1,5-Asymmetric induction of chirality: highly diastereoselective addition reactions of organoaluminium reagents into ketone groups in the side-chain of π-allyltricarbonyliron lactone complexes

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The utility of π-allyltricarbonyliron lactone complexes has been extended to include their use as chiral auxiliaries. Organoaluminium reagents add into ketone groups positioned in the side-chain of the allyl ligand to afford the corresponding tertiary alcohol complexes in good to excellent yield and with excellent diastereocontrol. Enantiomerically enriched complexes can be synthesised using the Sharpless asymmetric epoxidation protocol as the source of chirality. Addition products derived from *endo* ketones can be converted into the corresponding (*E*,*E*)-η⁴-dienetricarbonyliron complexes upon treatment with barium hydroxide solution without loss of diastereo- or enantio-purity.

Introduction

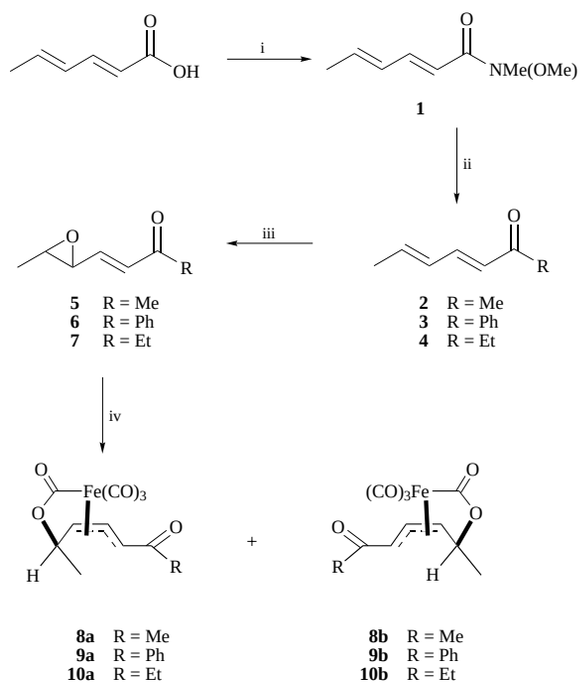
π-Allyltricarbonyliron lactone complexes[1] are readily synthesised from a variety of precursors including vinyl epoxides and cyclic sulfites. Application of Sharpless asymmetric epoxidation[2] (AE) and dihydroxylation[3] (AD) protocols provides routes to homochiral precursors and hence access to enantiomerically enriched complexes. Decomplexation of π-allyltricarbonyliron lactone complexes can be achieved in a variety of ways affording novel routes to important building blocks for organic synthesis, such as β-, γ- and δ-lactones.[1] In such decomplexation reactions the stereochemistry which has been incorporated into the complex is retained, in a defined way, in the product. π-Allyltricarbonyliron lactone complexes have consequently found wide application in the synthesis of a number of complex natural products.

An important extension to the synthetic utility of π-allyltricarbonyliron lactone complexes would be to employ their inherent chirality in controlling the stereochemical outcome of reactions carried out on functional groups appended to the periphery of the organic ligand. Just as the tricarbonyliron moiety in the related η⁴-dienetricarbonyliron complexes can act as a blocking agent controlling the addition of nucleophiles into carbonyl groups held in the side-chain of the diene ligand,[4] we reasoned that the combination of the rigidity of the lactone tether with the steric bulk provided by the tricarbonyliron group might too allow for diastereoselective addition reactions to proceed. This would also provide an example of what is formally a 1,5-asymmetric induction of chirality.

We set about testing this idea using the addition of organoaluminium reagents into ketone functional groups in the side-chain of the allyl ligand as the initial study and found that the reactions proceeded in a highly diastereoselective fashion providing a route to stereodefined secondary and tertiary alcohols. We now report our findings here in full.[5]

Results and discussion

Synthesis of π-allyltricarbonyliron lactone complexes bearing a ketone functionality in the side-chain of the allyl ligand proved relatively facile. One route which provides access to racemic complexes is outlined in Scheme 1. Thus starting from cheap and readily available (*E*,*E*)-hexa-2,4-dienoic acid, the corresponding epoxy enone precursors to the lactone complexes

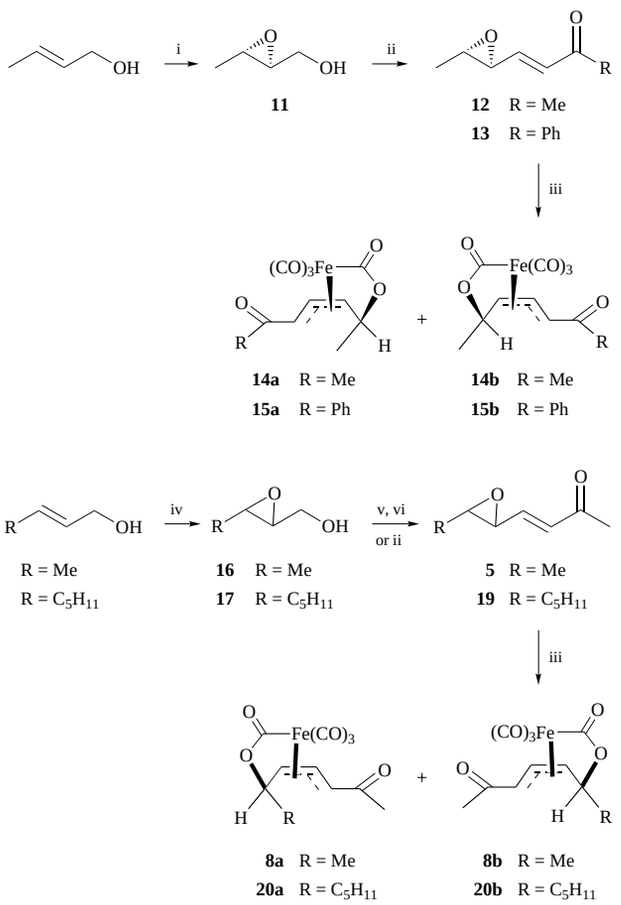


Scheme 1 *Reagents and conditions*: i, 1,1′-carbonyldiimidazole (1.2 equiv.), *N*,*O*-dimethylhydroxylamine hydrochloride (1.3 equiv.), DCM, 40 h, 90%; ii, RMgBr (1.1–1.6 equiv.), THF or Et_2O, 0 °C, 95% (**2**), 79% (**3**), 89% (**4**); iii, method A: dimethyldioxirane (*ca.* 1.1 equiv.), DCM, 0 °C, 3.5 h, 87% (**5**), or 3.5 h, 58% (**7**) or method B: $(CF_3CO)_2O$ (10 equiv.), $H_2NCONH_2{\cdot}H_2O_2$ (40 equiv.), K_2HPO_4, DCM, 1 h, 91% (**6**); iv, $Fe_2(CO)_9$ (1.8 equiv.), THF, 3 h, 41% (**8a**), 9% (**8b**), or 1.5 h, 67% (**9a**), 9% (**9b**), or 1.5 h, 50% (**10a**), 13% (**10b**)

were obtained in three steps. Synthesis of the Weinreb amide[6] **1** proceeded uneventfully and in high yield. From this, any number of ketones could be synthesised by addition of the appropriate Grignard reagent, regioselectively in a 1,2-fashion.[6] We chose to concentrate on three ketones, the methyl, phenyl and ethyl derivatives **2**, **3** and **4**. These were formed in high yield upon treating the Weinreb amide with MeMgBr, PhMgBr and EtMgBr respectively. Regioselective epoxidation of the more electron rich γ,δ-double bond of the resultant dienones was achieved either with dimethyldioxirane[7] or with *in situ*-

generated trifluoroperacetic acid[8] affording the desired epoxy enone precursors **5**, **6** and **7** to the lactone complexes. Treatment of the epoxy enones with diironnonacarbonyl [$Fe_2(CO)_9$] in tetrahydrofuran (THF)[9] at room temperature then gave rise to mixtures of *endo* and *exo* complexes **8a**, **9a** and **10a** and **8b**, **9b** and **10b** respectively which could be separated either by flash column chromatography or by preparative HPLC providing diastereoisomerically pure compounds.

An alternative approach to ketone complexes which permits the synthesis of both racemic and enantiomerically enriched derivatives is outlined in Scheme 2. For the enantiomerically



Scheme 2 *Reagents and conditions*: i, L-diisopropyl tartrate (0.18 equiv.), $Ti(OPr^i)_4$ (0.15 equiv.), 3 Å molecular sieves, Bu^{t}OOH (2 equiv.), DCM, 80%; ii, PDC (1.4 equiv.), 3 Å molecular sieves, DCM, 16 h then, $Ph_3P{=}CHC(O)CH_3$ (1.7 equiv.), THF–toluene (12 : 1), 0 °C, 2.75 h, 60% (**12**); or PDC (1.4 equiv.), 3 Å molecular sieves, DCM, 16 h then, $(EtO)_2P(O)CH_2C(O)Ph$ (2.2 equiv.), LiCl (2.2 equiv.), Pr^iNEt (2.0 equiv.), MeCN, 41% (**13**); iii, $Fe_2(CO)_9$ (1.8 equiv.), THF, 36% (**14a**), 9% (**14b**); 42% (**15a**), 10% (**15b**); iv, Bu^{t}OOH (2.0 equiv.), $Ti(OPr^i)_4$ (0.2 equiv.), 3 Å molecular sieves, DCM, 0 °C, 1 h, 42% (**16**), or Bu^{t}OOH (2.2 equiv.), $VO(acac)_2$ (0.1 equiv.), DCM, 0 °C, 1.5 h, 89% (**17**); see ii for transformation of **16** into **5**; v, CrO_3 (8.5 equiv.), pyridine (17 equiv.), Celite, DCM, then **17**, 0 °C, 45 min, 74% [(2*S**,3*R**)-2,3-epoxyoctanal **18**]; vi, $Ph_3P{=}CHC(O)CH_3$ (2.7 equiv.), DCM, 0 °C, 2 h, 44% (**19**); iii, $Fe_2(CO)_9$ (1.8 equiv.), THF, 59% (**20a**), 14% (**20b**)

enriched series the route takes advantage of the Sharpless AE reaction[2] to incorporate the required stereochemical information into the complex. Treatment of but-2-en-1-ol under the asymmetric epoxidation reaction conditions afforded the enantiomerically enriched epoxy alcohol **11**.[10] Oxidation to the corresponding aldehyde with pyridinium dichromate (PDC), Collins' reagent or using standard Swern conditions followed by homologation *via* a Wittig or Horner–Wadsworth–Emmons reaction generated the epoxy enone precursors **12** and **13** which reacted under the usual conditions of diironnonacarbonyl in THF to afford enantiomerically enriched complexes **14** and **15**. Using vanadium acetylacetonate–*tert*-butyl

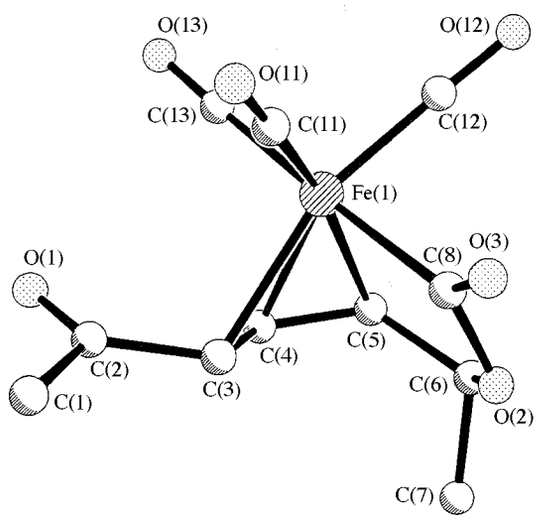


Fig. 1 X-Ray structure of complex **8a** showing the s-*cis* conformation adopted by the ketone in the side-chain of a π-allyltricarbonyliron lactone complex

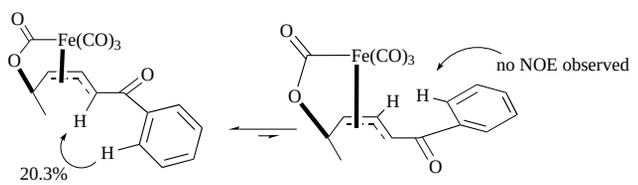


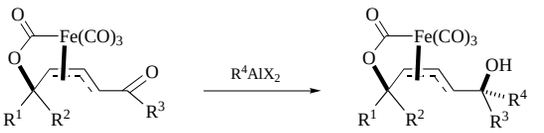
Fig. 2 Selected NOE data showing that the ketone prefers to adopt the s-*cis* conformation in the side-chain of π-allyltricarbonyliron lactone complexes

hydroperoxide in place of the AE conditions provided an alternative route to racemic complexes **8** and **20**.

For additions to the ketone functional groups to proceed with high diastereocontrol, two requirements must be fulfilled. The tricarbonyliron group must efficiently block *one* face of the carbonyl group such that the nucleophile adds from the opposite face *and* the ketone must adopt *one* reactive conformation in which the two prochiral faces can be distinguished by the iron moiety. Fortunately the ketone complex **8a** was crystalline and crystals suitable for solution by X-ray diffraction[11] were obtained. The results clearly show that, at least in the solid state, the ketone adopts one conformation, the s-*cis*, for reasons that remain undetermined although may be, at least in part, electrostatic in origin (Fig. 1). Furthermore the blocking ability of the $Fe(CO)_3$ unit appeared promising with one of the carbonyl ligands positioned directly over the ketone group preventing direct access to one of the faces of the prochiral ketone. The solution conformation was also investigated with the use of NOE experiments. These also clearly showed the preferential conformation of the ketone group to be s-*cis* (Fig. 2). Irradiation of the *ortho* aromatic protons in the phenyl ketone complex **9a** resulted in a strong enhancement of the resonance for the proton α to the carbonyl group. If the s-*trans* conformation was populated to any extent then an enhancement between the *ortho* protons on the phenyl ring and the allyl proton β to the carbonyl group would be expected. No such enhancement has been observed in any ketone complex synthesised to date. On the basis of these results a model predicting the stereochemical outcome of the addition of a nucleophile into the ketone group was proposed (Fig. 3): the approaching nucleophile would attack the ketone with the s-*cis* conformation *anti* to the tricarbonyliron moiety producing an alcohol chiral centre of predictable stereochemistry.

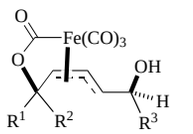
Due to the instability of π-allyltricarbonyliron lactone complexes to *strongly* Lewis basic nucleophiles such as Grignard and organolithium reagents it was decided to choose the more Lewis acidic organoaluminium reagents as nucleophiles. A wide

Table 1 Diastereoselective additions of organoaluminium reagents to racemic π-allyltricarbonyliron lactone complexes



8a R^1 = H, R^2 = Me, R^3 = Me
8b R^1 = Me, R^2 = H, R^3 = Me
9a R^1 = H, R^2 = Me, R^3 = Ph
9b R^1 = Me, R^2 = H, R^3 = Ph
10a R^1 = H, R^2 = Me, R^3 = Et
20a R^1 = H, R^2 = C_5H_{11}, R^3 = Me
20b R^1 = C_5H_{11}, R^2 = H, R^3 = Me

rac **21-25**, **27**, **29**, **31-40**



26, **28**, **30**

Complex	R^4AlX_2[a]	Product[b,c]	Yield (%)[d]
10a	$AlMe_3$	**21**	92
9a	$AlMe_3$	**22**	88
9b	$AlMe_3$	**23**	95
8a	$AlMe_3$	**24**	64
20a	$AlEt_3$	**25 (26)**	50 (33)
9a	$AlEt_3$	**27 (28)**	66 (21)
8a	$AlEt_3$	**29 (30)**	62 (37)
20a	$AlBu^i_3$	**26**	65
9a	$AlBu^i_3$	**28**	71
20a	$AlPr^n_3$	**31**[e] **(26)**	6 (93)
9a	Bu^n—≡—$AlMe_2$	**32**	70[f]
9b	Bu^n—≡—$AlMe_2$	**33**	64
8b	Bu^t—≡—$AlMe_2$	**34**	82
9a	Bu^t—≡—$AlMe_2$	**35**	58
8a	Bu^t—≡—$AlMe_2$	**36**	93
20b	$AlPhMe_2$	**37**	67
20b	Bu^n / $AlBu^i_2$	**38**	54
20b	Bu^n / $AlMe_2$	**38**	46
9a	Bu^n / $AlBu^i_2$	**39 (28)**	93 (5)
8a	Bu^n / $AlBu^i_2$	**40 (30)**	51 (9)

[a] $AlMe_3$, $AlEt_3$, $AlPr^n_3$, $AlBu^i_3$ reagents were obtained from Aldrich and used without further purification. [b] De of all products determined by ^{1}H NMR spectroscopy unless otherwise indicated and judged to be >95%. [c] Figures in parentheses refer to the reduction side-product. [d] Figures in parentheses refer to the isolated yield of the reduction side-product. [e] See ref. 22 for experimental data. [f] De >98%; determined by HPLC analysis (Daicel, OD column).

variety of organoaluminium reagents are available or easily prepared[12] thus potentially a wide range of addition products could be formed. The results obtained from the addition of a number of organoaluminium reagents into a variety of ketone complexes are outlined in Table 1. In all cases, with either *endo* or *exo* ketone complexes, the addition reaction proceeded in good to excellent yield and with excellent diastereoselectivity, only one diastereoisomeric product being observed by ^{1}H NMR (400 MHz) spectroscopic or HPLC analysis; 95% de is therefore a conservative estimate for the selectivity of the addition reaction.

