, J=5 Hz, CH_2), 5.45 (1 H, m, cis-CH), 6.05 (1 H, m, *cis-CH*); δ_C & DEPT ($CDC1_3$) 18 (Me), 56, 59 (2×CH), 62 (CH_2), 127, 134 (2×CH); m/z 113 (M^+-1, 2%), 97 (M^+-17, 8), 96 (M^+-H_20, 23), 70 (36), 54 (35), 43 (100). A second epoxide (<2% yield) was discarded.

(−)-(4*E*,2*R*,3*R*,5*R*)-[2-(Carbonyloxy-κC)-6-hydroxy-(3,4,5-η)-hex-4-en-3-yl]tricarbonyliron(0) (4) and (+)-(3*E*,2*S*,4*S*,5*R*)-[1-(carbonyloxy-κC)-5-hydroxy-(2,3,4-η)-hex-3-en-2-yl)]tricarbonyliron(0) (5). A mixture of (+)-(2*E*,4*R*,5*R*)-4,5-epoxyhex-2-en-l-ol (**3**) (1.14 g, 10 mmol) and $Fe_2(CO)_9$ (5.6 g, 18 mmol) in THF (200 ml) was sonicated in a 50 W ultrasound bath at rt for 3 h. The mixture was filtered through a pad of Celite and evaporated under reduced pressure. Flash chromatography (silica, gradient from 10 to 70% ethyl acetate in hexane) of the residue gave a mixture of two isomeric ferralactones (total 2.56 g, 91%), as a yellow oil which solidified on cooling. The ratio (nmr) of the ferralactones **4**:**5** was 47:53. Small portions could be separated by repeated flash chromatography using the same conditions, to afford pure samples of the two compounds: (−)-(4*E*,2*R*,3*R*,5*R*)-[2-(carbonyloxy-κC)-6-hydroxy-(3,4,5-η)-hex-4-en-3-yl]tricarbonyliron(0) (**4**)[33] (fast eluting): mp 81–83°C (dec), $[\alpha]_D^{25}$=−173 (*c*. 1.0, $CHC1_3$); Found: C, 42.74; H, 3.38; $C_{10}H_{10}O_6Fe$ requires C, 42.59; H, 3.57%; δ_C & DEPT ($CDCl_3$) 22 (CH_3), 62 (CH_2), 74, 78, 82 and 88 (CH), 207 (CO) (Lit.[21] 209, 207, 206, 203, 88, 82, 78, 74, 62, 22), and (+)-(3*E*,2*S*,4*S*,5*R*)-[1-(carbonyloxy-κC)-5-hydroxy-(2,3,4-η)-hex-3-en-2-yl)]tricarbonyliron(0) (**5**). (slow eluting): mp 130–133°C, $[\alpha]_D^{25}$=+55 (c=1, $CHCl_3$); δ_C & DEPT ($CDC1_3$) 25 (CH_3), 65 (CH_2), 67, 70, 88 and 90 (CH), 208 (CO) (Lit.[21] 209, 208, 207, 204, 90, 88, 71, 67, 65, 26). Single crystals of **5** were grown as follows: ferralactone **5** (~50 mg) was dissolved in minimum volume of dry acetone. This solution (contained in an open flask) was placed in a closed vessel charged with dry ether (100 ml). The system was left at rt for 5 days and the light yellow crystals were collected, dried under vacuum, and analysed by X-ray diffraction. Crystal data for (+)-5: $C_{10}H_{10}O_6Fe$; M=282.03; orthorhombic, $P2_12_12_1$; a=11.572(3), b=12.934(4), c=7.674(2) Å, U=1148.6(6) Å^3; Z=4; Dc=1.63 Mg m^{-3}; $F(000)$=576; μ(Mo-K_α)=1.33 mm^{-1}. Colourless crystal 0.10×0.15×0.25 mm; T=−80°C; 1193 independent reflections measured on Rigaku AFC7R diffractometer (Mo-K_α λ=0.71073 Å, 5°<2θ<50°, ω-scans). Refinement on F^2: wR_2=0.0740, R_1=0.0415, S=1.081 for all data; Flack χ=0.02(4). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre, reference 136760.

