1,5-Asymmetric induction of chirality: diastereoselective addition of organoaluminium reagents and allylstannanes into aldehyde groups in the side-chain of π-allyltricarbonyliron lactone complexes

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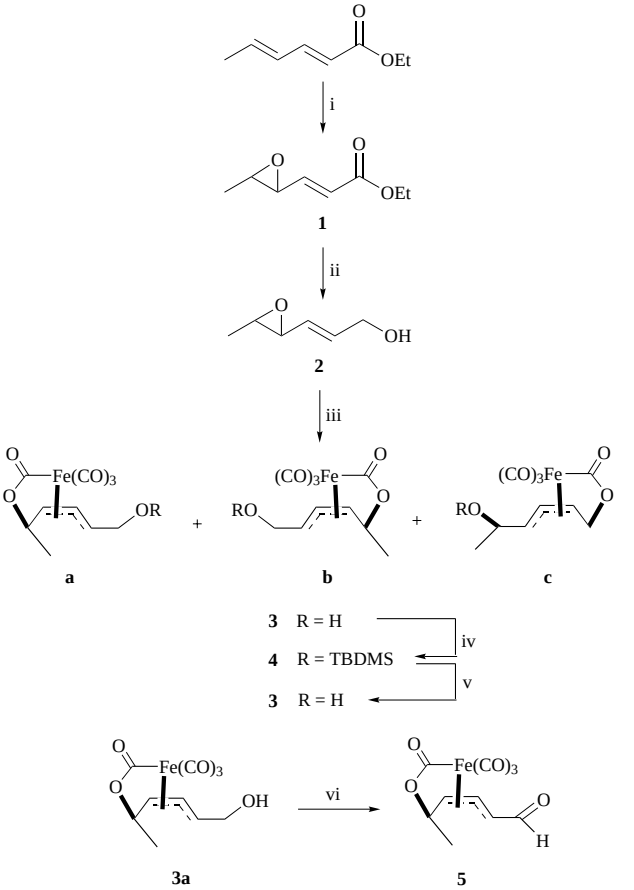
π-Allyltricarbonyliron lactone complex 5, bearing an aldehyde group in the side-chain, can be easily prepared from commercially available (2*E*,4*E*)-ethyl hexadienoate and reacts with organoaluminium and allylstannane nucleophiles to afford secondary alcohols. In analogy with the corresponding ketone-substituted complexes, the lactone tether acts *via* the $Fe(CO)_3$ moiety as a source of asymmetric induction. The levels of diastereoselectivity are generally reduced, however, compared with those obtained using ketone complexes. This can be attributed, at least in part, to the carbonyl appendage adopting both s-*cis* and s-*trans* conformations. The level of 1,5-asymmetric induction is strongly dependent upon the nature of the nucleophile in the case of the organoaluminium reactions and upon the reaction temperature in the case of BF_3-mediated addition of allylstannanes into the aldehyde group.

Introduction

In the previous two papers we reported the highly diastereoselective addition of both organoaluminium reagents[1a] and allylstannanes[1b] into ketone groups in the side-chain of π-allyltricarbonyliron lactone complexes. This provides a route to diastereoisomerically pure tertiary alcohols. While tertiary alcohols do occur in numerous, biologically important natural products, secondary alcohols are even more ubiquitous. We envisaged that aldehyde groups positioned in a similar position might also undergo addition reactions with a degree of diastereocontrol providing a route to synthetically more useful secondary alcohols *via* an analogous 1,5-asymmetric induction of chirality. Here we report in full our findings on the reaction of organoaluminium reagents and allylstannanes with formyl substituted π-allyltricarbonyliron lactone complexes.[2]