In the case of trialkylaluminium reagents, trimethylaluminium ($AlMe_3$) reacted as expected transferring a methyl group in very good yield and with excellent diastereoselectivity. In the cases of triethyl-, tripropyl- and triisobutyl-aluminium an alternative reaction pathway is available, that involving

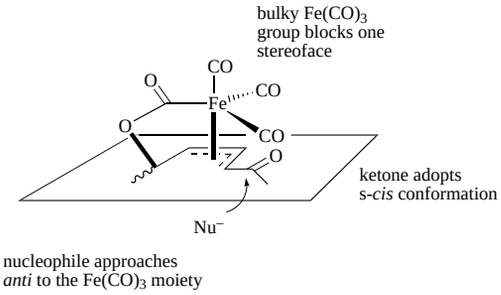


Fig. 3 Proposed model for the stereochemical outcome of the addition of nucleophiles into the ketone group in the side-chain of π-allyltricarbonyliron lactone complexes

β-hydride transfer, which would afford the secondary alcohol reduction product. While triethylaluminium ($AlEt_3$) afforded primarily the ethyl addition product upon reaction with complex **20a**, the reduction product **26** being isolated in lower yield (33%), the major product from the reaction of complex **20a** with tripropylaluminium ($AlPr^n_3$) was that resulting from the more facile β-hydride transfer; the propyl addition product **31** was only observed in very low yield (6%). In the case of triisobutylaluminium ($AlBu^i_3$), the reduction product **26** was isolated as the sole product (65%) again as a single diastereoisomer. This reflects the increased difficulty in transferring a very sterically demanding alkyl group compared with the relatively facile β-hydride transfer. Indeed $AlBu^i_3$ is now our reagent of choice if the secondary alcohol product is desired.[13] In the case of diisobutylalkenylaluminium reagents, synthesised by hydroalumination of the corresponding terminal alkynes, some reduction product was sometimes observed, albeit in small amounts. This could be prevented by using the dimethylalkenylaluminium analogues derived from the appropriate vinyllithium species and dimethylaluminium chloride. Similarly the use of dimethylalkynylaluminium reagents ensured that only the alkynyl group was transferred. With dimethylphenylaluminium the phenyl group was transferred preferentially.

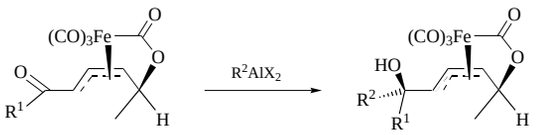
Complementary diastereoisomeric addition complexes were synthesised by the addition of $AlMe_3$ into the ethyl ketone complex **10a** and by addition of $AlEt_3$ into the methyl ketone complex **8a**. Conclusive evidence regarding the absolute stereochemistry of the tertiary alcohol centres in diastereoisomers **21** and **29** was obtained from X-ray crystal structures of the two complexes (Fig. 4).[11] These results, in conjunction with the NOE solution conformation studies (Fig. 2) and X-ray data on the ketone complex **9a** (Fig. 1) indicate that a common stereochemical pathway is operating in the addition of organoaluminium reagents to the ketone complexes. This is entirely consistent with our proposed model (Fig. 4). Thus the ketone adopts an s-*cis* conformation and the nucleophile adds *anti* to the bulky tricarbonyliron unit to afford one diastereoisomer.

The addition reactions were also carried out on enantiomerically enriched complexes and proceeded with the usual efficiency and selectivity. Importantly, no significant loss of optical purity was observed as determined by chiral shift reagents in NMR analysis or by chiral HPLC (Table 2).

Treatment of the *endo* complexes with a saturated aqueous solution of barium hydroxide in methanol results in a rapid decarboxylation reaction producing the corresponding η^4-dienetricarbonyliron complexes in good yield (Table 3). In this reaction, according to the mechanism proposed by Aumann *et al.*[14], initial attack by a hydroxide nucleophile on one of the carbonyl ligands cleaves the lactone tether producing an η^1-bound carboxylate ligand. This intermediate readily ejects carbon dioxide forming the (*E*,*E*)-η^4-dienetricarbonyliron complex by an *anti* elimination of water which is possible after an *endo* to *exo* transposition of the alkyl group bonded at the lactone tether.

Since π-allyltricarbonyliron lactone complexes are readily

Table 2 Diastereoselective additions of organoaluminium reagents to enantiomerically enriched π-allyltricarbonyliron lactone complexes



14a R^1 = Me **41–45**
15a R^1 = Ph

Complex[a]	R^2AlX_2	Product[b]	Yield (%)	ee(%)[c]
14a	Bu^n—≡—$AlMe_2$	**41**	75	84
15a	Bu^n—≡—$AlMe_2$	**42**	65	82
14a	Bu^t—≡—$AlMe_2$	**43**	70	86
15a	Bu^n / $AlBu^i_2$	**44**	67 (7)[d]	83[e]
15a	$AlMe_3$	**45**	85	85[f]

[a] Ee of **15a** measured as 87%, ee of **14a** not determined, ee of epoxy enone precursor **12** measured as 86%. [b] De of products determined by HPLC (Daicel OD column) unless stated otherwise and judged to be >98%. [c] Determined by HPLC unless stated otherwise. [d] Figure in parentheses refers to the isolated yield of the reduction side-product. [e] Determined using the chiral shift reagent Pr(hfc). [f] Determined on the decarboxylated product (see text).

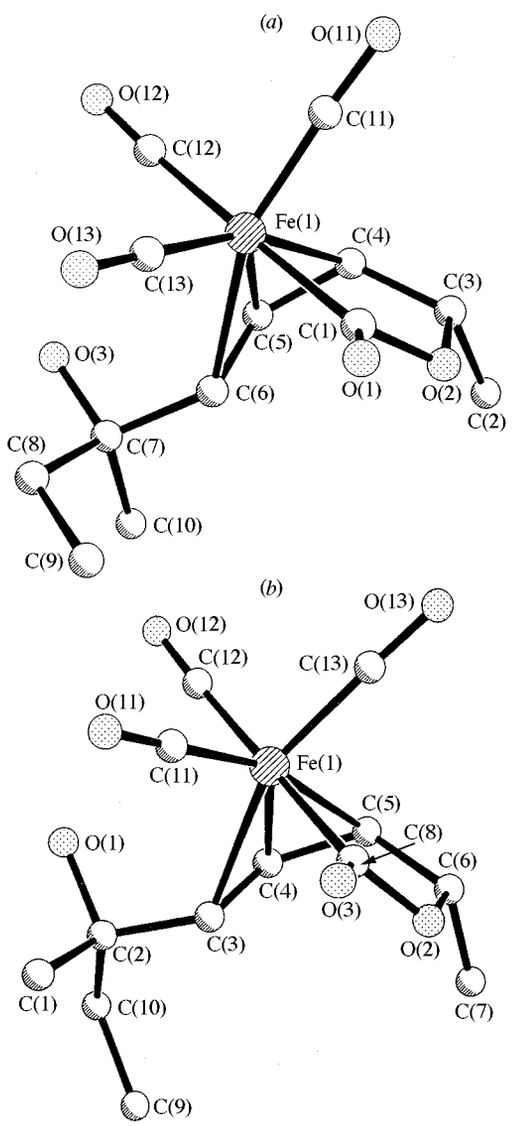
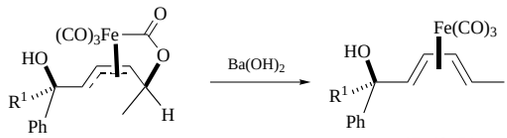


Fig. 4 X-Ray structures of diastereoisomeric addition complexes (*a*) **21** and (*b*) **29**

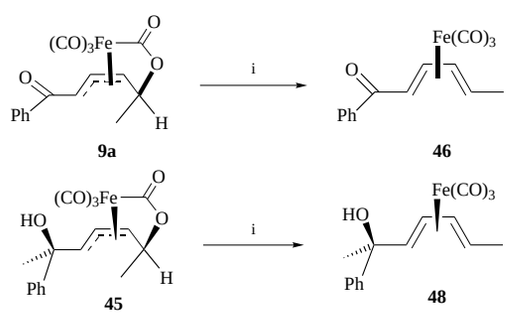
Table 3 Formation of η^4-dienetricarbonyliron complexes



47, 49–51

Complex	R^1	Product	Yield (%)
22	Me	**47**	80
39	Bu^n	**49**	81
35	Bu^t	**50**	80
28	H	**51**	94

synthesised in homochiral fashion, this decarboxylation reaction provides a facile route to homochiral η^4-dienetricarbonyliron complexes[4] thus eliminating the need for resolution, which is the commonest method for the preparation of enantiomerically enriched η^4-dienetricarbonyliron complexes.[15] With a number of *endo* addition complexes in hand, the $Ba(OH)_2$ reaction was tried and proved to be quite general (Table 3). The optically enriched addition complex **45**, prepared from epoxy enone **11** of 85% enantiomeric excess, was also treated with $Ba(OH)_2$ (Scheme 3) and the enantiomeric excess (ee) of the



Scheme 3 *Reagents and conditions*: i, $Ba(OH)_2$, MeOH, 10 min, 97% (**46**), 96% (**48**)

resulting diene complex **48** was also measured to be 85% indicating no racemisation at the tertiary stereocentre had occurred.

In summary, the synthetic utility of π-allyltricarbonyliron lactone complexes has been expanded to include their use as chiral auxiliaries in controlling the addition of nucleophiles into ketone groups in the side-chain of the allyl ligand. The addition reaction constitutes an example of 1,5-asymmetric induction of chirality with the chiral centre at the lactone tether acting, *via* the tricarbonyliron moiety, as the source of asymmetric induction. The functionalised complexes are accessible in a number of ways including one route which provides a source of enantiomerically enriched complexes. The addition of organoaluminium reagents into these complexes proceeds without loss of enantiopurity. Further the reaction of *endo* complexes with $Ba(OH)_2$ provides access to stereodefined, enantiomerically enriched η^4-dienetricarbonyliron complexes. Although much use is made of catalytic procedures involving transition metals, the use of a stoichiometric quantity of the cheap iron source in our complexes can be justified by its use to control two distinct elements of stereochemical information, namely the generation of an alcohol chiral centre and the synthesis of a stereodefined (*E,E*)-η^4-dienetricarbonyliron complex which upon decomplexation releases the free diene.[13,16]

Experimental

^1H NMR spectra were recorded in $CDCl_3$ unless stated otherwise on Bruker AC-200, Bruker AM-250, Bruker AC-250,

Bruker DPX-250, Bruker AM-400, Bruker DRX-500 or Bruker DRX-600 spectrometers and are reported as follows: chemical shift, δ (ppm), (number of protons, multiplicity, coupling constant J, and assignment). Residual protic solvent $CHCl_3$ (δ_H = 7.26 ppm) was used as the internal reference and coupling constants are quoted in Hz. ^{13}C NMR spectra were recorded in $CDCl_3$ unless stated otherwise, at 100 MHz, 62.5 MHz or 50 MHz on Bruker AM-400, Bruker DPX-250 or Bruker AM-200 spectrometers, respectively, using the central resonance of $CDCl_3$ (δ_C = 77.0 ppm) as the internal reference. Infra-red spectra were recorded as thin films between sodium chloride plates, deposited from chloroform solution or as a Nujol mull in the case of solids, on Perkin-Elmer 983G or FTIR 1620 spectrometers. Mass spectra were obtained on a Kratos MS890MS spectrometer at the Department of Chemistry, University of Cambridge, and at the EPSRC Mass Spectrometry service at Swansea. Microanalyses were determined in the microanalytical laboratories at the University of Cambridge. For those cases in which an inseparable mixture of compounds was produced, the data reported was obtained on the mixture. Where considerable assignment of ^1H NMR spectra of individual compounds in mixtures is possible, the interpretation is for each component; in other cases, ^1H NMR spectra are interpreted for the mixture. Optical rotations were measured with an Optical Activity AA-1000 polarimeter and $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}. Chiral HPLC analysis was performed on a Waters 3000 chromatographic system equipped with a Waters 990 photodiode array detector using a Daicel Chiralcel OD column. Chiral GLC analysis was performed on a Perkin-Elmer Sigma 3 gas chromatograph using a Lipodex E stationary phase.

Flash column chromatography was carried out using Merck Kieselgel (230–400 mesh) unless otherwise indicated. Analytical thin layer chromatography (TLC) was performed using precoated glass-backed plates (Merck Kieselgel 60 F254) and visualised by UV, acidic ammonium molybdate(IV) or acidic potassium permanganate solutions. Petrol refers to light petroleum bp 40–60 °C, which was distilled prior to use, and ether (Et_2O) refers to diethyl ether.

All reactions were carried out under an argon atmosphere in oven-dried glassware unless otherwise stated. Reactions involving preparation of the iron complexes were carried out using degassed tetrahydrofuran (THF). Solvents were degassed by successively evacuating and purging the solvent three times with argon whilst simultaneously subjecting the solvent to sonication using a 80 W 55 kHz cleaning bath. Diethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl; dichloromethane (DCM) from calcium hydride. Other reagents and solvents were purified using standard procedures.[17] Aqueous solutions are saturated unless otherwise specified.

Note in the synthesis of the iron lactone ketone complexes, diironnonacarbonyl [$Fe_2(CO)_9$] is used. This is extremely toxic. Furthermore, ironpentacarbonyl is a highly toxic by-product from the reaction. All work involving the handling of these species was carried out in a well ventilated hood. All glassware was treated with bleach to destroy any iron carbonyl residues before re-use.

(2*E*,4*E*)-*N*-Methoxy-*N*-methylhexa-2,4-dienamide 1

1,1′-Carbonyldiimidazole (16.7 g, 103 mmol) was added portionwise to (2*E*,4*E*)-hexa-2,4-dienoic acid (10.0 g, 89 mmol) in DCM (200 cm^3). After stirring for 1 h at room temperature, argon was bubbled through the solution for 30 min and then *N*,*O*-dimethylhydroxylamine hydrochloride (11.3 g, 114 mmol) was added and stirring was continued for a further 40 h. The reaction mixture was then poured into aqueous NH_4Cl (150 cm^3). The layers were separated and the aqueous fraction extracted with DCM (1 × 200 cm^3, 3 × 100 cm^3). The combined organic extracts were washed with brine (200 cm^3), dried ($MgSO_4$) and concentrated *in vacuo*. Purification by flash column chromatography (eluent: Et_2O–petrol 2:1) afforded *amide* **1** as a yellow oil (12.5 g, 90%) (Found: C, 61.79; H, 9.13; N, 6.42. $C_8H_{13}NO_2$ requires C, 61.95; H, 8.98; N, 6.57%); ν_{max}(film)/cm^{-1} 2965, 2936, 2914, 1660 (C=O), 1631 (C=C), 1608 (C=C), 1462, 1414, 1372, 1292, 1179, 1150, 1116, 1078; δ_H(400 MHz) 1.84 (3H, d, *J* 6.7, 6-H × 3), 3.23 (3H, s, N−Me), 3.68 (3H, s, O−Me), 6.12 (1H, dq, *J* 15.2, 6.7, 5-H), 6.23 (1H, dd, *J* 15.2, 10.5, 4-H), 6.35 (1H, d, *J* 15.2, 2-H), 7.29 (1H, dd, *J* 15.2, 10.5, 3-H); δ_C(100 MHz) 18.3 (CH_3, 6-C), 32.1 (CH_3, N−Me), 61.4 (CH_3, O−Me), 116.5 (CH), 130.1 (CH), 138.1 (CH), 143.4 (CH), 167.2 (C=O); *m*/*z* (EI) 155 (M$^+$, 72%), 124 (100, M − OMe), 95 [37, M − N(Me)OMe], 67 [56, M − C(O)N(Me)OMe].

General procedure for the synthesis of ketones 2–4

The Grignard reagent (solution in Et_2O or THF, 32–45 mmol, 1.1–1.6 equiv.) was added dropwise to a solution of the Weinreb amide **1** (29 mmol) in THF (100 cm^3) at 0 °C and the resultant solution stirred at this temperature for 30 min to 2 h. Upon completion of the reaction, the mixture was quenched by slow addition of aqueous NH_4Cl (20 cm^3) at 0 °C. The layers were separated and the aqueous fraction extracted with Et_2O (3 × 100 cm^3). The combined organic fractions were washed with brine (30 cm^3), dried ($MgSO_4$) and then concentrated *in vacuo*. Purification of the residue by flash column chromatography (eluent: Et_2O–petrol) afforded the dienone.

(3*E*,5*E*)-Hepta-3,5-dien-2-one 2

Compound **2** was synthesised according to the general procedure described above using MeMgBr (33.2 cm^3 of a 3.0 mol dm^{-3} solution in Et_2O, 100 mmol) and Weinreb amide **1** (14.05 g, 90 mmol) in THF (300 cm^3). Work-up as described and purification by flash column chromatography (eluent: Et_2O–petrol 1:3) afforded dienone **2** (9.50 g, 95%); ν_{max}(film)/cm^{-1} 1666 (C=O), 1643 (C=C), 1593 (C=C); δ_H(250 MHz) 1.85 (3H, d, *J* 5.1, 7-H × 3), 2.23 (3H, s, 1-H × 3), 6.00 (1H, d, *J* 15.2, 3-H), 6.07–6.22 (2H, m, 5-H, 6-H), 7.07 (1H, dd, *J* 15.2, 8.2, 4-H); *m*/*z* (EI) 110 (M$^+$, 36%), 95 (100, M − Me), 67 [58, M − C(O)CH$_3$] [Found (M$^+$) 110.0731. $C_7H_{10}O$ requires *M*, 110.0731].

(2*E*,4*E*)-1-Phenylhexa-2,4-dien-1-one 3

Compound **3** was synthesised according to the general procedure described above using PhMgBr (15 cm^3 of a 3.0 mol dm^{-3} solution in Et_2O, 45 mmol) and Weinreb amide **1** (4.47 g, 29 mmol) in THF (100 cm^3). Work-up as described and purification by flash column chromatography (eluent: Et_2O–petrol 1:10) afforded dienone **3** as a yellow solid (3.57 g, 79%) (Found: C, 83.77; H, 7.03. $C_{12}H_{12}O$ requires C, 83.68; H, 7.02%); ν_{max}(film)/cm^{-1} 3020, 3010, 2970, 2860, 1661 (C=O), 1630 (C=C), 1590 (C=C), 1447, 1329, 1250, 1190, 1120, 1060, 1020; δ_H(400 MHz) 1.90 (3H, d, *J* 6.0, 6-H × 3), 6.30 (1H, dq, *J* 15.0, 6.0, 5-H), 6.34 (1H, dd, *J* 15.0, 9.9, 4-H), 6.86 (1H, d, *J* 15.1, 2-H), 7.40 (1H, dd, *J* 15.1, 9.9, 3-H), 7.46 (2H, apparent t, *J* 7.8, *m*-Ph-*H*), 7.54 (1H, tt, *J* 7.8, 1.4, *p*-Ph-*H*), 7.93 (2H, dd, *J* 7.8, 1.4, *o*-Ph-*H*); δ_C(100 MHz) 18.9 (CH_3, 6-C), 123.4 (CH), 128.3 (CH), 128.5 (CH), 128.6 (CH), 130.6 (CH), 132.5 (quat. C), 141.1 (CH), 145.3 (CH), 190.9 (CO); *m*/*z* (EI) 172 (M$^+$, 62%), 105 [100, M − Me(CH)$_4$], 95 (7, M − Ph), 77 [75, M − Me(CH)$_4$C(O)], 51 (32) [Found (M$^+$) 172.0895. $C_{12}H_{12}O$ requires *M*, 172.0888].