(+)-(2*R*,5*S*)-Tricarbonyl[(2,3,4,5-η)-hexa-2,4-dien-l-ol]-iron(0) (6) and (−)-(2*R*,3*S*)-tricarbonyl[(3,4,5,6-η)-hexa-3,5-dien-2-ol]iron(0) (7). Using the ultrasound procedure described above, (+)-(2*E*,4*R*,5*R*)-4,5-epoxyhex-2-en-l-ol (**3**) (1.14 g, 10 mmol) was converted into a crude mixture of ferralactone complexes which were taken on into the next step without purification. By the method of Aumann,[15] the ferralactone complexes were dissolved in methanol (50 ml) at rt. Saturated aqueous barium hydroxide (25 ml) was added and the mixture was allowed to stand for 15 h. Water was added and the product was extracted in pentane. The combined extracts were dried with $MgSO_4$, concentrated and flash chromatography (silica, 20% ethyl acetate in hexane) afforded (+)-(2*R*,5*S*)-tricarbonyl[(2,3,4,5-η)-hexa-2,4-dien-l-ol]iron(0) (**6**). (0.99 g, 42%), and (−)-(2*R*,3*S*)-tricarbonyl-[(3,4,5,6-η)-hexa-3,5-dien-2-ol]iron(0) (**7**) (1.13 g, 48%). (+)-(2*R*,5*S*)-tricarbonyl[(2,3,4,5-η)-hexa-2,4-dien-l-ol]iron(0) (**6**) (slow eluting): $[\alpha]_D^{25}$=+8.3 (*c* 1, $CHCl_3$); Found: C, 45.7, H 4.15; $C_9H_{10}O_4Fe$ requires C, 45.41; H, 4.23%; ν_{max}(film)/cm^{-1} 3325 (OH), 2048, 1980 and 1970 (CO), 1442, 1380, 1101, 609, 568, [(lit.[24] ν_{max} (film)/cm^{-1} 3340 (OH), 2049, 1982, 1975)]; δ_H($CDCl_3$) 1.10 (1 H, m, 2-H), 1.26 (1 H, q, J=6 Hz, 5-H), 1.42 (3 H, d, J=6 Hz, Me), 1.61 (1 H, br s, OH), 3.55–3.80 (2 H, m, CH_2), 5.0–5.20 (2 H, m, 3-H and 4-H); δ_C & DEPT ($CDCl_3$) 19 (CH_3), 58 (CH_2), 60, 65, 82, 86 (CH), 212 (CO). (−)-(2*R*,3*S*)-tricarbonyl[(3,4,5,6-η)-hexa-3,5-dien-2-ol]iron(0) (**7**) (fast eluting): $[\alpha]_D^{25}$=−46.4 (*c* 1, $CHCl_3$); (Found: C, 45.74; H, 4.04; $C_9H_{10}O_4Fe$ requires C, 45.42; H, 4.23%); ν_{max}(CH_2Cl_2)/cm^{-1} 3605 (free OH), 2048, 1980 and 1968 (CO), 1374, 1147, 1085, 1034; δ_H($CDC1_3$) 0.35 (1 H, dd, J=2 Hz, 9, CH_{anti}), 1.09 (1 H, t, J=8 Hz, CH), 1.35 (3 H, d, J=6 Hz, Me), 1.46 (1 H, br. s, OH), 1.81 (1 H, ddd, J=1, 2, 7 Hz, CH_{syn}), 3.78 (1 H, t, J=6 Hz, HC–Me), 5.28 (2 H, m, CH-internal); δ_C & DEPT ($CDCl_3$) 26 (CH_3), 40 (CH_2), 70, 71, 81 and 85 (CH), 211 (CO); m/z 238 (M^+, 22%), 210 (M^+-CO, 55), 182 (M^+-2CO, 34), 154

(M^+-3CO, 39), 136 (80), 134 (100), 81 (26); *m/z* (EI) 237.9928 (M^+), $C_9H_{10}O_4Fe$ required 237.9928. By the same procedure, small portions of purified ferralactone complexes could be converted into η^4-diene complexes. Ferralactone **4** (0.330 g, 1.17 mmol) in methanol (9 ml) was treated with saturated aq. Barium hydroxide (4.5 ml) to give the η^4-complex **6** (0.262 g, 94%) as a brown oil. Ferralactone **5** (0.332 g, 1.18 mmol) afforded corresponding η^4-complex **7** as bright yellow needles (0.126 g, 45%) after crystallisation from hexane. mp 70–72°C, (hexane) (lit.[38] 65°C, petroleum ether).