Results and discussion

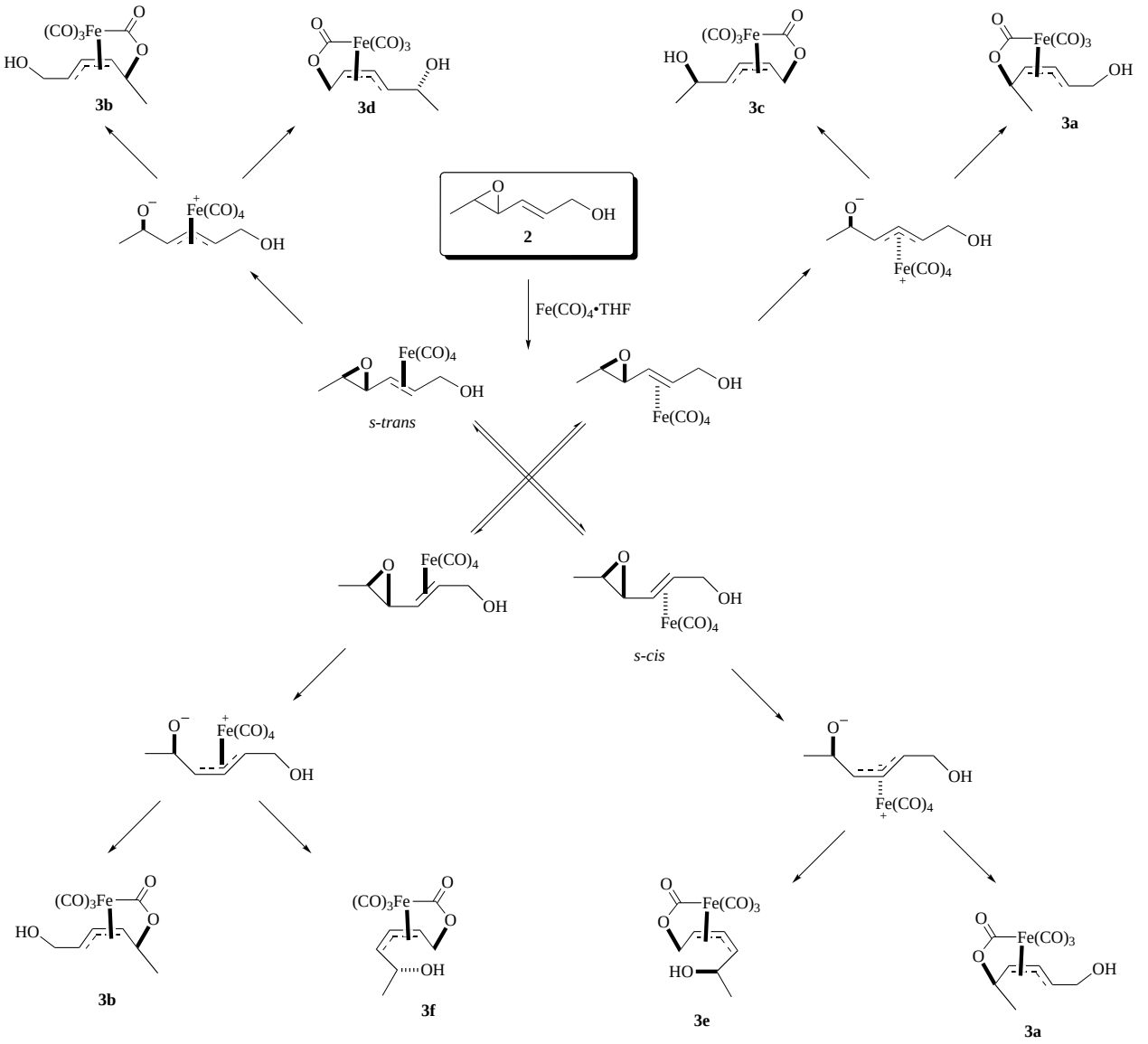
For the purpose of the study, the racemic *endo* aldehyde complex **5** was prepared from readily available (2*E*,4*E*)-ethyl hexadienoate.† The first approach to **5** is outlined in Scheme 1. Regioselective epoxidation of the more electron rich γ,δ double bond of (2*E*,4*E*)-ethyl hexadienoate proceeded smoothly using *in situ* generated trifluoroperacetic acid.[3] Uneventful reduction of the ester functionality with diisobutylaluminim hydride then afforded the precursor **2** to the lactone complexes in 58% over the two steps.‡ Treatment of the vinyl epoxide **2** with diironnonacarbonyl, $[Fe_2(CO)_9]$ in tetrahydrofuran (THF) under standard conditions[4] yielded not only a mixture of the expected *endo* and *exo* complexes **3a** and **3b**, but also the secondary alcohol complex **3c**, in a ratio of 20:2:7. The presence of such a secondary alcohol product can be accounted for by considering the proposed mechanism for the formation of π-allyltricarbonyliron lactone complexes (Scheme 2):[5] $Fe_2(CO)_9$ in THF produces the reactive tetracarbonyliron intermediate $Fe(CO)_4$·THF.[6] Complexation of this species to either face of the alkene of the vinyl epoxide, which can adopt both s-*cis* and s-*trans* conformations, then initiates product formation: coordination