(4*E*,6*E*)-Octa-4,6-dien-3–one 4

Compound **4** was synthesised according to the general procedure described above using EtMgBr (21.4 cm^3 of a 1.0 mol dm^{-3} solution in THF, 21 mmol) and Weinreb amide **1** (2.22 g, 14 mmol) in THF (40 cm^3). After the aqueous work-up as described, the organic solvent was removed by distillation. The residue was then filtered through a pad of silica, washing with Et_2O–petrol (30–40 °C boiling point fraction) (300 cm^3, 1:1).

The solvents were removed by distillation at atmospheric pressure to provide dienone **4** as a colourless oil (1.57 g, 89%); ν_{max}(film)/cm^{-1} 3028, 2970, 2820, 2790, 1667 (C=O), 1640 (C=C), 1597, 1459, 1440, 1414, 1361, 1200, 1117, 1065, 997, 916; δ_H(200 MHz) 1.06 (3H, t, *J* 7.3, 1-H × 3), 1.81 (3H, dd, *J* 5.2, 2.0, 8-H × 3), 2.51 (2H, q, *J* 7.3, 2-H × 2), 5.98–6.17 (3H, m, 4-H, 6-H, 7-H), 7.03–7.18 (1H, m, 5-H); δ_C(50 MHz) 8.1 (CH_3, 8-C), 18.6 (CH_3, 1-C), 33.5 (CH_2, 7-C), 127.3 (CH), 130.2 (CH), 139.8 (CH), 142.4 (CH), 201.1 (CO); *m*/*z* (EI) 124 (M^+, 32%), 109 (25, M − Me), 95 (83, M − Et), 77 (21), 67 (29), 57 [100, M − Me(CH)$_4$] [Found (M^+) 124.0894. $C_8H_{12}O$ requires *M*, 124.0888].

General procedure for the synthesis of epoxy enones 5–7

Method A. Dimethyldioxirane[7] (DMDO) (140 cm^3 of a *ca*. 0.05 mol dm^{-3} solution in acetone, *ca*. 7 mmol) was added *via* cannula to a stirred solution of the dienone (6.65 mmol) in DCM (40 cm^3) at 0 °C. The reaction mixture was stirred at this temperature or warmed to room temperature (as appropriate). Upon completion of reaction, $MgSO_4$ was added and the resultant suspension stirred vigorously for 20 min. Filtration and removal of the solvents afforded the crude product which was purified by flash column chromatography to afford the epoxy enone.

Method B. Trifluoroacetic anhydride (2.94 mmol) was added dropwise to a stirred suspension of the dienone (0.29 mmol), urea–hydrogen peroxide addition complex (11.70 mmol) and dipotassium hydrogen phosphate (5.13 mmol) in DCM (4 cm^3) at 0 °C. The resulting slurry was warmed to room temperature and stirred for 1 h, after which time aqueous $NaHCO_3$ (20 cm^3) was added and stirring was continued until effervescence ceased. (Note: on a larger scale it is advantageous to add the reaction mixture to stirred aqueous $NaHCO_3$ at 0 °C.) The layers were separated and the aqueous fraction was extracted with DCM (3 × 20 cm^3). The combined organic extracts were then washed with brine (30 cm^3), dried ($MgSO_4$) and concentrated *in vacuo* to afford the epoxy enone after purification by flash column chromatography.

(3*E*,5*R,6*R**)-5,6-Epoxyhept-3-en-2-one 5**

Compound **5** was prepared according to method A (*vide supra*) from dienone **2** (1.00 g, 9.09 mmol) and DMDO (95 cm^3 of a *ca*. 0.1 mol dm^{-3} solution in acetone, *ca*. 9.50 mmol). After 3.5 h at 0 °C, work-up as described and purification by flash column chromatography (eluent: Et_2O–hexane 1:3) yielded *epoxy enone* **5** as a volatile, yellow liquid (1.00 g, 7.94 mmol, 87%); ν_{max}(film)/cm^{-1} 2954, 1676 (C=O), 1630 (C=C), 1593, 1420, 1259, 1186, 1142, 1006, 973, 940, 864, 804; δ_H(250 MHz) 1.38 (3H, d, *J* 5.2, 7-H × 3), 2.24 (3H, s, 1-H × 3), 2.99 (1H, qd, *J* 5.2, 2.0, 6-H), 3.17 (1H, dd, *J* 6.6, 2.0, 5-H), 6.33 (1H, d, *J* 16.0, 3-H), 6.45 (1H, dd, *J* 16.0, 6.6, 4-H); *m*/*z* (CI) 127 (MH^+, 2%), 82 (100, $C_5H_{10}O$) [Found (MH^+) 127.0761. $C_7H_{11}O_2$ requires *M*H, 127.0758].

An alternative method which is also applicable to the preparation of enantiomerically enriched material is described below.

Epoxy alcohol **16** (0.50 g, 5.7 mmol) was added to a vigorously stirred suspension of pyridinium dichromate (3.00 g, 8.0 mmol) and activated 3 Å powdered molecular sieves (*ca.* 6 g) in DCM (40 cm^3). After 16 h at room temperature the reaction mixture was filtered through a pad of silica/$MgSO_4$/silica and washed with Et_2O (400 cm^3). The combined filtrates were concentrated *in vacuo* to a small volume and transferred into a reaction vessel containing THF–toluene (65 cm^3, 12:1). 1-(Triphenylphosphoranylidene)propan-2-one (3.00 g, 9.43 mmol) was added to the cooled (0 °C) solution. After stirring for 2.75 h, the reaction mixture was filtered through a pad of silica, eluting with Et_2O–petrol (30–40 °C boiling point fraction) (100 cm^3, 3:1). The filtrate was concentrated and then subjected to purification by flash column chromatography [eluent: Et_2O–petrol (30–40 °C boiling point fraction) 1:2→neat Et_2O; gradient] to give epoxy enone **5** as a yellow liquid (0.43 g, 60%), which had identical spectroscopic properties to material prepared earlier (*vide supra*).

(4*E*,6*R,7*R**)-6,7-Epoxyoct-4-en-3-one 7**

Compound **7** was prepared according to method A (*vide supra*) from dienone **4** (0.825 g, 6.65 mmol). After 1 h at 0 °C and then 3.5 h at room temperature, work-up as described and purification by flash column chromatography [eluent: Et_2O–petrol (boiling point fraction 30–40 °C) 1:7] yielded *epoxy enone* **7** as a colourless liquid (0.534 g, 58%); ν_{max}(film)/cm^{-1} 3020, 2989, 1677 (C=O), 1633 (C=C), 1459, 1417, 1378, 1235, 1201, 1119, 1036, 1007, 978, 942; δ_H(200 MHz) 1.09 (3H, t, *J* 7.3, 1-H × 3), 1.38 (3H, d, *J* 5.2, 8-H × 3), 2.56 (2H, q, *J* 7.3, 2-H × 2), 2.97 (1H, qd, *J* 5.2, 2.0, 7-H), 3.17 (1H, dd, *J* 6.4, 2.0, 6-H), 6.37 (1H, d, *J* 15.9, 4-H), 6.52 (1H, dd, *J* 15.9, 6.4, 5-H); *m*/*z* (EI), 141 (MH^+, 15%), 124 (8, M − O), 111 (39, M − Et), 96 (45), 81 (100), 57 [32, M − MeCH(O)CH(CH)$_2$] [Found (MH^+) 141.0906. $C_8H_{13}O_2$ requires *M*H, 141.0915].

(2*E*,4*R,5*R**)-4,5-Epoxy-1-phenylhex-2-en-1-one 6**

Compound **6** was prepared according to method B (*vide supra*) from the dienone **3** (0.050 g, 0.29 mmol). After 1 h at room temperature, work-up as described and purification by flash column chromatography (eluent: Et_2O–petrol 1:7) afforded *epoxy enone* **6** as a yellow oil (0.051 g, 91%) (Found: C, 76.47; H, 6.56. $C_{12}H_{12}O_2$ requires C, 76.57; H, 6.43%); ν_{max}(film)/cm^{-1} 3013, 2930, 1672 (C=O), 1625 (C=C), 1579, 1448, 1380, 1345, 1269, 1238, 1177, 1017, 965, 971, 906; δ_H(400 MHz) 1.40 (3H, d, *J* 5.1, 6-H × 3), 3.01 (1H, qd, *J* 5.1, 2.1, 5-H), 3.28 (1H, dd, *J* 6.7, 2.1, 4-H), 6.79 (1H, dd, *J* 15.1, 6.7, 3-H), 7.18 (1H, d, *J* 15.1, 2-H), 7.45 (2H, apparent t, *J* 7.9, *m*-Ph-*H*), 7.55 (1H, tt, *J* 7.9, 1.5, *p*-Ph-*H*), 7.93 (2H, dd, *J* 7.9, 1.5, *o*-Ph-*H*); δ_C(100 MHz) 17.7 (CH_3), 57.8 (CH), 58.0 (CH), 127.1 (CH), 128.7 (CH), 128.8 (CH), 133.2 (CH), 137.4 (quat. C), 144.8 (CH), 189.5 (C=O); *m*/*z* (EI) 188 (M^+, 83%), 172 (20, M − O), 144 [100, M − MeCH(O)], 77 [90, M − MeCH(O)(CH)$_3$C(O)], 51 (36) [Found (M^+) 188.0841. $C_{12}H_{12}O_2$ requires *M*, 188.0837].

(2*R,3*R**)-2,3-Epoxybutan-1-ol 16**

tert-Butyl hydroperoxide (93.0 cm^3 of a 3 mol dm^{-3} solution in 2,2,4-trimethylpentane, 0.279 mol), (2*E*)-but-2-en-1-ol (11.8 cm^3, 0.139 mol) in DCM (200 cm^3) and titanium(IV) isopropoxide (8.2 cm^3, 0.028 mol) in DCM (200 cm^3) were all stirred separately over activated 3 Å powdered molecular sieves at room temperature for 30 min. The *tert*-butyl hydroperoxide and alcohol solutions were then added sequentially *via* cannula to the titanium(IV) isopropoxide solution at 0 °C and the resulting mixture was stirred efficiently and allowed to warm to room temperature. After 2 h, a solution of citric acid (5.2 g, 0.028 mol) in Et_2O–acetone (330 cm^3, 10:1) was added to the reaction mixture at 0 °C *via* cannula and the solution stirred for 1 h at 0 °C. The reaction mixture was then filtered through a pad of Celite and washed with Et_2O (200 cm^3). The filtrate was concentrated by first evacuating the rotary evaporator and then isolating the system to ensure minimal loss of the fairly volatile product. Flash column chromatography of the concentrate [eluent: Et_2O–petrol (30–40 °C boiling point fraction) 2:3→9:1; gradient] afforded epoxy alcohol **16** as a colourless oil (5.2 g, 42%), which was spectroscopically identical to that reported in the literature.[10]

(2*R,3*R**)-2,3-Epoxyoctan-1-ol 17**

tert-Butyl hydroperoxide (25.0 cm^3 of a 3 mol dm^{-3} solution in 2,2,4-trimethylpentane, 76 mmol), which had been dried over activated 4 Å powdered molecular sieves for 30 min prior to use, was added *via* cannula to (2*E*)-oct-2-en-1-ol (5.00 g, 35.0 mmol) in DCM (106 cm^3) at 0 °C. Vanadium(III) acetylacetonate (0.72 g, 3.5 mmol) was then added in one portion and the solution was stirred at 0 °C for 1.5 h. Aqueous Na_2SO_3 (100 cm^3) was

added and the reaction mixture stirred for 30 min and gradually warmed to room temperature. The solution was then filtered through a pad of Celite and then poured into brine (100 cm^3). The layers were separated and the aqueous phase was extracted with Et_2O (3 × 100 cm^3). The combined organic extracts were washed with brine (50 cm^3), dried ($MgSO_4$) and concentrated *in vacuo*. Purification of the residue by flash column chromatography (eluent: Et_2O–petrol 1:9→1:1; gradient) provided the epoxy alcohol **17** as a white solid (5.02 g, 89%) which was spectroscopically identical to that reported in the literature.[10]

(2*S,3*R**)-2,3-Epoxyoctanal 18**

Chromium(VI) oxide (24.94 g, 250 mmol) was added to a solution of pyridine (41 cm^3, 507 mmol) in DCM (420 cm^3). After stirring the suspension for 15 min, Celite (30 g) was added and the resultant slurry was stirred vigorously for a further 5 min before cooling to 0 °C. A solution of the epoxy alcohol **17** (4.21 g, 29 mmol) in DCM (50 cm^3) was then added *via* cannula. After warming to room temperature and stirring for a further 45 min, $NaHSO_4$ (60 g) and Et_2O (400 cm^3) were added and the mixture was stirred vigorously for 15 min before being filtered through a sandwich of silica/$MgSO_4$/silica washing with Et_2O (1500 cm^3). Concentration of the filtrate *in vacuo* followed by flash column chromatography [eluent: Et_2O–petrol (30–40 °C boiling point fraction) 1:32→1:19; gradient] provided aldehyde **18** as a colourless oil (3.06 g, 74%); ν_{max}(film)/cm^{-1} 2957, 2930, 2860, 2733, 1729 (C=O), 1467, 1436, 1380, 1150, 1050, 981; δ_H(200 MHz) 0.90 (3H, t, *J* 7.1, 8-H × 3), 1.30–1.62 (8H, m, 4-H × 2, 5-H × 2, 6-H × 2, 7-H × 2), 3.12 (1H, dd, *J* 6.2, 2.0, 2-H), 3.21 (1H, td, *J* 5.3, 2.0, 3-H), 9.01 (1H, d, *J* 6.2, 1-H); δ_C(100 MHz) 13.9 (CH_3), 22.5 (CH_2), 25.4 (CH_2), 31.2 (CH_2), 31.4 (CH_2), 56.8 (CH), 59.2 (CH), 198.5 (C=O); *m*/*z* (EI) 142 (M^+, 25%), 113 (52, M − CHO), 83 (72), 71 [100, M − Me$(CH)_4$], 69 (55), 55 (90) [Found (M^+) 142.0987. $C_8H_{14}O_2$ requires *M*, 142.0993].

(3*E*,5*R,6*R**)-5,6-Epoxyundec-3-en-2-one 19**

1-(Triphenylphosphoranylidene)propan-2-one (4.86 g, 15.3 mmol) in DCM (35 cm^3) was added *via* cannula to a stirred solution of the epoxy aldehyde **18** (0.81 g, 5.7 mmol) in DCM (45 cm^3) at 0 °C and the reaction mixture was stirred for 2 h and then warmed to room temperature. The mixture was then poured into H_2O (50 cm^3) and the layers were separated. The aqueous phase was extracted with Et_2O (2 × 80 cm^3). The combined organic phases were washed with brine (75 cm^3), dried ($MgSO_4$) and concentrated *in vacuo*. The residue was repeatedly triturated with petrol to separate the Ph_3PO by filtration. Purification of the residue by flash column chromatography (eluent: Et_2O–petrol 1:7) afforded *epoxy enone* **19** as a colourless liquid (0.45 g, 44%); ν_{max}(film)/cm^{-1} 2955, 2929, 2857, 1698, 1679 (C=O), 1629 (C=C), 1466, 1432, 1360, 1298, 1256, 1180, 1146, 976, 883, 827, 728; δ_H(200 MHz) 0.88 (3H, t, *J* 7.2, 11-H × 3), 1.22–1.64 (8-H, m, 7-H × 2, 8-H × 2, 9-H × 2, 10-H × 2), 2.24 (3H, s, 1-H × 3), 2.89 (1H, td, *J* 5.3, 2.1, 6-H), 3.20 (1H, dd, *J* 6.7, 2.1, 5-H), 6.32 (1H, d, *J* 16.8, 3-H), 6.47 (1H, dd, *J* 16.8, 6.7, 4-H); δ_C(62.5 MHz) 13.9 (CH_3), 22.5 (CH_2), 25.4 (CH_2), 27.2 (CH_3), 31.4 (CH_2), 31.8 (CH_2), 56.4 (CH), 61.5 (CH), 132.4 (CH), 143.6 (CH), 197.3 (C=O); *m*/*z* (CI) 200 [$(M + NH_4)^+$, 33%], 183 (58, MH), 167 (35, MH − O), 95 (23), 82 (100) [Found (MH^+) 183.1388. $C_{11}H_{19}O_2$ requires *M*H, 183.1385].

General procedure for the synthesis of ketone complexes 8–10 and 20

THF (28 cm^3) was added to diironnonacarbonyl (3.21 g, 8.82 mmol) *via* cannula and the mixture stirred vigorously in the absence of light for 15–20 min at room temperature after which time the epoxy enone (4.89 mmol) was added and the reaction mixture stirred vigorously. Upon completion of the reaction (usually 1.5–3 h), the mixture was filtered through a pad of Celite washing with Et_2O (60 cm^3). Toluene (2 cm^3) was added and the solution was concentrated *in vacuo*. (CARE: iron-pentacarbonyl is a highly toxic and volatile by-product from the reaction). Purification of the residue by flash column chromatography [eluent: petrol (to elute off the triiron-dodecacarbonyl)→Et_2O–petrol; gradient] afforded in order of elution, the *endo* complex and then the *exo* complex.