(−)-(5*S*)-Tricarbonyl[(1,2,3,4,5-η)-hexadienyl]iron(1+) hexafluorophosphate(1−) (2). Using Howell's procedure,[36] the diene complex (+)-**6** (0.238 g, 1 mmol) was dissolved in dry ether (50 ml) in a PTFE vessel, and the solution was cooled to 0°C. HPF_6 (75% aq. solution, 0.12 ml, 1 mmol) was added and the mixture was stirred for 2 h at 0°C. The solid product was collected by filtration and washed with ether. The filtrate was concentrated and further precipitated material was collected. The combined solids were dried under vacuum (0.306 g, 80%): $[\alpha]_D^{25}=-19$ (c=1, CH_3CN). $\nu_{max}(C_2H_6CO)/cm^{-1}$ 2115, 2065 (CO); $\delta_H(C_2D_6CO)$ 1.88 (3 H, d, J=6 Hz, Me), 2.62 (1 H, dd, J=3 Hz, 12, 1-H$_{anti}$), 3.78 (2 H, m, 5-H and 1-H$_{syn}$), 6.26 and 6.24 (2 H, m, inner CH), 7.19, (1 H, t, J=7 Hz, middle CH); δ_C & DEPT (C_2D_6CO) 21 (Me), 64 (CH_2), 92, 96, 105, 106 (CH). The same product {$[\alpha]_D^{25}=-24$ (c=1, CH_3CN)} was obtained in 31% yield from (−)-**7**. IR indicated that in this case the reaction did not proceed to completion.

Racemisation during the preparation of tricarbonyl-[(1,2,3,4,5-η)-hexadienyl]iron(1+) hexafluoro-phosphate(1−) (2)

A solution of neutral η^4-complex **7** (0.056 g, 0.23 mmol) in acetic anhydride (3 ml) was cooled to 0°C and HPF_6 (60% aqueous solution) was added in portions until the IR spectrum of the reaction mixture no longer showed absorption bands at 2048 and 1975 cm^{-1} (bands due to the neutral complex). A total of 0.3 ml HPF_6, solution was required. The mixture was poured into dry ether (30 ml). The precipitated salt was filtered, washed with ether and dried (0.022 g, 25%). $[\alpha]_D^{25}=0.0$ (c=0.15, CH_3CN); $\nu_{max}(C_2H_6CO)/cm^{-1}$ 2116, 2065 (CO).

(−)-(2*R*,5*S*)-Tricarbonyl[(2,3,4,5-η)-hexa-2,4-dien-1-al]-iron(0) (10). A slurry of pyridinium dichromate (PDC) (0.131 g, 0.37 mmol) in CH_2Cl_2 (3 ml) was cooled to 0°C and tricarbonyliron complex (+)-**6** (0.096 g, 0.4 mmol) in CH_2Cl_2 (1 ml) was added. The mixture was warmed to rt and stirred for 2 h and then at 30°C for further 2 h. After addition of ether (50 ml) the mixture was filtered through a pad of Celite and the filtrate was concentrated. The residue was subjected to flash chromatography (10% ether in hexane) to afford a yellow oil (0.036 g, 38%). $[\alpha]_D^{25}=-114$ (c=1.5, $CHCl_3$) (lit.[28] $[\alpha]_D^{25}=-112$ at ~99% e.e. by NMR) ν_{max}(hexane)/cm^{-1} 2063, 2004, 1989 (CO), 1688 (CH═O), 1459, 1171, 1121, 605, 565; $\delta_H(CDCl_3)$ 1.26 (1H, m, 2-H), 1.50 (3 H, d, J=7 Hz, CH_3),1.70 (1 *H*, *m*, 5-H), 5.30 (1 H, dd, J=5 Hz, 9, 4-H), 5.78 (1 H, m, 3-H); δ_C & DEPT ($CDC1_3$) 19 (CH_3), 129, 130, 142 and 153 (CH), 194 (CHO).

(+)-(3*S*)-Tricarbonyl[(3,4,5,6-η)-hexa-3,5-dien-2-one]-iron(0) (11). A slurry of pyridinium dichromate (PDC) (0.131 g, 0.37 mmol) in CH_2Cl_2 (3 ml) was cooled to 0°C and tricarbonyliron complex **7** (0.060 g, 0.25 mmol) in CH_2Cl_2 (1 ml) was added. The mixture was warmed to rt and stirred for 2 h and then at 30°C for further 2 h. After addition of ether (50 ml) the mixture was filtered through a pad of Celite and the filtrate was concentrated. The residue was subjected to flash chromatography (10% ether in hexane) to afford yellow oil (0.054 g, 91%). $[\alpha]_D^{25}=+358$ (c=1.5, $CHCl_3$); ν_{max}(hexane)/cm^{-1} 2065, 2005 and 1994 (CO), 1678 (C═O), 1465, 1357, 1310, 1180, 619, 598, 564; $\delta_H(CDCl_3)$ 0.73 (1 H, dd, J=2 Hz, 10, 6$_{anti}$), 1.25 (1 H, d, J=8 Hz, 3-H), 2.02 (1 H, dd, J=2 Hz, 7, 6-H$_{syn}$), 2.14 (3 H, s, CH_3), 5.4 (1 H, m, 5-H), 5.96 (1 H, dd, J=6 Hz, 8, 4-H); δ_C & DEPT ($CDC1_3$) 30 (CH_3), 41 (CH_2), 55, 85, 86 (CH), 203 (CO); *m/z* 236 (M^+, 9%) 208 (M^+-CO, 17) 180 (M^+-2CO, 34), 152 (M^+-3CO, 100), 134 (43).

(+)-(2*R*,5*S*)-Tricarbonyl[(2,3,4,5-η)-1-acetoxyhexa-2,4-diene]iron(0) (8). Using the procedure of Howell,[36] the η^4-complex **6** (0.238 g, 1.0 mmol) was dissolved in dry pyridine (3.5 ml) under nitrogen and cooled to 0°C. Acetic anhydride (0.106 ml, 1.1 mmol) was added and the reaction stirred at rt overnight. After removal of the solvent, the residue was purified by flash chromatography (20% ethyl acetate in hexane) to give the acetate as a yellow oil (0.250 g, 88.4%). $[\alpha]_D^{25}=+18$ [(lit.[24] for enantiomer $[\alpha]_D^{25}=-17$, c=1, $CHCl_3$)]; ν_{max}(film)/cm^{-1} 2043, 1964 (CO), 1740 (C═O), 1231, 1023, 610, 579; $\delta_H(CDCl_3)$, 1.00 (1 H, q, J=7 Hz, 2-H), 1.26 (1 H, m, 5-H), 1.42 (3 H, d, J=6 Hz, CH_3), 2.06 (3 H, s, $COCH_3$), 4.08 (2 H, J=7 Hz, CH_2), 5.06 (1 h, dd, J=5 Hz, 9, 4-H), 5.20 (1 H, dd, J=5, 8 Hz, 3-H); [lit.,[24] (C_6H_6), 0.6–0.8, (2 H, m, 2-H and 5-H), 0.96 (1 H, d, J=6 Hz, 6-H), 1.69 (3 H, s, OAc), 3.99 ((1 H, d, J=8 Hz, 1 b-H), 4.28 (1 H, m, 4-H), 4.58 (1 H, m, 3-H); δ_C and DEPT ($CDCl_3$) 19 and 21 (CH_3), 54 (CH_2), 58, 66, 83 and 87 (CH), 171 (C═O), 211 (CO); *m/z* 280 (M^+ 1%), 252 (M^+-CO, 21), 224 (M^+-2CO, 37), 196 (M^+-3CO, 100), 181 (14), 136 (51), 134 (75), 81 (25). The racemic tricarbonyliron complex (±)-**6** (0.144 g, 0.6 mmol) was reacted with acetic anhydride in a similar manner to afford the racemic acetate (±)-**8** (0.105 g, 62%).