[(4*E*,2*R,3*S**)-2-(Carbonyloxy-κ*C*)-6-oxo-(3,4,5-η)-hept-4-en-3-yl]tricarbonyliron 8a and [(4*E*,2*R**,3*R**)-2-(carbonyloxy-κ*C*)-6-oxo-(3,4,5-η)-hept-4-en-3-yl]tricarbonyliron 8b**

Complexes **8a** and **8b** were prepared according to the general procedure using epoxy enone **5** (0.50 g, 4.0 mmol) and diironnonacarbonyl (3.00 g, 8.2 mmol) in THF (20 cm^3). After 3 h, work-up as described and purification by flash column chromatography (eluent: petrol→Et_2O–petrol 3:7; gradient) afforded, in order of elution, *ketone* **8a** as a yellow solid (0.48 g, 41%) (Found: C, 44.92; H, 3.52. $C_{11}H_{10}FeO_6$ requires C, 44.93; H, 3.43%); ν_{max}(film)/cm^{-1} 2923, 2853, 2088 (CO), 2019 (CO), 1682 (C=O), 1661 (C=O), 1462, 1377, 1309, 1182, 1169, 1088, 1049, 1001, 946, 905, 721, 654; δ_H(500 MHz) 1.39 (3H, d, *J* 6.4, 1-H × 3), 2.44 (3H, s, 7-H × 3), 3.90 (1H, d, *J* 11.1, 5-H), 4.53 (1H, qd, *J* 6.4, 4.6, 2-H), 5.06 (1H, dd, *J* 8.7, 4.6, 3-H), 5.54 (1H, dd, *J* 11.1, 8.7, 4-H); δ_C(100 MHz; C_6D_6) 21.5 (CH_3), 29.4 (CH_3), 66.1 (CH), 72.4 (CH), 85.8 (CH), 91.6 (CH), 198.9 (CO), 200.3 (CO × 2), 205.9 (CO), 208.9 (CO); *m*/*z* (FAB) 295 (MH^+, 43%), 211 (8, MH − 3CO), 154 (100, M − 3CO − Fe) [Found (MH^+) 294.9931. $C_{11}H_{11}FeO_6$ requires *M*H, 294.9905]; and then *ketone* **8b** as a pale yellow solid (0.10 g, 9%); ν_{max}(film)/cm^{-1} 2923, 2853, 2088 (CO), 2024 (CO), 1682 (C=O), 1661 (C=O), 1462, 1377, 1309, 1182, 1169, 1088, 1049, 1001, 946, 905, 721, 654; δ_H(500 MHz) 1.43 (3H, d, *J* 6.4, 1-H × 3), 2.41 (3H, s, 7-H × 3), 3.76 (1H, d, *J* 11.1, 5-H), 4.30 (1H, q, *J* 6.4, 2-H), 4.83 (1H, d, *J* 8.3, 3-H), 5.70 (1H, dd, *J* 11.1, 8.3, 4-H); δ_C(100 MHz; C_6D_6) 23.9 (CH_3), 29.3 (CH_3), 65.1 (CH), 69.9 (CH), 84.7 (CH), 92.9 (CH), 198.8 (CO), 200.3 (CO), 200.6 (CO), 205.8 (CO), 209.1 (CO); *m*/*z* (FAB) 295 (MH^+, 35%), 211 (15, MH − 3CO) [Found (MH^+) 294.9896. $C_{11}H_{11}FeO_6$ requires *M*H, 294.9905].

[(4*E*,2*R,3*S**)-2-(Carbonyloxy-κ*C*)-6-oxo-(3,4,5-η)-oct-4-en-3-yl]tricarbonyliron 10a and [(4*E*,2*R**,3*R**)-2-(carbonyloxy-κ*C*)-6-oxo-(3,4,5-η)-oct-4-en-3-yl]tricarbonyliron 10b**

Complexes **10a** and **10b** were prepared according to the general procedure using epoxy enone **7** (0.43 g, 3.0 mmol) and diironnonacarbonyl (2.00 g, 5.5 mmol) in THF (14 cm^3). After 1.5 h, work-up as described and purification by flash column chromatography (eluent: petrol→Et_2O–petrol 1:1; gradient) afforded, in order of elution, *ketone* **10a** as a bright yellow solid (0.47 g, 50%) (Found: C, 46.44; H, 3.95. $C_{12}H_{12}FeO_6$ requires C, 46.60; H, 4.24%); ν_{max}(film)/cm^{-1} 3054, 2985, 2091 (CO), 2025 (CO), 1671 (C=O), 1499, 1421, 1360, 1265, 1086, 1053, 1001, 946; δ_H(200 MHz) 1.20 (3H, t, *J* 7.3, 8-H × 3), 1.38 (3H, d, *J* 6.4, 1-H × 3), 2.75 (2H, q, *J* 7.3, 7-H × 2), 3.89 (1H, d, *J* 11.3, 5-H), 4.52 (1H, qd, *J* 6.4, 4.7, 2-H), 5.04 (1H, dd, *J* 8.7, 4.7, 3-H), 5.54 (1H, dd, *J* 11.3, 8.7, 4-H); δ_C(50 MHz) 7.9, 21.8, 36.5, 65.5, 72.9, 85.4, 92.0, 199.7, 202.6, 204.6, 205.0, 207.9; *m*/*z* (FAB) 309 (MH^+, 37%), 275 (22), 239 (15), 225 (10, MH − 3CO), 186 (100), 183 (25), 167 (24, M − CH_3CH_2CO − 3CO), 125 (17, MH − 4CO − Fe − O) [Found (MH^+) 309.0052. $C_{12}H_{13}FeO_6$ requires *M*H, 309.0061]; and then *ketone* **10b** as a yellow solid (0.12 g, 13%); ν_{max}(film)/cm^{-1} 3052, 2977, 2092 (CO), 2025 (CO), 1665 (C=O), 1493, 1451, 1411, 1379, 1307, 1216, 1172, 1089, 1046, 1006, 952; δ_H(200 MHz) 1.17 (3H, t, *J* 7.3, 8-H × 3), 1.41 (3H, d, *J* 6.5, 1-H × 3), 2.71 (2H, q, *J* 7.3, 7-H × 2), 3.74 (1H, d, *J* 11.0, 5-H), 4.29 (1H, q, *J* 6.5, 2-H), 4.81 (1H, d, *J* 8.5, 3-H), 5.70 (1H, dd, *J* 11.0, 8.5, 4-H); δ_C(100 MHz) 7.9 (CH_3), 24.1 (CH_3), 36.6 (CH_2), 64.9 (CH), 70.8 (CH), 84.4 (CH), 93.6 (CH), 200.0 (CO), 202.5 (CO), 204.7 (CO), 204.9 (CO), 208.2

(CO); *m/z* (FAB) 309 (MH^+, 95%), 281 (17, MH − CO), 253 (7, MH − 2CO), 225 (42, MH − 3CO), 197 (100, MH − 2CO − Fe), 179 (26), 125 (15, MH − 4CO − Fe − O), 121 (32) [Found (MH^+) 309.0062. $C_{12}H_{13}FeO_6$ requires *M*H, 309.0061].

[(4*E*,2*R,3*S**)-2-(Carbonyloxy-κ*C*)-6-oxo-6-phenyl-(3,4,5-η)-hex-4-en-3-yl]tricarbonyliron 9a and [(4*E*,2*R**,3*R**)-2-(carbonyloxy-κ*C*)-6-oxo-6-phenyl-(3,4,5-η)-hex-4-en-3-yl]-tricarbonyliron 9b**

Complexes **9a** and **9b** were prepared according to the general procedure using epoxy enone **6** (0.11 g, 0.59 mmol) and diironnonacarbonyl (0.36 g, 0.98 mmol) in THF (10 cm^3). After 1.5 h, work-up as described and purification by flash column chromatography (eluent: petrol→Et_2O–petrol 1 : 3; gradient) afforded a mixture of *ketones* **9a** and **9b** as a yellow solid. Preparative HPLC (Dynamax 25.2 mm column; eluent: EtOAc–hexane 1 : 6; flow rate 15 $cm^3\ min^{-1}$) afforded, in order of elution, *ketone* **9a** as a yellow solid (0.12 g, 67%) (Found: C, 53.68; H, 3.52. $C_{16}H_{12}FeO_6$ requires C, 53.95; H, 3.40%); ν_{max}(film)/cm^{-1} 3050, 3010, 2950, 2093 (CO), 2025 (CO), 1659 (C=O), 1598, 1580, 1500, 1449, 1418, 1359, 1341, 1325, 1304, 1240, 1110, 1054; δ_H(400 MHz) 1.43 (3H, d, *J* 6.3, 1-H × 3), 4.60 (1H, d, *J* 10.9, 5-H), 4.62 (1H, qd, *J* 6.3, 4.5, 2-H), 5.14 (1H, dd, *J* 8.4, 4.5, 3-H), 5.86 (1H, dd, *J* 10.9, 8.4, 4-H), 7.54 (2H, apparent t, *J* 7.8, *m*-Ph-*H*), 7.64 (1H, tt, *J* 7.8, 1.5, *p*-Ph-*H*), 8.07 (2H, dd, *J* 7.8, 1.5, *o*-Ph-*H*); δ_C(50 MHz) 21.9, 62.2, 73.1, 85.9, 92.5, 128.4, 129.1, 134.0, 136.0, 193.4, 199.8, 203.2, 204.4, 207.9; *m/z* (FAB) 357 (MH^+, 100%), 329 (10, MH − CO), 273 (20, MH − 3CO), 245 (90) [Found (MH^+) 357.0061. $C_{16}H_{13}FeO_6$ requires *M*H, 357.0061]; and then *ketone* **9b** as a yellow solid (0.04 g, 9%); ν_{max}(film)/cm^{-1} 3047, 3009, 2950, 2094 (CO), 2048 (CO), 2030 (CO), 1658 (C=O), 1598, 1580, 1500, 1448, 1417, 1320, 1220, 1119; δ_H(400 MHz) 1.47 (3H, d, *J* 6.5, 1-H × 3), 4.40 (1H, q, *J* 6.5, 2-H), 4.46 (1H, d, *J* 10.4, 5-H), 4.91 (1H, d, *J* 8.3, 3-H), 6.03 (1H, dd, *J* 10.4, 8.3, 4-H), 7.53 (2H, apparent t, *J* 7.8, *m*-Ph-*H*), 7.63 (1H, tt, *J* 7.8, 1.6, *p*-Ph-*H*), 8.05 (2H, dd, *J* 7.8, 1.6, *o*-Ph-*H*); δ_C(50 MHz) 23.9, 61.4, 70.8, 84.9, 94.0, 128.2, 129.0, 133.9, 135.8, 193.2, 199.0, 202.8, 204.2, 208.1; *m/z* (FAB) 357 (MH^+, 40%), 329 (24, MH − CO), 301 (21, MH − 2CO), 245 (78) [Found (MH^+) 357.0061. $C_{16}H_{13}FeO_6$ requires *M*H, 357.0061].

[(3*E*,5*S,6*R**)-6-(Carbonyloxy-κ*C*)-2-oxo-(3,4,5-η)-undec-3-en-5-yl]tricarbonyliron 20a and [(3*E*,5*R**,6*R**)-6-(carbonyloxy-κ*C*)-2-oxo-(3,4,5-η)-undec-3-en-5-yl]tricarbonyliron 20b**

Complexes **20a** and **20b** were prepared according to the general procedure using epoxy enone **19** (0.89 g, 4.89 mmol) and diironnonacarbonyl (3.21 g, 8.82 mmol) in THF (28 cm^3). After 3 h, work-up as described and purification by flash column chromatography (eluent: petrol→Et_2O–petrol 7 : 3; gradient) afforded, in order of elution, *ketone* **20a** as a brown solid (1.01 g, 59%) (Found: C, 51.29; H, 5.15. $C_{15}H_{18}FeO_6$ requires C, 51.42; H, 5.18%); ν_{max}(film)/cm^{-1} 3017, 2931, 2860, 2091 (CO), 2025 (CO), 1676 (C=O), 1498, 1466, 1418, 1362, 1310, 1216, 1174, 1020; δ_H(200 MHz) 0.88 (3H, t, *J* 6.5, 11-H × 3), 1.20–1.64 (8H, m, 7-H × 2, 8-H × 2, 9-H × 2, 10-H × 2), 2.43 (3H, s, 1-H × 3), 3.85 (1H, d, *J* 10.9, 3-H), 4.34 (1H, td, *J* 6.4, 4.8, 6-H), 5.03 (1H, dd, *J* 8.8, 4.8, 5-H), 5.55 (1H, dd, *J* 10.9, 8.8, 4-H); δ_C(100 MHz) 13.9 (CH_3, 11-C), 22.4 (CH_2), 26.5 (CH_2), 30.2 (CH_3, 1-C), 31.5 (CH_2), 36.7 (CH_2), 65.8 (CH), 77.4 (CH), 84.7 (CH), 92.0 (CH), 199.7 (CO), 201.6 (CO), 202.4 (CO), 204.9 (CO), 207.8 (CO); *m/z* (FAB) 351 (MH^+, 100%), 323 (12, MH − CO), 267 (14, MH − 3CO), 239 (92), 222 (5, M − 4CO − O), 208 (12, MH − 4CO − O − Me), 167 (13, MH − 4CO − Fe − O) [Found (MH^+) 351.0547. $C_{15}H_{19}FeO_6$ requires *M*H, 351.0531]; and then *ketone* **20b** as a brown solid (0.24 g, 14%); ν_{max}(film)/cm^{-1} 3019, 2930, 2858, 2094 (CO), 2048 (CO), 2029 (CO), 1660 (C=O), 1522, 1423, 1215, 1015; δ_H(200 MHz) 0.89 (3H, t, *J* 7.2, 11-H × 3), 1.23–1.68 (8H, m, 7-H × 2, 8-H × 2, 9-H × 2, 10-H × 2), 2.30 (3H, s, 1-H × 3), 3.74 (1H, d, *J* 11.2, 3-H), 4.05 (1H, t, *J* 5.9, 6-H), 4.86 (1H, d, *J* 8.3, 5-H), 5.73 (1H, dd, *J* 11.2, 8.3, 4-H); δ_C(100 MHz) 13.9 (CH_3, 11-C), 22.5 (CH_2), 25.1 (CH_2), 30.2 (CH_3), 31.3 (CH_2), 38.1 (CH_2), 64.9 (CH), 74.4 (CH), 83.5 (CH), 93.6 (CH), 199.9 (CO), 201.5 (CO), 202.1 (CO), 204.8 (CO), 208.0 (CO); *m/z* (FAB) 351 (MH^+, 100%), 323 (10, MH − CO), 267 (52, MH − 3CO), 239 (72), 222 (13, M − 4CO − O), 208 (7, MH − 4CO − O − Me), 167 (32, MH − 4CO − Fe − O) [Found (MH^+) 351.0526. $C_{15}H_{19}FeO_6$ requires *M*H, 351.0531].

General procedure for the addition of alkyl organoaluminium reagents into ketone complexes: synthesis of complexes 21–31

Trialkylaluminium (0.40 mmol) was added dropwise to a cooled (0 °C unless stated otherwise) solution of the ketone complex (0.19 mmol) in DCM (unless stated otherwise) (1.5 cm^3). Stirring was continued until complete consumption of starting material was noted as judged by TLC analysis of aliquots taken from the reaction mixture. Aqueous NH_4Cl (0.5 cm^3) was then added dropwise and the resultant biphasic mixture stirred vigorously for 10 to 20 min. $MgSO_4$ (excess) was then added and the slurry stirred vigorously for a further 10–15 min. Filtration of the reaction mixture through a pad of Celite washing the residue with DCM (30 cm^3), followed by concentration of the filtrate *in vacuo* afforded the crude product which was then purified by flash column chromatography.

[(4*E*,2*R,3*S**,6*S**)-2-(Carbonyloxy-κ*C*)-6-hydroxy-6-methyl-(3,4,5-η)-oct-4-en-3-yl]tricarbonyliron 21**

Complex **21** was prepared according to the general procedure from the ethyl ketone complex **10a** (0.058 g, 0.19 mmol) using $AlMe_3$ (0.200 cm^3 of a 2.0 mol dm^{-3} solution in toluene, 0.40 mmol) and benzene–toluene (2 cm^3; 1 : 1) as solvent. After 1 h, work-up as described followed by purification by flash column chromatography (eluent: Et_2O–petrol 1 : 1) afforded the *alcohol* **21** as a white solid (0.056 g, 92%); ν_{max}(film)/cm^{-1} 3452 (OH), 3020, 2990, 2895, 2082 (CO), 2027 (CO), 1652 (C=O), 1458, 1374, 1216, 1180, 1131, 1084, 1045, 999, 945; δ_H(200 MHz) 1.05 (3H, t, *J* 7.3, 8-H × 3), 1.32 (3H, d, *J* 6.3, 1-H × 3), 1.47 (3H, s, 6-Me), 1.80 (2H, q, *J* 7.3, 7-H × 2), 1.92 (1H, s, OH), 4.14 (1H, d, *J* 12.3, 5-H), 4.42 (1H, qd, *J* 6.3, 4.8, 2-H), 4.61 (1H, dd, *J* 8.2, 4.8, 3-H), 4.87 (1H, dd, *J* 12.3, 8.2, 4-H); δ_C(50 MHz) 8.5, 21.8, 29.1, 37.8, 73.3 (overlapping signals), 76.2, 86.6, 93.7, 203.4, 206.3, 206.8, 209.5; *m/z* (FAB) 325 (MH^+, 44%), 297 (11, MH − CO), 268 (22, MH − 3CO), 263 (16, M − CO_2 − OH), 251 (6, M − 2CO − OH), 241 (22, MH − 3CO), 197 (7, MH − 3CO − CO_2), 123 (100, M − 4CO − Fe − O − OH) [Found (MH^+) 325.0375. $C_{13}H_{17}FeO_6$ requires *M*H, 325.0374].

[(4*E*,2*R,3*S**,6*R**)-2-(Carbonyloxy-κ*C*)-6-hydroxy-6-phenyl-(3,4,5-η)-hept-4-en-3-yl]tricarbonyliron 22**

Complex **22** was prepared according to the general procedure from phenyl ketone complex **9a** (0.040 g, 0.11 mmol) using $AlMe_3$ (0.127 cm^3 of a 2.0 mol dm^{-3} solution in toluene, 0.25 mmol) and benzene (3 cm^3) as solvent. After 30 min, work-up as described followed by purification by flash column chromatography (eluent: Et_2O–petrol 1 : 1→neat Et_2O; gradient) afforded *alcohol* **22** as a white solid (0.036 g, 88%) (Found: C, 55.14; H, 4.49. $C_{17}H_{16}FeO_6$ requires C, 54.87; H, 4.33%); ν_{max}(film)/cm^{-1} 3420 (OH), 3002, 2981, 2930, 2088 (CO), 2002 (CO), 1656 (C=O), 1493, 1446, 1374, 1356, 1311, 1150, 1076, 980; δ_H(200 MHz) 1.40 (3H, d, *J* 11.9, 1-H × 3), 1.87 (3H, s, 7-H × 3), 2.30 (1H, s, OH), 4.36–4.47 {2H, m, [including 4.45 (1H, d, *J* 11.9, 5-H)], 2-H, 5-H}, 4.63 (1H, dd, *J* 8.4, 4.6, 3-H), 5.08 (1H, dd, *J* 11.9, 8.4, 4-H), 7.28 (1H, tt, *J* 7.1, 1.6, *p*-Ph-*H*), 7.38 (2H, apparent t, *J* 7.1, *m*-Ph-*H*), 7.51 (2H, dd, *J* 7.1, 1.6, *o*-Ph-*H*); δ_C(50 MHz) 22.0, 35.0, 73.2, 74.8, 76.6, 86.7, 92.1, 123.8, 127.6, 128.7, 147.2, 203.4, 204.4, 206.1, 209.4; *m/z* (FAB) 373 (MH^+, 60%), 345 (15, MH − CO), 317 (12, MH − 2CO), 307 (62), 289 (52), 260 (38), 242 (35), 226 (42), 171 (100,

M − 4CO − Fe − O − OH) [Found (MH^+) 373.0374. $C_{17}H_{17}FeO_6$ requires *M*H, 373.0375].

[(4*E*,2*S,3*S**,6*R**)-2-(Carbonyloxy-κ*C*)-6-hydroxy-6-phenyl-(3,4,5-η)-hept-4-en-3-yl]tricarbonyliron 23**

Complex **23** was prepared according to the general procedure from phenyl ketone complex **9b** (0.026 g, 0.07 mmol) using $AlMe_3$ (0.082 cm^3 of a 2.0 mol dm^{-3} solution in toluene, 0.16 mmol) and benzene (1.3 cm^3) as solvent. After 30 min, work-up as described followed by purification by flash column chromatography (eluent: Et_2O–petrol 1:1→neat Et_2O; gradient) afforded *alcohol* **23** as a white solid (0.026 g, 95%); ν_{max}(film)/cm^{-1} 3416 (OH), 3002, 2965, 2899, 2085 (CO), 2011 (CO), 1652 (C=O), 1493, 1446, 1380, 1337, 1307, 1147, 1080, 1050; δ_H(400 MHz) 1.36 (3H, d, *J* 6.0, 1-H × 3), 1.85 (3H, s, 7-H × 3), 2.31 (1H, s, OH), 4.28 (1H, q, *J* 6.0, 2-H), 4.31 (1H, d, *J* 12.0, 5-H), 4.40 (1H, d, *J* 8.0, 3-H), 5.21 (1H, dd, *J* 12.0, 8.0, 4-H), 7.28 (1H, tt, *J* 8.0, 1.5, *p*-Ph-*H*), 7.39 (2H, apparent t, *J* 8.0, *m*-Ph-*H*), 7.49 (2H, dd, *J* 8.0, 1.5, *o*-Ph-*H*); δ_C(50 MHz) 23.8, 34.9, 71.0, 74.6, 75.7, 88.3, 91.2, 123.8, 127.5, 128.6, 149.0, 203.6, 204.4, 205.8, 209.7; *m*/*z* (FAB) 373 (MH^+, 64%), 345 (15, MH − CO), 317 (19, MH − 2CO), 288 (22, M − 3CO), 271 (35, M − 3CO − OH), 226 (38), 171 (100, M − 3CO − Fe − OH), 105 (45) [Found (MH^+) 373.0380. $C_{17}H_{17}FeO_6$ requires *M*H, 373.0375].

[(4*E*,2*R,3*S**)-2-(Carbonyloxy-κ*C*)-6-hydroxy-6-methyl-(3,4,5-η)-hept-4-en-3-yl]tricarbonyliron 24**

Complex **24** was prepared according to the general procedure from methyl ketone complex **8a** (0.025 g, 0.09 mmol) using $AlMe_3$ (0.045 cm^3 of a 2.0 mol dm^{-3} solution in toluene, 0.18 mmol) and benzene (2 cm^3) as solvent. After 30 min at 0 °C and then 2.5 h at room temperature, work-up as described followed by purification by flash column chromatography (eluent: Et_2O–hexane 50%) afforded *alcohol* **24** as a yellowish solid (0.017 g, 64%); ν_{max}(film)/cm^{-1} 2083 (CO), 2028 (CO), 2015 (CO), 1654 (C=O); δ_H(200 MHz) 1.35 (3H, d, *J* 6.2, 1-H × 3), 1.59 (6H, s, 7-H × 3 and 6-Me), 4.14 (1H, d, *J* 12.2, 5-H), 4.44 (1H, qd, *J* 6.2, 6.1, 2-H), 4.64 (1H, dd, *J* 8.2, 6.1, 3-H), 4.85 (1H, dd, *J* 12.2, 8.2, 4-H); δ_C(100 MHz) 21.9 (CH_3), 32.1 (CH_3), 33.5 (CH_3), 70.9 (quat. C), 73.3 (CH), 76.5 (CH), 86.6 (CH), 94.1 (CH), 203.8 (CO), 206.3 (CO), 207.0 (CO), 209.4 (CO); *m*/*z* (FAB) 311 (MH^+, 21%), 283 (3, MH − CO), 254 (4, M − 2CO), 227 (7, MH − 3CO), 109 (45, C_8H_{13}) [Found (MH^+) 311.0225. $C_{12}H_{16}FeO_6$ requires *M*H, 311.0218].

[(4*E*,3*R,6*S**,7*R**)-7-(Carbonyloxy-κ*C*)-3-hydroxy-3-methyl-(4,5,6-η)-dodec-4-en-6-yl]tricarbonyliron 25 and [(3*E*,2*S**, 5*S**,6*R**)-6-(carbonyloxy-κ*C*)-2-hydroxy-(3,4,5-η)-undec-3-en-5-yl]tricarbonyliron 26**

Complex **25** was prepared according to the general procedure from methyl ketone complex **20a** (0.406 g, 1.16 mmol) using $AlEt_3$ (3.12 cm^3 of a 1.0 mol dm^{-3} solution in hexanes, 3.12 mmol) and DCM (12 cm^3) as solvent. After 1.5 h, work-up as described followed by purification by flash column chromatography (eluent: Et_2O–petrol 1:1) afforded in order of elution, the tertiary *alcohol* **25** as a yellow solid (0.219 g, 50%) (Found: C, 53.62; H, 6.05. $C_{17}H_{24}FeO_6$ requires C, 53.67; H, 6.36%); ν_{max}(film)/cm^{-1} 3430 (OH), 3013, 2963, 2933, 2860, 2083 (CO), 2007 (CO), 1639 (C=O), 1461, 1379, 1323, 1216, 1167, 1118, 957; δ_H(200 MHz) 0.89 (3H, t, *J* 6.5, 12-H × 3), 1.06 (3H, t, *J* 7.5, 1-H × 3), 1.17–1.63 (12H, m, OH, 3-Me, 8-H × 2, 9-H × 2, 10-H × 2, 11-H × 2), 1.81 (2H, q, *J* 7.5, 2-H × 2), 4.02 (1H, d, *J* 12.5, 4-H), 4.22–4.29 (1H, m, 7-H), 4.61 (1H, dd, *J* 8.3, 4.6, 6-H), 4.85 (1H, dd, *J* 12.5, 8.3, 5-H); δ_C(100 MHz) 8.8 (CH_3), 13.9 (CH_3), 22.5 (CH_2), 26.6 (CH_2), 30.1 (CH_2), 31.6 (CH_2), 36.7 (CH_2), 38.8 (CH_2), 73.1 (quat. C, 4-C), 75.0 (CH), 77.4 (CH), 87.1 (CH), 93.0 (CH), 203.5 (CO), 206.1 (CO), 207.2 (CO), 209.7 (CO); *m*/*z* (FAB) 381 (MH^+, 57%), 353 (6, MH − CO), 324 (8, M − 2CO), 297 (12, MH − 3CO), 179 (100, M − 4CO − Fe − O − OH); and then the secondary *alcohol* **26** as a pale yellow oil (0.135 g, 33%) (Found: C, 51.02; H, 5.61. $C_{15}H_{20}FeO_6$ requires C, 51.14; H, 5.68%); ν_{max}(film)/cm^{-1} 3421 (OH), 3020, 2980, 2967, 2856, 2083 (CO), 2008 (CO), 1634 (C=O), 1458, 1373, 1216, 1145, 1118, 857; δ_H(200 MHz) 0.88 (3H, t, *J* 7.2, 11-H × 3), 1.20–1.59 (8H, m, 7-H × 2, 8-H × 2, 9-H × 2, 10-H × 2), 1.52 (3H, d, *J* 6.4, 1-H × 3), 1.83 (1H, d, *J* 4.6, OH), 4.00 (1H, dd, *J* 12.1, 3.4, 3-H), 4.24 (1H, td, *J* 5.6, 4.7, 6-H), 4.33–4.47 (1H, m, 2-H), 4.61 (1H, dd, *J* 8.3, 4.7, 5-H), 4.79 (1H, dd, *J* 12.1, 8.3, 4-H); δ_C(50 MHz) 13.5, 22.5, 25.8, 26.6, 31.5, 36.7, 67.5, 76.0, 77.2, 87.8, 88.6, 200.4, 203.5, 205.8, 206.7; *m*/*z* (FAB) 353 (MH^+, 51%), 325 (47, MH − CO), 291 (41, M − OH − CO_2), 269 (100, MH − 3CO), 151 (82, M − 4CO − Fe − O − OH).

[(4*E*,2*R,3*S**,6*R**)-2-(Carbonyloxy-κ*C*)-6-hydroxy-6-phenyl-(3,4,5-η)-oct-4-en-3-yl]tricarbonyliron 27 and [(4*E*,2*R**,3*S**,6*R**)-2-(carbonyloxy-κ*C*)-6-hydroxy-6-phenyl-hex-4-en-3-yl]tricarbonyliron 28**

Complex **27** was prepared according to the general procedure from phenyl ketone complex **9a** (0.056 g, 0.16 mmol) using $AlEt_3$ (0.352 cm^3 of a 1.0 mol dm^{-3} solution in toluene, 0.35 mmol) and DCM (3.8 cm^3) as solvent. After 70 min, work-up as described followed by purification by flash column chromatography (eluent: Et_2O–petrol 2:3→neat Et_2O; gradient) afforded in order of elution, the tertiary *alcohol* **27** as a white solid (0.040 g, 66%); ν_{max}(film)/cm^{-1} 3428 (OH), 3010, 2980, 2870, 2087 (CO), 2008 (CO), 1656 (C=O), 1495, 1448, 1374, 1356, 1239, 1145, 1084, 1040, 998, 945; δ_H(400 MHz) 0.91 (3H, t, *J* 7.0, 8-H × 3), 1.40 (3H, d, *J* 6.0, 1-H × 3), 2.01–2.18 (2H, m, 7-H × 2), 2.19 (1H, s, OH), 4.40 (1H, d, *J* 12.0, 5-H), 4.43 (1H, apparent quintet, *J* 6.0, 2-H), 4.61 (1H, dd, *J* 8.2, 6.0, 3-H), 5.08 (1H, dd, *J* 12.0, 8.2, 4-H), 7.28 (1H, tt, *J* 8.0, 1.5, *p*-Ph-*H*), 7.38 (2H, apparent t, *J* 8.0, *m*-Ph-*H*), 7.43 (2H, dd, *J* 8.0, 1.5, *o*-Ph-*H*); δ_C(50 MHz) 8.5, 22.0, 29.7, 39.6, 73.1, 76.2, 86.9, 91.0, 124.0, 127.5, 128.6, 146.3, 203.5, 204.0, 206.3, 209.5; *m*/*z* (FAB) 387 (MH^+, 82%), 359 (10, MH − CO), 329 (13, M − CO − Et), 307 (72), 289 (42), 274 (17, MH − 3CO − Et), 229 (12, M − 4CO − O − Et), 185 (37, M − 4CO − Fe − O − OH), 154 (100), 136 (83) [Found (MH^+) 387.0538. $C_{18}H_{19}FeO_6$ requires *M*H, 387.0531]; and then the secondary *alcohol* **28** as a white solid (0.012 g, 21%) (Found: C, 53.77; H, 3.80. $C_{16}H_{14}FeO_6$ requires C, 53.66; H, 3.94%); ν_{max}(film)/cm^{-1} 3412 (OH), 2980, 2930, 2078 (CO), 2014 (CO), 1650 (C=O), 1552, 1507, 1453, 1321, 1202; δ_H(200 MHz) 1.33 (3H, d, *J* 6.4, 1-H × 3), 2.68 (1H, d, *J* 4.1, OH), 4.31 (1H, dd, *J* 12.0, 4.1, 5-H), 4.44 (1H, apparent quintet, *J* 6.4, 2-H), 4.62 (1H, dd, *J* 8.3, 6.4, 3-H), 4.81 (1H, dd, *J* 12.0, 8.3, 4-H), 5.20 (1H, apparent t, *J* 4.1, 6-H), 7.29–7.49 (5H, m, Ph-*H*); δ_C(50 MHz) 21.6, 73.2, 74.6, 77.6, 86.2, 88.8, 125.5, 128.4, 128.9, 142.7, 203.0, 205.4, 205.6, 209.1; *m*/*z* (CI) 313 (M − H − CO_2, 25%), 297 (15), 192 (13), 173 (100, M − 4CO − Fe − O − H), 157 (72, M − 4CO − Fe − O − OH), 129 (62), 105 (68), 77 (74, Ph), 51 (43).

[(4*E*,2*R,3*S**,6*R**)-2-(Carbonyloxy-κ*C*)-6-hydroxy-6-methyl-(3,4,5-η)-oct-4-en-3-yl]tricarbonyliron 29 and [(4*E*,2*R**,3*S**,6*S**)-2-(carbonyloxy-κ*C*)-6-hydroxy-(3,4,5-η)-hept-4-en-3-yl]tricarbonyliron 30**

Complex **29** was prepared according to the general procedure from methyl ketone complex **8a** (0.028 g, 0.10 mmol) using $AlEt_3$ (0.200 cm^3 of a 1.0 mol dm^{-3} solution in toluene, 0.20 mmol) and DCM (2.4 cm^3) as solvent. After 1 h, work-up as described followed by purification by flash column chromatography (eluent: Et_2O–petrol 50%) afforded in order of elution, the tertiary *alcohol* **29** as a colourless solid (0.020 g, 62%) (Found: C, 48.40; H, 4.97. $C_{13}H_{16}FeO_6$ requires C, 48.18; H, 4.98%); ν_{max}(film)/cm^{-1} 3422 (OH), 2079 (CO), 2003 (CO), 1644 (C=O); δ_H(200 MHz; C_6D_6) 0.75 (3H, t, *J* 7.3, 8-H × 3), 1.05

(3H, d, *J* 6.3, 1-H × 3), 1.15 (1H, s, OH), 1.20 (3H, s, 6-Me), 1.15–1.35 (2H, m, 7-H × 2), 3.68 (1H, ddd, *J* 8.3, 4.5, 0.5, 3-H), 3.93 (1H, ddq, *J* 6.3, 4.5, 0.5, 2-H), 3.97 [1H, d (+ unresolved fine coupling), *J* 12.5, 5-H], 4.38 (1H, ddd, *J* 12.5, 8.3, 0.5, 4-H); δ_C(100 MHz; C_6D_6) 8.6, 21.7, 29.7, 38.2, 72.4, 72.8, 76.3, 86.8, 93.8, 202.7, 204.2, 208.1, 210.9; *m*/*z* (FAB) 325 (MH^+, 100%), 307 (52, M − OH), 268 (19, M − 2CO), 241 (20, MH − 3CO) [Found (MH^+) 325.0346. $C_{13}H_{17}FeO_6$ requires *M*H, 325.0374]; and then the secondary *alcohol* **30** (0.011 g, 37%) (Found: C, 44.63; H, 4.19. $C_{11}H_{12}FeO_6$ requires C, 44.63; H, 4.09%); ν_{max}(film)/cm^{-1} 3358 (OH), 2081 (CO), 2022 (CO), 1993 (CO), 1626 (C=O); δ_H(200 MHz) 1.35 (3H, d, *J* 6.4, 1-H × 3), 1.53 (3H, d, *J* 6.4, 7-H × 3), 1.94 (1H, d, *J* 4.6, OH), 4.05 (1H, dd, *J* 12.0, 3.4, 5-H), 4.41–4.47 (1H, m, 6-H), 4.54 (1H, qd, *J* 6.4, 4.6, 2-H), 4.63 (1H, dd, *J* 8.3, 4.6, 3-H), 4.79 (1H, dd, *J* 12.0, 8.3, 4-H); δ_C(100 MHz) 21.7, 25.6, 67.3, 73.2, 77.0, 87.6, 88.6, 203.3, 206.1, 206.5, 209.2; *m*/*z* (FAB) 297 (MH^+, 100%), 269 (13, MH − CO), 240 (8, M − 2CO), 213 (20, MH − 3CO) [Found (MH^+) 297.0081. $C_{11}H_{13}FeO_6$ requires *M*H, 297.0061].