(+)-(2*R*,3*S*)-Tricarbonyl[(3,4,5,6-η)-2-acetoxyhexa-3,5-diene]iron (9). η^4-Complex (−)-**7** (0.238 g, 1 mmol) was reacted with acetic anhydride in a similar manner to that used for the η^4-complex **6** to afford the corresponding acetate (+)-**9** as a yellow oil (0.180 g, 65%) which crystallised on cooling at −20°C. mp 44.5–46.5°C; $[\alpha]_D^{25}=+99$ (c 1, $CHCl_3$); ν_{max}(film)/cm^{-1} 2048, 1972 and 1964 (3 CO), 1739 (C═O), 1372, 1240, 1048, 613, 572; $\delta_H(CDCl_3)$ 0.30 (1 H, dd, J=3, 8 Hz, 6-H$_{anti}$), 0.98 (1 H, t, J=7 Hz, 3-H), 1.36 (3 H, d, J=6 Hz, CH_3), 1.75 (1 H, m, 6-H$_{syn}$), 2.07 (3 H, d, J=1 Hz, $COCH_3$), 4.91 (1 H, quintet J=6 Hz, 2-H), 5.20 (2 H, m, 4-H and 5-H); $\delta_C(CDCl_3)$ 21 & 22 (CH_3), 41 (CH_2), 62, 73, 83, 87, 170 (CO); *m/z* 252 (M^+-CO, 18%), 224 (M^+-2CO, 31), 196 (M^+-3CO, 100), 181 (12), 136 (35), 134 (50), M^+ 280.

Synthesis of the racemic acetoxy η^4-complex (±)-9 from tricarbonyl(η^4-butadiene)iron(0) by acylation and reduction

Following the method described by Knox,[39] a solution of a Perrier complex in CH_2Cl_2 was prepared by gentle warming of acetyl chloride (1.2 ml) and anhydrous $AlCl_3$ (2.94 g), followed by addition of CH_2Cl_2 (10 ml) to the cooled melt. To a stirred solution of tricarbonyl(η^4-butadiene)iron(0) (0.213 g, 1.1 mmol) in CH_2Cl_2 (10 ml) at −78°C, a portion Perrier complex solution (1 ml) was added. At 30 min intervals, two further portions (1 ml) of the Pierrer complex were added. After the last addition, the mixture was stirred for 10 min, diluted with dry ether at −78°C, and poured onto ice. The organic layer was separated, washed with water (4×15 ml), brine (20 ml), dried with $MgSO_4$ and solvent evaporated to give oily product (0.149 g, 56%). ν_{max}(film)/cm^{-1} 2065, 2005, 1994 (CO), 1677 (C═O); δ_H($CDCl_3$) 0.72 (1 H, dd, J=2, 10 Hz, 6-H$_{anti}$), 1.25 (1 H, d, J=7 Hz, 3-H), 2.04 (1 H, dd. J=3, 8 Hz, 6-H$_{syn}$) 2.14 (3 H, s, CH_3), 5.4 (1 H, m, 5-H). 5.97 (1 H, q, J=5, 7 Hz, 4-H). The product was reduced to corresponding secondary alcohol complex (±)-**7** with $NaBH_4$ and the alcohol was reacted with acetic anhydride/pyridine as described earlier which gave racemic acetate complex (±)-**9**.

Circular dichroism measurements

Volumetric and spectroscopic measurements were performed in air without special precautions. Accurately weighed samples of the complexes (10–20 mg) were dissolved in $CHCl_3$, CH_3OH or CH_3CN in 2 ml volumetric flasks. CD spectra were recorded at 22°C and with 0.2 cm path-length, at a scan rate of 100 nm min^{-1} at 0.2 nm resolution and a 1 nm bandwidth at the following concentrations: **8**: 0.032 M; **9**: 0.018 M; **10**: 0.038 M; **11**: 0.−038 M. Plots of $\Delta\epsilon$ (mol^{-1} dm^2) against λ (nm) are shown in Fig. 1.

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35. A long-standing strategic objective in our work is the demonstration of routes to specific dienyl complexes without recourse to chromatography so that they can be made easily available on a large scale; for an example in the cyclohexadienyl series, see: Meng, W. D.; Stephenson, G. R. *J. Organometal. Chem.* **1989**, *371*, 355.
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