[(3*E*,2*S,5*S**,6*R**)-6-(Carbonyloxy-κ*C*)-2-hydroxy-(3,4,5-η)-undec-3-en-5-yl]tricarbonyliron 26**

Complex **26** was prepared according to the general procedure from methyl ketone complex **20a** (0.632 g, 1.81 mmol) using $AlBu^i_3$ (4.16 cm^3 of a 1.0 mol dm^{-3} solution in toluene, 4.16 mmol) and benzene–toluene (14 cm^3; 6:1) as solvent. After 1 h, work-up as described followed by purification by flash column chromatography (eluent: Et_2O–petrol 1:1→neat Et_2O; gradient) afforded *alcohol* **26** as a pale yellow oil (0.417 g, 65%) which had identical spectroscopic data to material prepared earlier (*vide supra*).

[(4*E*,2*R,3*S**,6*R**)-2-(Carbonyloxy-κ*C*)-6-hydroxy-6-phenyl-hex-4-en-3-yl]tricarbonyliron 28**

Complex **28** was prepared according to the general procedure from phenyl ketone complex **9a** (0.060 g, 0.17 mmol) using $AlBu^i_3$ (0.389 cm^3 of a 1.0 mol dm^{-3} solution in toluene, 0.40 mmol) and benzene (5 cm^3) as solvent. After 30 min, work-up as described followed by purification by flash column chromatography (eluent: Et_2O–petrol 1:1→neat Et_2O; gradient) afforded *alcohol* **28** as a white solid (0.043 g, 71%) which had identical spectroscopic data to material prepared earlier (*vide supra*).

General procedure for the addition of alkynyl organoaluminium reagents into ketone complexes: synthesis of complexes 32–36

Bu^nLi (1.6 mol dm^{-3} solution in hexanes, 0.59 mmol) was added dropwise to the alkyne (0.59 mmol) in toluene (3.5 cm^3) at 0 °C and stirred at this temperature for 45 min whereupon Me_2AlCl (1.0 mol dm^{-3} solution in hexanes, 0.59 mmol) was slowly added. The resultant solution was stirred at 0 °C for a further 45 min after which time formation of the alkynylaluminium reagent was assumed to be complete. A solution of the ketone complex (0.17 mmol) in DCM (3 cm^3) was added and stirring continued until complete consumption of starting material was noted as judged by TLC analysis of aliquots taken from the reaction mixture. Work-up and purification as described earlier (*vide supra*) for the addition of alkyl organoaluminium reagents afforded the diastereoisomerically pure addition product.

[(4*E*,2*R,3*S**,6*R**)-2-(Carbonyloxy-κ*C*)-6-hydroxy-6-phenyl-(3,4,5-η)-dodec-4-en-7-yn-3-yl]tricarbonyliron 32**

Complex **32** was prepared according to the general procedure from the phenyl ketone **9a** (0.060 g, 0.17 mmol) in DCM (3 cm^3). The alkynylaluminium reagent was prepared from hex-1-yne (0.067 cm^3, 0.59 mmol), Bu^nLi (0.59 mmol) and Me_2AlCl (0.59 mmol). After 30 min, work-up as described followed by purification by flash column chromatography (eluent: Et_2O–petrol 2:3→1:1; gradient) afforded *alcohol* **32** as a light brown foam (0.051 g, 70%). Chiral HPLC analysis revealed the presence of one diastereoisomer (>98% de) [eluent: Pr^iOH–hexane 5%; flow rate 0.5 cm^3 min^{-1}; retention times 20.93 min (first enantiomer), 28.14 min (second enantiomer)] (Found: C, 60.21; H, 5.07. $C_{22}H_{22}FeO_6$ requires C, 60.29; H, 5.06%); ν_{max}(film)/cm^{-1} 3326 (OH), 3020, 2970, 2910, 2860, 2239 (C≡C), 2085 (CO), 2032 (CO), 1660 (C=O), 1488, 1466, 1448, 1376, 1329, 1236, 1230, 1184, 1131; δ_H(400 MHz) 0.89 (3H, t, *J* 7.0, 12-H × 3), 1.17 (3H, d, *J* 6.0, 1-H × 3), 1.38 (2H, apparent sextet, *J* 7.0, 11-H × 2), 1.50 (2H, apparent quintet, *J* 7.0, 10-H × 2), 2.22 (2H, t, *J* 7.0, 9-H × 2), 2.94 (1H, s, OH), 4.33 (1H, d, *J* 12.0, 5-H), 4.37 (1H, apparent quintet, *J* 6.0, 2-H), 4.58 (1H, dd, *J* 8.3, 6.0, 3-H), 4.98 (1H, dd, *J* 12.0, 8.3, 4-H), 7.31 (1H, tt, *J* 7.1, 1.5, *p*-Ph-*H*), 7.38 (2H, apparent t, *J* 7.1, *m*-Ph-*H*), 7.69 (2H, dd, *J* 7.1, 1.5, *o*-Ph-*H*); δ_C(50 MHz) 13.5, 18.3, 21.8, 22.0, 30.2, 73.1, 74.1, 76.4, 80.7, 88.1, 89.9, 90.8, 124.9, 128.3, 128.7, 145.0, 203.5, 205.2, 205.3, 209.1; *m*/*z* (FAB) 439 (MH^+, 80%), 411 (12, MH − CO), 399 (23), 355 (22, MH − 3CO), 337 (29, M − 3CO − OH), 326 (25), 309 (42, M − H − 4CO − O), 237 (100, M − 4CO − Fe − O − OH), 181 (96) [Found (MH^+) 439.0845. $C_{22}H_{23}FeO_6$ requires *M*H, 439.0844].

[(4*E*,2*S,3*S**,6*R**)-2-(Carbonyloxy-κ*C*)-6-hydroxy-6-phenyl-(3,4,5-η)-dodec-4-en-7-yn-3-yl]tricarbonyliron 33**

Complex **33** was prepared according to the general procedure from phenyl ketone **9b** (0.030 g, 0.08 mmol) in DCM (1.5 cm^3). The alkynylaluminium reagent was prepared from hex-1-yne (0.034 cm^3, 0.30 mmol), Bu^nLi (0.30 mmol) and Me_2AlCl (0.30 mmol). After 90 min, work-up as described followed by purification by flash column chromatography (eluent: Et_2O–petrol 1:1) afforded *alcohol* **33** as a brown gum (0.022 g, 64%); ν_{max}(film)/cm^{-1} 3360 (OH), 3015, 2987, 2932, 2855, 2337 (C≡C), 2085 (CO), 2038 (CO), 2008 (CO), 1650 (C=O), 1489, 1448, 1307, 1216, 1048, 1002, 950; δ_H(400 MHz) 0.90 (3H, t, *J* 7.0, 12-H × 3), 1.31 (3H, d, *J* 6.2, 1-H × 3), 1.39 (2H, apparent sextet, *J* 7.0, 11-H × 2), 1.50 (2H, apparent quintet, *J* 7.0, 10-H × 2), 2.24 (2H, t, *J* 7.0, 9-H × 2), 2.77 (1H, s, OH), 4.12 (1H, q, *J* 6.2, 2-H), 4.17 (1H, d, *J* 12.0, 5-H), 4.32 (1H, d, *J* 8.3, 3-H), 5.10 (1H, dd, *J* 12.0, 8.3, 4-H), 7.33 (1H, tt, *J* 7.1, 1.5, *p*-Ph-*H*), 7.39 (2H, apparent t, *J* 7.1, *m*-Ph-*H*), 7.70 (2H, dd, *J* 7.1, 1.5, *o*-Ph-*H*); δ_C(50 MHz) 13.5, 18.4, 22.1, 23.7, 30.2, 71.0, 74.2, 75.6, 80.6, 89.6, 89.9, 90.1, 125.0, 128.4, 128.8, 145.0, 203.8, 204.8, 205.3, 209.4; *m*/*z* (FAB) 439 (MH^+, 77%), 383 (12, MH − 2CO), 355 (24, MH − 3CO), 292 (27), 237 (52, M − 4CO − Fe − O − OH), 181 (100), 165 (67) [Found (MH^+) 439.0823. $C_{22}H_{23}FeO_6$ requires *M*H, 439.0844].

[(4*E*,2*S,3*S**,6*S**)-2-(Carbonyloxy-κ*C*)-6-hydroxy-6-methyl-(3,4,5-η)-dodec-4-en-7-yn-3-yl]tricarbonyliron 34**

Complex **34** was prepared according to the general procedure from methyl ketone **8b** (0.041 g, 0.14 mmol) in DCM (1.6 cm^3). The alkynylaluminium reagent was prepared from hex-1-yne (0.057 cm^3, 0.50 mmol), Bu^nLi (0.50 mmol) and Me_2AlCl (0.50 mmol). After 30 min, work-up as described followed by purification by flash column chromatography (eluent: Et_2O–hexane 1:1) afforded *alcohol* **34** (0.043 g, 82%); ν_{max}(film)/cm^{-1} 3414 (OH), 2250 (C≡C), 2081 (CO), 2004 (CO), 1646 (C=O); δ_H(200 MHz) 0.89 (3H, t, *J* 7.0, 12-H × 3), 1.35 (3H, d, *J* 6.5, 1-H × 3), 1.31–1.46 (4H, m, 10-H × 2, 11-H × 2), 1.77 (3H, s, 6-Me), 2.14 (2H, t, *J* 7.0, 9-H × 2), 2.60 (1H, s, OH), 4.03 (1H, d, *J* 12.1, 5-H), 4.24 (1H, br q, *J* 6.5, 2-H), 4.38 (1H, ddd, *J* 7.8, 1.5, 0.6, 3-H), 5.04 (1H, ddd, *J* 12.1, 7.8, 0.9, 4-H); δ_C(100 MHz) 13.5, 18.2, 21.9, 23.7, 30.3, 33.7, 68.7, 71.1, 75.8, 81.8, 87.0, 89.6, 89.9, 203.5, 205.4, 205.9, 209.5; *m*/*z* (FAB) 377 (MH^+, 100%), 321 (50, MH − 2CO), 293 (38, MH − 3CO) [Found (MH^+) 377.0670. $C_{17}H_{21}FeO_6$ requires *M*H, 377.0687].

[(4*E*,2*R,3*S**,6*R**)-2-(Carbonyloxy-κ*C*)-6-hydroxy-9,9-dimethyl-6-phenyl-(3,4,5-η)-dec-4-en-7-yn-3-yl]tricarbonyliron 35**

Complex **35** was prepared according to the general procedure

from phenyl ketone **9a** (0.072 g, 0.20 mmol) in DCM (3 cm^3). The alkynylaluminium reagent was prepared from 3,3-dimethylbut-1-yne (0.054 cm^3, 0.44 mmol), Bu^{n}Li (0.44 mmol) and Me_2AlCl (0.44 mmol). After 1 h, work-up as described followed by purification by flash column chromatography (eluent: Et_2O–hexane 1:1) afforded *alcohol* **35** as a dark yellow foam (0.051 g, 58%) (Found: C, 60.45; H, 5.12. $C_{22}H_{22}FeO_6$ requires C, 60.29; H, 5.06%); ν_{max}(film)/cm^{-1} 3330 (OH), 3063, 3036, 3010, 2985, 2876, 2239 (C≡C), 2087 (CO), 2031 (CO), 1664 (C=O), 1488, 1449, 1364, 1326, 1261, 1240, 1202, 1040, 998; δ_H(400 MHz) 1.20 (3H, d, *J* 6.3, 1-H × 3), 1.23 (9H, s, 10-H × 3, 9-Me × 2), 2.85 (1H, s, OH), 4.33 (1H, d, *J* 12.0, 5-H), 4.34–4.41 (1H, m, 2-H), 4.58 (1H, dd, *J* 8.2, 4.7, 3-H), 5.00 (1H, dd, *J* 12.0, 8.2, 4-H), 7.31 (1H, tt, *J* 7.1, 1.6, *p*-Ph-*H*), 7.38 (2H, apparent t, *J* 7.1, *m*-Ph-*H*), 7.69 (2H, dd, *J* 7.1, 1.6, *o*-Ph-*H*); δ_C(50 MHz) 21.8, 27.7, 30.5, 73.0, 73.7, 76.3, 79.5, 88.0, 90.4, 97.9, 125.0, 128.3, 128.6, 145.1, 203.5, 205.0, 205.2, 209.1; *m*/*z* (FAB) 439 (MH^+, 100%), 411 (8, MH − CO), 399 (17), 382 (10, M − 2CO), 355 (22, MH − 3CO), 337 (27, M − 3CO − OH), 326 (41), 309 (44), 293 (23, M − 4CO − O − OH), 237 (73, M − 4CO − Fe − O − OH), 181 (16), 165 (14) [Found (MH^+) 439.0838. $C_{22}H_{23}FeO_6$ requires *M*H, 439.0844].

[(4*E*,2*R,3*S**,6*S**)-2-(Carbonyloxy-κ*C*)-6-hydroxy-6,9,9-trimethyl-(3,4,5-η)-dec-4-en-7-yn-3-yl]tricarbonyliron 36**

Complex **36** was prepared according to the general procedure from methyl ketone **8a** (0.043 g, 0.14 mmol) in DCM (1 cm^3). The alkynylaluminium reagent was prepared from 3,3-dimethylbut-1-yne (0.041 cm^3, 0.33 mmol), Bu^{n}Li (0.33 mmol) and Me_2AlCl (0.33 mmol). After 35 min, work-up as described followed by purification by flash column chromatography (eluent: Et_2O–hexane 1:1) afforded *alcohol* **36** as a gum (0.050 g, 93%) (Found: C, 54.30; H, 5.47. $C_{17}H_{21}FeO_6$ requires C, 54.28; H, 5.36%); ν_{max}(film)/cm^{-1} 3386 (OH), 2238 (C≡C), 2082 (CO), 2041 (CO), 2004 (CO), 1644 (C=O); δ_H(200 MHz) 1.18 (9H, s, 10-H × 3, 9-Me × 2), 1.35 (3H, d, *J* 6.3, 1-H × 3), 1.79 (3H, s, 6-Me), 2.46 (1H, s, OH), 4.17 (1H, d, *J* 12.1, 5-H), 4.43 (1H, br dq, *J* 6.0, 5.0, 2-H), 4.64 (1H, dd, *J* 8.2, 4.7, 3-H), 4.95 (1H, dd, *J* 12.1, 8.2, 4-H); δ_C(100 MHz) 22.0, 27.5, 30.7, 33.8, 68.4, 73.3, 76.7, 80.6, 88.0, 90.4, 95.1, 203.5, 205.9, 206.2, 209.3; *m*/*z* (FAB) 377 (MH^+, 75%), 349 (9, MH − CO), 321 (18, MH − 2CO), 293 (35, MH − 3CO), 57 (39, Bu^t) [Found (MH^+) 377.0723. $C_{17}H_{21}FeO_6$ requires *M*H, 377.0687].

Procedure for the addition of phenyl organoaluminium reagents into ketone complexes: synthesis of complex 37

[(3*E*,2*S,5*S**,6*S**)-6-(Carbonyloxy-κ*C*)-2-hydroxy-2-phenyl-(3,4,5-η)-undec-3-en-5-yl]tricarbonyliron 37**

Me_2AlCl (0.860 cm^3 of a 1.0 mol dm^{-3} solution in hexanes, 0.86 mmol) was added dropwise to a solution of PhLi (0.480 cm^3 of a 1.8 mol dm^{-3} solution in hexanes, 0.86 mmol) in toluene (2 cm^3) at 0 °C. After stirring at 0 °C for 45 min when formation of the organoaluminium reagent was assumed to be complete, ketone complex **20b** (0.100 g, 0.29 mmol) in DCM (2 cm^3) was added dropwise and stirring continued at 0 °C. After 3 h the reaction was quenched by the addition of aqueous HCl (5 cm^3 of a 1 mol dm^{-3} solution, ice cold) and the biphasic mixture stirred for 5 min at 0 °C. The layers were separated and the aqueous fraction extracted with DCM (3 × 5 cm^3). The combined organic fractions were dried ($MgSO_4$) and the solvent removed *in vacuo*. Purification of the residue by flash column chromatography (eluent: Et_2O–petrol 1:4) afforded *alcohol* **37** as an off-white solid (0.082 g, 67%) (Found: C, 58.90; H, 5.66. $C_{21}H_{24}FeO_6$ requires C, 58.87; H, 5.65%); ν_{max}(film)/cm^{-1} 3420 (OH), 2932, 2084 (CO), 2031 (CO), 2015 (CO), 1649 (C=O), 1458, 1378; δ_H(600 MHz) 0.86 (3H, t, *J* 6.8, 11-H × 3), [1.22–1.36 (4H, m), 1.38–1.44 (1H, m), 1.52–1.64 (3H, m), 7-H × 2, 8-H × 2, 9-H × 2, 10-H × 2], 1.95 (3H, s, 1-H × 3), 2.01 (1H, s, OH), 3.88 (1H, br t, *J* 6.6, 6-H), 4.18 (1H, d, *J* 12.1, 3-H), 4.34 (1H, d, *J* 8.1, 5-H), 4.97 (1H, dd, *J* 12.1, 8.1, 4-H), 7.30 (1H, t, *J* 7.3, *p*-Ph-*H*), 7.39 (2H, apparent t, *J* 7.3, *m*-Ph-*H*), 7.54 (2H, d, *J* 7.3, *o*-Ph-*H*); δ_C(50 MHz) 13.9 (CH_3, 11-C), 22.4 (CH_2), 25.1 (CH_2), 31.4 (CH_2), 32.3 (CH_3, 1-C), 37.7 (CH_2), 73.8 (quat. C, 2-C), 74.5 (CH), 74.8 (CH), 88.7 (CH), 92.5 (CH), 124.4 (CH), 127.5 (CH), 128.8 (CH), 147.5 (quat. C), 203.3 (CO), 205.5 (CO), 206.8 (CO), 209.7 (CO); *m*/*z* (FAB) 429 (MH^+, 15%), 389 (15), 371 (5, M − H − 2CO), 345 (18, MH − 3CO), 339 (20), 327 (13, MH − 3CO − H_2O), 317 (11, MH − 4CO), 299 (22, MH − 4CO − H_2O), 282 (25, MH − 4CO − O − H_2O), 227 (100, MH − 4CO − Fe − O − OH), 143 (19), 105 (34) [Found (MH^+) 429.1004. $C_{21}H_{25}FeO_6$ requires *M*H, 429.1000].

General procedure for the addition of alkenyl diisobutylaluminium reagents into ketone complexes: synthesis of complexes 38–40

Bu^i_2AlH (1.5 mol dm^3 solution in toluene, 0.76 mmol) was added dropwise to a solution of hex-1-yne (0.76 mmol) in hexane (3 cm^3) at 0 °C. The reaction mixture was stirred for 20 min at 0 °C, at room temperature for 20 min and then heated to 60 °C for 4 h. After allowing the reaction mixture to cool to ambient temperature, Et_2O (1 cm^3) was added and the solution was then cooled to 0 °C. A solution of the ketone complex (0.14 mmol) in DCM (1 cm^3) was then added dropwise. The reaction mixture was stirred until TLC analysis of aliquots taken from the reaction indicated consumption of starting material. Work-up as described previously for the addition of alkyl organoaluminium reagents (*vide supra*) and purification by flash column chromatography afforded the diastereoisomerically pure, tertiary alcohol addition product.

[(8*E*,11*E*,6*S,7*S**,10*R**)-6-(Carbonyloxy-κ*C*)-10-hydroxy-10-methyl-(7,8,9-η)-hexadeca-8,11-dien-7-yl]tricarbonyliron 38**

Complex **38** was prepared according to the general procedure from methyl ketone **20b** (0.078 g, 0.22 mmol) in hexane (5 cm^3). The alkenylaluminium reagent was prepared from hex-1-yne (0.137 cm^3, 1.19 mmol) and Bu^i_2AlH (1.140 cm^3 of a 1.0 mol dm^{-3} solution in hexanes, 1.14 mmol). After 30 min, work-up as described followed by purification by flash column chromatography (eluent: Et_2O–petrol 1:9→1:2; gradient) afforded tertiary *alcohol* **38** as a cream-coloured gum (0.052 g, 54%); ν_{max}(film)/cm^{-1} 3450 (OH), 2959, 2930, 2858, 2083 (CO), 2029 (CO), 2013 (CO), 1652 (C=O), 1464; δ_H(200 MHz) 0.84–0.92 (6H, m, 1-H × 3, 16-H × 3), 1.22–1.67 {15H, m, [including 1.59 (3H, s, 10-Me)], 2-H × 2, 3-H × 2, 4-H × 2, 5-H × 2, 14-H × 2, 15-H × 2, 10-Me}, 1.85 (1H, s, OH), 2.02 (2H, apparent q, *J* 6.6, 13-H × 2), 3.89 (1H, d, *J* 11.4, 9-H), 3.97 (1H, br t, *J* 6.5, 6-H), 4.35 (1H, dd, *J* 8.0, 1.1, 7-H), 4.87 (1H, ddd, *J* 11.4, 8.0, 0.8, 8-H), 5.56 (1H, d, *J* 15.6, 11-H), 5.75 (1H, dt, *J* 15.6, 6.2, 12-H); δ_C(50 MHz) 13.81 (CH_3, 1-C or 16-C), 13.88 (CH_3, 16-C or 1-C), 22.2 (CH_2), 22.4 (CH_2), 25.2 (CH_2), 30.2 (CH_3, 10-Me), 31.1 (CH_2), 31.4 (CH_2), 31.8 (CH_2), 37.8 (CH_2, 13-C), 72.2 (quat. C, 10-C), 74.4 (CH), 74.9 (CH), 88.7 (CH), 91.5 (CH), 129.7 (CH, 11-C or 12-C), 136.0 (CH, 12-C or 11-C), 203.7 (CO), 205.7 (CO), 206.7 (CO), 209.8 (CO); *m*/*z* (FAB) 435 (MH^+, 17%), 395 (9), 377 (8, M − H − 2CO), 351 (17, MH − 3CO), 333 (6, MH − 3CO − H_2O), 321 (9, M − H − 4CO), 305 (14), 233 (100) [Found (MH^+) 435.1470. $C_{21}H_{31}FeO_6$ requires *M*H, 435.1463].

[(4*E*,7*E*,2*R,3*S**,6*R**)-2-(Carbonyloxy-κ*C*)-6-hydroxy-6-phenyl-(3,4,5-η)-dodeca-4,7-dien-3-yl]tricarbonyliron 39**

Complex **39** was prepared according to the general procedure from phenyl ketone **9a** (0.050 g, 0.14 mmol) in DCM (1 cm^3). The alkenylaluminium reagent was prepared from hex-1-yne (0.086 cm^3, 0.76 mmol) and Bu^i_2AlH (0.509 cm^3 of a 1.5 mol dm^{-3} solution in toluene, 0.76 mmol). After 20 min, work-up as described followed by purification by flash column chromatography (eluent: Et_2O–petrol 3:7→neat Et_2O; gradient) afforded in order of elution, tertiary *alcohol* **39** as a cream-

coloured foam (0.058 g, 93%) (Found: C, 59.85; H, 5.50. $C_{22}H_{24}FeO_6$ requires C, 60.02; H, 5.49%); ν_{max}(film)/cm^{-1} 3393 (OH), 3062, 3018, 2960, 2930, 2859, 2085 (CO), 2012 (CO), 1659 (C=O), 1491, 1466, 1448, 1375, 1356, 1340, 1312, 1085, 1042, 997, 945; δ_H(400 MHz) 0.90 (3H, t, *J* 7.0, 12-H × 3), 1.24–1.34 (4H, m, 10-H × 2, 11-H × 2), 1.39 (3H, d, *J* 6.0, 1-H × 3), 2.05 (2H, apparent q, *J* 7.0, 9-H × 2), 2.34 (1H, s, OH), 4.40–4.47 {2H, m, [including 4.44 (1H, d, *J* 12.0, 5-H)], 2-H, 5-H}, 4.62 (1H, dd, *J* 8.1, 5.3, 3-H), 5.01 (1H, dd, *J* 12.0, 8.1, 4-H), 5.71 (1H, dt, *J* 15.2, 7.0, 8-H), 5.88 (1H, d, *J* 15.2, 7-H), 7.29 (1H, tt, *J* 7.6, 1.5, *p*-Ph-*H*), 7.39 (2H, t, *J* 7.6, *m*-Ph-*H*), 7.50 (2H, dd, *J* 7.7, 1.5, *o*-Ph-*H*); δ_C(50 MHz; C_6D_6) 14.0, 21.8, 22.5, 31.2, 32.1, 72.8, 76.8, 76.9, 87.5, 91.4, 125.5, 127.7, 128.3, 128.7, 131.1, 136.9, 203.1, 204.3, 205.3, 210.6; *m*/*z* (FAB) 441 (MH^+, 22%), 339 (14, M − 3CO − OH), 327 (10), 311 (17), 295 (13, M − 4CO − O − OH), 239 (100, M − 4CO − Fe − O − OH), 105 (33) [Found (MH^+) 441.1001. $C_{22}H_{25}FeO_6$ requires *M*H, 441.1010]; and then the secondary alcohol reduction product **28** (0.002 g, 5%) which was spectroscopically identical to material prepared earlier (*vide supra*).

[(4*E*,7*E*,2*R,3*S**,6*R**)-2-(Carbonyloxy-κ*C*)-6-hydroxy-6-methyl-(3,4,5-η)-dodeca-4,7-dien-3-yl]tricarbonyliron 40**

Complex **40** was prepared according to the general procedure from methyl ketone **8a** (0.023 g, 0.08 mmol) in DCM (0.4 cm^3). The alkenylaluminium reagent was prepared from hex-1-yne (0.057 cm^3, 0.50 mmol) and Bu$^i_2$AlH (0.327 cm^3 of a 1.5 mol dm^{-3} solution in toluene, 0.50 mmol). After 20 min, work-up as described followed by purification by flash column chromatography (eluent: Et_2O–hexane 60%) afforded in order of elution, the tertiary *alcohol* **40** as a clear gum (0.015 g, 51%) (Found: C, 54.30; H, 5.80. $C_{17}H_{23}FeO_6$ requires C, 53.96; H, 5.86%); ν_{max}(film)/cm^{-1} 3407 (OH), 2080 (CO), 2061 (CO), 2004 (CO), 1644 (C=O); δ_H(400 MHz) 0.89 (3H, t, *J* 7.0, 12-H × 3), 1.17–1.46 (4H, m, 10-H × 2, 11-H × 2), 1.36 (3H, d, *J* 6.3, 1-H × 3), 1.64 (3H, s, 6-Me), 1.67 (1H, s, OH), 2.06 (2H, br t, *J* 6.6, 9-H × 2), 4.09 (1H, d, *J* 12.3, 5-H), 4.42 (1H, br qd, *J* 6.3, 4.6, 2-H), 4.60 (1H, dd, *J* 8.2, 4.6, 3-H), 4.76 (1H, dd, *J* 12.3, 8.2, 4-H), 5.66 (1H, d, *J* 15.5, 7-H), 5.76 (1H, dt, *J* 15.5, 6.6, 8-H); δ_C(100 MHz) 13.9, 21.9, 22.1, 30.4, 31.2, 31.8, 72.5, 73.3, 76.5, 87.0, 92.5, 129.8, 136.2, 203.5, 206.3, 206.9, 209.5; *m*/*z* (FAB) 379 (MH^+, 65%), 351 (5, MH − CO), 295 (10, MH − 3CO), 177 [100, $(C_{13}H_{21})^+$] [Found (MH^+) 379.0844. $C_{17}H_{23}FeO_6$ requires *M*H, 379.0844]; and then the secondary *alcohol* reduction product **30** as an off-white solid (0.002 g, 9%) which was spectroscopically identical to material prepared earlier (*vide supra*).

General procedure for the addition of alkenyldimethylaluminium reagents into ketone complexes: synthesis of complex 38

[(8*E*,11*E*,6*S,7*S**,10*R**)-6-(Carbonyloxy-κ*C*)-10-hydroxy-10-methyl-(7,8,9-η)-hexadeca-8,11-dien-7-yl]tricarbonyliron 38**

Bu^{n}Li (0.430 cm^3 of a 1.6 mol dm^{-3} solution in hexanes, 0.69 mmol) was added dropwise to a solution of (1*E*)-1-iodohex-1-ene (0.145 g, 0.69 mmol) in toluene (3 cm^3) at 0 °C and the mixture was maintained at this temperature for 20 min. Me_2AlCl (0.690 cm^3 of a 1.0 mol dm^{-3} solution in hexanes, 0.69 mmol) was added dropwise and stirring at 0 °C was continued for a further 45 min after which time formation of the alkenylaluminium reagent was assumed to be complete. A solution of ketone **20b** (0.076 g, 0.22 mmol) in DCM (3 cm^3) was added and the reaction mixture stirred at 0 °C for 2.5 h. The reaction was quenched by the addition of HCl (1 mol dm^{-3}, 5 cm^3; ice cold). The two phases were separated and the aqueous layer extracted with DCM (3 × 5 cm^3). The combined organic fractions were dried ($MgSO_4$) and the solvent removed *in vacuo*. Purification of the residue by flash column chromatography (eluent: Et_2O–petrol 1:4) yielded the alcohol **38** (0.043 g, 46%) which was spectroscopically identical to material prepared earlier (*vide supra*).

(2*S*,3*S*)-2,3-Epoxybutan-1-ol 11

(2*E*)-But-2-en-1-ol (10.0 cm^3, 118 mmol) was treated with L-diisopropyl tartrate (4.97 g, 21.2 mmol), titanium(IV) isopropoxide (5.73 cm^3, 17.7 mmol), activated 3 Å powdered molecular sieves (4.20 g) and *tert*-butyl hydroperoxide (79 cm^3 of a 3 mol dm^{-3} solution in 2,2,4-trimethylpentane, 236 mmol) according to literature procedure[10] to provide the crude product. Purification by flash column chromatography [eluent: Et_2O–petrol (30–40 °C boiling point fraction) 2:3] followed by removal of the solvent by distillation at atmospheric pressure (40–45 °C) provided the epoxy alcohol **11** as a colourless liquid (8.31 g, 80%) which had identical spectroscopic properties to those reported in the literature,[10] $[\alpha]_D^{24}$ −50.9 (*c* 1.30, C_6H_6) {lit.,[10] $[\alpha]_D^{24}$ −55.0 (*c* 0.22, C_6H_6)}. Analysis by chiral GLC, and comparison of the racemate prepared in an analogous manner (*vide supra*) (Macherey-Nagel Lipodex E column, 25 m × 0.25 mm internal diameter; 70 °C isotherm; carrier gas: helium; flow rate: 100 cm^3 min^{-1}) revealed **11** to have 85% ee [retention times 17.80 min (minor), 18.54 min (major)].

(2*E*,5*S*,6*S*)-5,6-Epoxyhept-3-en-2-one 12

Compound **12** was prepared from epoxy alcohol **11** according to the procedure described (*vide supra*) and had identical spectroscopic properties to those reported for the racemic compound, $[\alpha]_D^{22}$ −31.9 (*c* 0.50, $CHCl_3$). Chiral GLC analysis of **12** (Macherey-Nagel Lipodex E column, 25 m × 0.25 mm internal diameter; 90 °C isotherm; carrier gas: helium; flow rate: 100 cm^3 min^{-1}) revealed **12** to have an ee of 86% [retention times 23.10 min (major), 24.42 min (minor)].

(2*E*,4*S*,5*S*)-4,5-Epoxy-1-phenylhex-2-en-1-one 13

A solution of the epoxy alcohol **11** (0.200 g, 1.14 mmol) in DCM (1 cm^3) was added *via* cannula to a stirred suspension of pyridinium dichromate (0.680 g, 1.81 mmol) and activated 4 Å powdered molecular sieves (*ca*. 0.2 g) in DCM (13 cm^3) at room temperature. After stirring for 16 h, the reaction mixture was filtered through a pad of $MgSO_4$ and Celite, and the residue was washed with Et_2O (20 cm^3). The solution was concentrated by removal of solvents by distillation at atmospheric pressure (35–40 °C) and the crude aldehyde was used without further purification. A solution of diethyl (2-oxo-2-phenylethyl)-phosphonate[18] (0.635 g, 2.51 mmol) in MeCN (1 cm^3) was added *via* cannula to a solution of LiCl (dried *in vacuo* for 16 h at 120 °C immediately prior to use, 0.120 g, 2.51 mmol) in MeCN (15 cm^3). After stirring for 10 min, diisopropylethylamine (0.394 cm^3, 2.28 mmol) and the crude aldehyde were added sequentially. After stirring for 30 min, H_2O (20 cm^3) and DCM (20 cm^3) were added. The biphasic mixture was poured into NH_4Cl solution (30 cm^3) and the layers were separated. The aqueous layer was extracted with DCM (3 × 30 cm^3). The combined organic fractions were washed with brine (30 cm^3) and dried ($MgSO_4$). Concentration *in vacuo* followed by purification by flash column chromatography afforded *epoxy enone* **13** as a light yellow oil (0.870 g, 41%) which had identical spectroscopic properties to the racemic material prepared earlier (*vide supra*), $[\alpha]_D^{24}$ −20.6 (*c* 0.48, $CHCl_3$).

[(4*E*,2*S*,3*R*)-2-(Carbonyloxy-κ*C*)-6-oxo-(3,4,5-η)-hept-4-en-3-yl]tricarbonyliron 14a and [(4*E*,2*S*,3*S*)-2-(carbonyloxy-κ*C*)-6-oxo-(3,4,5-η)-hept-4-en-3-yl]tricarbonyliron 14b

Complexes **14a** and **14b** were prepared as in the racemic pathway (*vide supra*) from epoxy enone **12**. Purification as described afforded enantiomerically enriched *endo ketone complex* **14a**; $[\alpha]_D^{22}$ +438.9 (*c* 0.70, $CHCl_3$), and *exo ketone complex* **14b**; $[\alpha]_D^{24}$ +18.0 (*c* 0.51, $CHCl_3$). Both complexes had identical spectroscopic properties to those reported for the racemates.

[(4*E*,2*S*,3*R*)-2-(Carbonyloxy-κ*C*)-6-oxo-6-phenyl-(3,4,5-η)-hex-4-en-3-yl]tricarbonyliron 15a and [(4*E*,2*S*,3*S*)-2-(carbonyloxy-κ*C*)-6-oxo-6-phenyl-(3,4,5-η)-hex-4-en-3-yl]tricarbonyliron 15b

Complexes **15a** and **15b** were prepared as in the racemic path-

way (*vide supra*) from epoxy enone **13**. Purification by HPLC as described afforded enantiomerically enriched *endo ketone complex* **15a**; $[\alpha]_D^{24}$ +172.7 (*c* 0.17, $CHCl_3$), and *exo ketone complex* **15b**. Both complexes had identical spectroscopic properties to those reported for the racemates. Chiral HPLC analysis revealed **15a** to have 87% ee [eluent: Pr^iOH–hexane 5%; flow rate 0.5 cm^3 min^{-1}; retention times 34.97 min (major), 40.26 min (minor)].

Reaction of enantiomerically enriched ketone complexes with organoaluminium reagents: synthesis of complexes 41–45

Reactions of ketones **14a** and **15a** with organoaluminium reagents were carried out under analogous conditions to their racemates (*vide supra*). Work-up and purification by flash column chromatography afforded the enantiomerically enriched complexes which were spectroscopically identical to the complexes prepared from racemic material.

[(4*E*,2*S*,3*R*,6*R*)-2-(Carbonyloxy-κ*C*)-6-hydroxy-6-methyl-(3,4,5-η)-dodec-4-en-7-yn-3-yl]tricarbonyliron 41

Treatment of ketone **14a** (0.143 mmol) with dimethylhex-1-ynylaluminium under standard conditions afforded the tertiary *alcohol* **41** as a light brown gum (75%); $[\alpha]_D^{25}$ +136.2 (*c* 0.21, $CHCl_3$). HPLC analysis revealed **41** to have an ee of 84% [eluent: Pr^iOH–hexane 4%; flow rate 0.5 cm^3 min^{-1}; retention times 17.55 min (major), 21.20 min (minor)].

[(4*E*,2*S*,3*R*,6*S*)-2-(Carbonyloxy-κ*C*)-6-hydroxy-6-phenyl-(3,4,5-η)-dodec-4-en-7-yn-3-yl]tricarbonyliron 42

Treatment of ketone **15a** (0.11 mmol) with dimethylhex-1-ynylaluminium under standard conditions afforded the tertiary *alcohol* **42** as a cream-coloured gum (65%); $[\alpha]_D^{24}$ +144.5 (*c* 0.13, $CHCl_3$). HPLC analysis revealed **42** to have an ee of 82% [eluent: Pr^iOH–hexane 5%; flow rate 0.5 cm^3 min^{-1}; retention times 20.40 min (major), 28.14 min (minor)].

[(4*E*,2*S*,3*R*,6*R*)-2-(Carbonyloxy-κ*C*)-6-hydroxy-6,9,9-trimethyl-(3,4,5-η)-dec-4-en-7-yn-3-yl]tricarbonyliron 43

Treatment of ketone **14a** (0.061 mmol) with (3,3-dimethylbut-1-ynyl)dimethylaluminium under standard conditions afforded the tertiary *alcohol* **43** as a gum (70%); $[\alpha]_D^{24}$ +103.6 (*c* 0.28, $CHCl_3$). HPLC analysis revealed **43** to have an ee of 86% [eluent: Pr^iOH–hexane 4%; flow rate 0.5 cm^3 min^{-1}; retention times 17.05 min (major), 19.85 min (minor)].

[(4*E*,7*E*,2*S*,3*R*,6*S*)-2-(Carbonyloxy-κ*C*)-6-hydroxy-6-phenyl-(3,4,5-η)-dodeca-4,7-dien-3-yl]tricarbonyliron 44

Treatment of ketone **15a** (0.130 mmol) with diisobutylhex-1-enylaluminium under standard conditions afforded the tertiary *alcohol* **44** as a cream-coloured gum (67%); $[\alpha]_D^{24}$ +113.6 (*c* 0.84, $CHCl_3$). Analysis of the ^1H NMR (200 MHz) spectrum using the shift reagent praseodymium(III) tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphoride] (13 mol%) indicated an ee of 83% for **44**. A small quantity of the reduction product [(4*E*,2*S*,3*R*,6*S*)-2-(carbonyloxy-κ*C*)-6-hydroxy-6-phenyl-(3,4,5-η)-hex-4-en-3-yl]tricarbonyliron was also obtained as a white solid (7%); $[\alpha]_D^{24}$ +20.4 (*c* 1.10, $CHCl_3$).

[(4*E*,2*S*,3*R*,6*S*)-2-(Carbonyloxy-κ*C*)-6-hydroxy-6-phenyl-(3,4,5-η)-hept-4-en-3-yl]tricarbonyliron 45

Treatment of ketone **15a** (0.060 mmol) with trimethylaluminium under standard conditions afforded the tertiary *alcohol* **45** as a white solid (85%); $[\alpha]_D^{24}$ +97.6 (*c* 0.95, $CHCl_3$). The level of enantiopurity of the η^4-dienetricarbonyliron complex **48** obtained directly from **45** indicated **45** to have an ee of 85% (*vide infra*).

General procedure for the preparation of η^4-dienetricarbonyliron complexes: synthesis of complexes 46–51

A saturated aqueous solution of $Ba(OH)_2$ (2 cm^3) was added dropwise to a solution of the alcohol (0.06 mmol) in MeOH (4 cm^3). The resultant solution was stirred for 10 min and then poured into H_2O (20 cm^3). The layers were separated and the aqueous fraction was extracted with Et_2O (3 × 15 cm^3). The combined organic extracts were washed with brine (20 cm^3), dried ($MgSO_4$) and concentrated *in vacuo*. Purification of the residue by flash column chromatography (eluent: Et_2O–petrol) afforded the corresponding η^4-dienetricarbonyliron complex.

[(3*Z*,2*R,5*R**)-1-Oxo-1-phenyl-(2,3,4,5-η)-hex-3-en-2,5-diyl]-tricarbonyliron 46**

Complex **46** was prepared according to the general procedure from ketone complex **9a** (0.068 g, 0.19 mmol). Work-up after 10 min followed by purification by flash column chromatography (eluent: Et_2O–petrol 1:4) afforded *ketone* **46** as a bright yellow solid (0.058 g, 97%) (Found: C, 57.76; H, 3.95. $C_{15}H_{12}FeO_4$ requires C, 57.73; H, 3.86%); ν_{max}(film)/cm^{-1} 3090, 3010, 2945, 2860, 2054 (CO), 2003 (CO), 1646 (C=O), 1598, 1578, 1495, 1460, 1344, 1298, 1239, 1183, 1128, 1011; δ_H(200 MHz) 1.53 (3H, d, *J* 6.2, 6-H × 3), 1.71–1.82 (1H, m, 5-H), 1.93 (1H, d, *J* 8.0, 2-H), 5.36 (1H, dd, *J* 8.0, 5.1, 4-H), 6.06 (1H, dd, *J* 8.0, 5.1, 3-H), 7.39–7.56 (3H, m, *m*-Ph-*H*, *p*-Ph-*H*), 7.91 (2H, dd, *J* 6.8, 1.2, *o*-Ph-*H*); δ_C(50 MHz) 19.1, 49.9, 59.4, 82.2, 89.3, 127.5, 128.5, 132.6, 137.3, 195.2, 209.7 (br); *m*/*z* (CI) 313 (MH^+, 75%), 256 (15, M − 2CO), 228 (40, M − 3CO), 172 (15, M − 3CO − Fe), 157 (40), 105 [100, PhC(O)], 77 (58, Ph).

[(3*Z*,2*R,5*R**,6*R**)-6-Hydroxy-6-phenyl-(2,3,4,5-η)-hept-3-en-2,5-diyl]tricarbonyliron 47**

Complex **47** was prepared according to the general procedure from alcohol complex **22** (0.049 g, 0.13 mmol). Work-up after 10 min followed by purification by flash column chromatography (eluent: Et_2O–petrol 1:4) afforded *alcohol* **47** as a bright yellow gum (0.033 g, 80%) (Found: C, 58.80; H, 5.05. $C_{16}H_{16}FeO_4$ requires C, 58.56; H, 4.91%); ν_{max}(film)/cm^{-1} 3610 (OH), 2967, 2932, 2857, 2798, 2043 (CO), 1980 (CO), 1493, 1446, 1380, 1334, 1231, 1202, 1147, 1069, 1028; δ_H(400 MHz) 1.01 (1H, dq, *J* 8.3, 6.4, 2-H), 1.27 (1H, d, *J* 8.8, 5-H), 1.36 (3H, d, *J* 6.4, 1-H × 3), 1.69 (3H, s, 7-H × 3), 1.71 (1H, s, OH), 5.01 (1H, dd, *J* 8.3, 5.1, 3-H), 5.45 (1H, dd, *J* 8.8, 5.1, 4-H), 7.28 (1H, tt, *J* 7.2, 1.1, *p*-Ph-*H*), 7.38 (2H, apparent t, *J* 7.2, *m*-Ph-*H*), 7.42 (2H, dd, *J* 7.2, 1.1, *o*-Ph-*H*); δ_C(100 MHz) 19.0 (CH_3), 33.9 (CH_3), 56.7 (CH), 74.6 (quat. C), 74.9 (CH), 79.3 (CH), 83.8 (CH), 123.8 (CH), 126.8 (CH), 128.3 (CH), 149.0 (quat. C), 212.1 (br, CO); *m*/*z* (EI) 300 [(M − CO)$^+$, 8%], 272 (5, M − 2CO), 244 (5, M − 3CO), 226 (40), 171 (100, M − 3CO − Fe − OH), 143 (95), 128 (82), 77 (43, Ph) [Found (M^+) 328.0398. $C_{16}H_{16}FeO_4$ requires 328.0398].

[(3*Z*,2*R*,5*R*,6*R*)-6-Hydroxy-6-phenyl-(2,3,4,5-η)-hept-3-en-2,5-diyl]tricarbonyliron 48

Complex **48** was prepared according to the general procedure from alcohol complex **45** (0.016 g, 0.04 mmol). Work-up after 10 min followed by purification by flash column chromatography (eluent: Et_2O–petrol 1:4) afforded *alcohol* **48** (0.014 g, 96%) which was spectroscopically identical to the racemic material prepared earlier (*vide supra*); $[\alpha]_D^{24}$ −84.7 (*c* 1.35, CH_2Cl_2). Analysis by chiral HPLC revealed **48** to have 85% ee [eluent: Pr^iOH–hexane 5%; flow rate 0.5 cm^3 min^{-1}; retention times 17.39 min (minor), 24.67 min (major)].

[(3*Z*,7*E*,2*R,5*R**,6*R**)-6-Hydroxy-6-phenyl-(2,3,4,5-η)-dodeca-3,7-dien-2,5-diyl]tricarbonyliron 49**

Complex **49** was prepared according to the general procedure from alcohol complex **39** (0.028 g, 0.07 mmol). Work-up after 10 min followed by purification by flash column chromatography (eluent: Et_2O–petrol 1:10) afforded *alcohol* **49** as an orange gum (0.021 g, 81%); ν_{max}(film)/cm^{-1} 3602 (OH), 3007,

Table 4 Crystal data for complexes **8a**, **21** and **29**[a]

	8a	**29**	**21**
Molecular formula	$C_{11}H_{10}FeO_6$	$C_{13}H_{16}FeO_6$	$C_{13}H_{16}FeO_6$
M	294.04	324.11	324.11
T/K	153(2)	293(2)	293(2)
Crystal system	orthorhombic	orthorhombic	monoclinic
a/Å	9.822(2)	14.160(3)	8.543(3)
b/Å	10.326(2)	14.263(3)	16.017(3)
c/Å	11.814(2)	14.697(3)	10.906(2)
α/°	90	90	90
β/°	90	90	90.74(3)
γ/°	90	90	90
U/Å^3	1198.2(4)	2968.2(11)	1492.2(5)
Space group	$P2_12_12_1$	*Pbca*	$P2_1/n$
Z	4	8	4
D_c/Mg m^{-3}	1.630	1.451	1.443
Crystal size/mm	0.45 × 0.29 × 0.21	0.39 × 0.36 × 0.20	0.31 × 0.30 × 0.28
F(000)	600	1344	672
μ/mm^{-1}	1.274	1.036	1.031
Data collection range/°	$3.95 < \theta < 22.49$	$3.98 < \theta < 22.51$	$2.54 < \theta < 22.50$
Reflections measured	1846	1929	2100
Independent reflections	1559 (R_{int} = 0.0130)	1929	1951 (R_{int} = 0.0288)
Parameters, restraints	169, 0	185, 0	229, 0
*wR*2 (all data)[b]	0.1095	0.1107	0.0870
x, *y*[b]	0.08224, 0.0158	0.0565, 3.555	0.0298, 0.322
$R1[I > 2\sigma(I)]$[b]	0.0275	0.0375	0.0365
Observed reflections $[I > 2\sigma(I)]$	1509	1621	1535
Goodness-of-fit on F^2 (all data)[b]	1.229	1.055	1.018
Maximum shift/*σ*	0.003	0.001	0.002
Peak, hole in final difference map/e Å^{-3}	0.427, −0.584	0.515, −0.321	0.190, −0.223

[a] Data in common: Graphite-monochromated Mo-Kα radiation, $\lambda = 0.710\ 73$ Å. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{\frac{1}{2}}$, $w = 1/[\sigma^2(F_o)^2 + (xP)^2 + yP]$, $P = (F_o^2 + 2F_c^2)/3$, where *x* and *y* are constants adjusted by the program; Goodness-of-fit = $[\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)]^{\frac{1}{2}}$ where *n* is the number of reflections and *p* the number of parameters.

2947, 2879, 2043 (CO), 1976 (CO), 1600, 1491, 1447, 1380, 1216, 974, 758; δ_H(500 MHz) 0.87 (3H, t, *J* 7.0, 12-H × 3), 1.02 (1H, dq, *J* 8.6, 6.3, 2-H), 1.21–1.32 (5H, m, 5-H, 10-H × 2, 11-H × 2), 1.36 (3H, d, *J* 6.3, 1-H × 3), 1.77 (1H, s, OH), 2.02 (2H, dt, *J* 6.7, 6.0, 9-H × 2), 5.02 (1H, dd, *J* 8.6, 5.1, 3-H), 5.40 (1H, dd, *J* 8.8, 5.1, 4-H), 5.64 (1H, dt, *J* 15.3, 6.7, 8-H), 5.81 (1H, d, *J* 15.3, 7-H), 7.27 (1H, tt, *J* 7.1, 1.2, *p*-Ph-*H*), 7.36 (2H, apparent t, *J* 7.1, *m*-Ph-*H*), 7.39 (2H, dd, *J* 7.1, 1.2, *o*-Ph-*H*); δ_C(50 MHz) 13.9, 19.0, 22.2, 29.7, 31.2, 31.9, 56.3, 73.2, 79.7, 83.8, 124.6, 126.7, 128.1, 130.7, 136.8, 147.4, 211.9 (br); *m*/*z* (EI) 396 (M^+, 10%), 379 (15, M − OH), 368 (25, M − CO), 351 (20, M − CO − OH), 340 (20, M − 2CO), 323 (27, M − 2CO − OH), 312 (10, M − 3CO), 239 (54, M − 3CO − Fe − OH), 181 (53), 91 (100), 77 (22, Ph), 55 (34) [Found (M^+) 396.1031. $C_{21}H_{24}FeO_4$ requires *M*, 396.1024].

[(3*Z*,2*R,5*R**,6*S**)-6-Hydroxy-9,9-dimethyl-6-phenyl-(2,3,4,5-η)-dec-3-en-7-yn-2,5-diyl]tricarbonyliron 50**

Complex **50** was prepared according to the general procedure from alcohol complex **35** (0.027 g, 0.06 mmol). Work-up after 10 min followed by purification by flash column chromatography (eluent: Et_2O–petrol 1:11) afforded *alcohol* **50** as a yellow gum (0.019 g, 80%); ν_{max}(film)/cm^{-1} 3584 (OH), 3021, 3002, 2989, 2965, 2241 (C≡C), 2043 (CO), 1971 (CO), 1600, 1489, 1448, 1262, 1216, 1030, 758; δ_H(200 MHz) 1.04 (1H, dq, *J* 8.7, 6.3, 2-H), 1.20–1.27 (10H, m, 5-H, 9-Me × 2, 10-H × 3), 1.38 (3H, d, *J* 6.3, 1-H × 3), 2.23 (1H, s, OH), 5.03 (1H, dd, *J* 8.7, 5.0, 3-H), 5.53 (1H, dd, *J* 8.7, 5.0, 4-H), 7.27–7.38 (3H, m, *m*-Ph-*H*, *p*-Ph-*H*), 7.62 (2H, dd, *J* 7.8, 1.6, *o*-Ph-*H*); δ_C(50 MHz) 18.9, 27.6, 30.7, 57.4, 73.3, 73.9, 79.4, 81.4, 84.2, 96.6, 124.9, 127.4, 128.2, 146.5, 211.7 (br); *m*/*z* (CI) 377 (M − OH, 37%), 338 (5, M − 2CO), 310 (72, M − 3CO), 237 (100, M − 3CO − Fe − OH), 173 (57), 102 (18), 52 (27) {Found [$(M - OH)^+$] 377.0840. $C_{21}H_{21}FeO_3$ requires *M* − OH, 377.0839}.

[(3*Z*,1*R,2*R**,5*R**)-1-Hydroxy-1-phenyl-(2,3,4,5-η)-hex-3-en-2,5-diyl]tricarbonyliron 51**

Complex **51** was prepared according to the general procedure from alcohol complex **28** (0.053 g, 0.15 mmol). Work-up after 10 min followed by purification by flash column chromatography (eluent: Et_2O–petrol 1:11) afforded *alcohol* **51** as a bright yellow foam (0.047 g, 94%); ν_{max}(film)/cm^{-1} 3455 (OH), 3063, 3016, 2969, 2920, 2859, 2044 (CO), 1974 (CO), 1601, 1493, 1452, 1380, 1318, 1285, 1169, 1133, 1076, 924, 883, 847; δ_H(200 MHz) 1.31–1.18 (2H, m, 2-H, 5-H), 1.41 (3H, d, *J* 6.3, 6-H × 3), 1.87 (1H, d, *J* 2.6, OH), 4.44 (1H, dd, *J* 8.3, 2.6, 1-H), 5.04 (1H, dd, *J* 8.7, 4.9, 4-H), 5.20 (1H, dd, *J* 8.7, 4.9, 3-H), 7.25–7.38 (5H, m, Ph-*H*); δ_C(50 MHz) 19.0, 58.3, 68.5, 76.7, 80.6, 85.8, 125.4, 127.8, 128.6, 144.6, 211.9 (br); *m*/*z* (CI) 313 [$(M - H)^+$, 10%], 297 (55, M − OH), 286 (8, M − CO), 258 (6, M − 2CO), 247 (10), 231 (15, MH − 3CO), 212 (22), 157 (17, M − 3CO − Fe − OH), 84 (58), 49 (100) {Found [$(M - H)^+$] 313.0180. $C_{15}H_{13}FeO_4$ requires *M* − H, 313.0163}.

X-Ray crystallography

Crystals of compounds **9a**, **21** and **27** were grown, in all cases, from Et_2O–petrol. Diffraction intensities were measured on a Stoe-Siemens diffractometer using graphite monochromated Mo-Kα radiation in the *ω*–*θ* scan mode. The refined cell parameters and additional crystallographic details for **9a**, **21** and **27** are summarised in Table 4. No corrections for absorption or crystal decay were applied during data processing. The structures were solved by automatic direct methods (SHELXS-86).[19] Subsequent refinements were performed using full matrix least-squares on F^2 (SHELXS-93)[20] with all non-H atoms anisotropic. H-atoms were placed geometrically in idealised positions and refined as riding atoms. Methyl groups were refined as rigid bodies. Figs. 1 and 4 were produced using SHELXTL/PC.[21] The final positional parameters with *U*, the thermal parameters U_{ij}, bond lengths and bond angles for **9a**, **21** and **27** have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc.*, *Perkin Trans. 1*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 207/148.

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