Scheme 1 *Reagents and conditions*: i, $(CF_3CO)_2O$ (10 equiv.), $H_2NCONH_2{\cdot}H_2O_2$ (40 equiv.), K_2HPO_4 (20 equiv.), DCM, 0.5 h, 65%; ii, DIBAL-H (2.3 equiv.), THF, −78 °C, 1 h, 89%; iii, $Fe_2(CO)_9$ (2.1 equiv.), THF, 1 h, 83% (**3a**:**3b**:**3c**; 20:2:7); iv, TBDMSCl (1.1 equiv.), imidazole (1.4 equiv.), DMF, 10 min, 45% (from **2**) (**4a**), 4% (from **2**) (**4b**), 15% (from **2**) (**4c**); v, HF·pyridine, THF, 3 h, 70% (**3a**), or 5 h, 67% (**3b**), or 72 h, 26% (**3c**); vi, Dess–Martin periodinane (1.7 equiv.), DCM, 0 °C, 1 h, 98%, or PDC (1.5 equiv.), 4 Å molecular sieves, DCM, 2 h, 77%

† Obtained from Aldrich Inc. and used without further purification.

‡ Initial studies showed that formation of the aldehyde complexes from an epoxy enal precursor resulted in low yields of the desired complexes, hence oxidation after complexation was preferable. Similarly although the epoxy ester **1** can be used to synthesise lactone complexes bearing an ester in the side-chain, all attempts to subsequently reduce the ester to the desired aldehyde or to an alcohol resulted in extensive decomposition.



Scheme 2 Mechanism of formation of π-allyltricarbonyliron lactone complexes

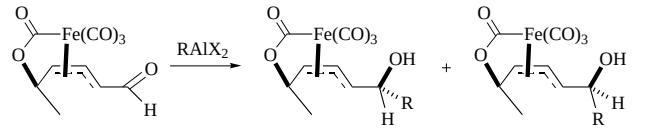
to the double bond labilises the epoxide to ring opening, affording an intermediate cationic η^3-allyltetracarbonyliron species. Intramolecular attack of the generated alkoxide on a carbonyl ligand then gives rise to the *endo* and *exo* lactone complexes **3a** and **3b** respectively.§ Alternatively, attack of the less nucleophilic primary alcohol would give rise to four possible secondary alcohol complexes **3c**–**f** (Scheme 2) of which only one, **3c**, was isolated. In accord with earlier work,[4] *endo* complex **3a** is the major product, deriving from initial coordination of the tetracarbonyliron species to the stereoface of the double bond *anti* to the epoxide. Extensive NMR experiments have confirmed the structure of the isolated secondary alcohol complex **3c**. Although the relative stereochemistry remains undetermined, it is most probably that shown; like the *endo* complex, also deriving from initial complexation of the tetracarbonyliron moiety to the s-*trans*-conformation of the epoxy alkene *anti* to the epoxide. The other possible complexes **3d**, **3e** and **3f** may have been too unstable or been present in such small quantities that they were overlooked. The fact that *endo* and *exo* complexes predominate over the four possible secondary alcohol isomers also implies that epoxide ring opening is rate determining and subsequent attack of an alcohol/alkoxide nucleophile on a carbonyl ligand must be rapid. The observed ratio of products then reflects the increased nucleophilicity of the secondary alkoxide over the primary alcohol.

Separation of the alcohol complexes unfortunately proved to be an arduous task. Oxidation of the mixture with either Dess–Martin periodinane or pyridinium dichromate (PDC) allowed, after careful chromatographic separation from the other complexes, more facile access to the desired *endo* aldehyde complex **5** required for the study. To ease separation of the mixture of alcohols **3a**–**c**, these were silyl protected with *tert*-butyldimethylsilyl chloride in dimethylformamide (DMF) affording the silyl protected complexes **4a**–**c**. These were more readily separable by chromatography. Silyl deprotection with HF–pyridine then furnished the pure alcohol complexes which could be oxidised to the respective carbonyl compounds as before.

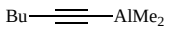
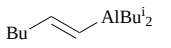
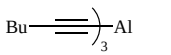
Silyl protection of the epoxy alcohol precursor **2** would not only preclude formation of the secondary alcohol complex **3c** but would also enable more facile separation of diastereoisomeric *endo* and *exo* complexes. A modified route to complex **5** is outlined in Scheme 3. Protection of the alcohol **2** with *tert*-butyldimethylsilyl chloride in DMF yielded the silyl ether **6** in high yield. Standard conditions for complexation were then applied to form complexes **4a** and **4b** in good yield and a ratio of 5:1. After facile separation of the *endo* and *exo* diastereo-

§ Formation of *transoid* complexes from the s-*trans*-conformation of the vinyl epoxide has been observed in a small number of cases, but on this substrate, isomerisation to the less strained *cisoid* complexes occurs under the reaction conditions.

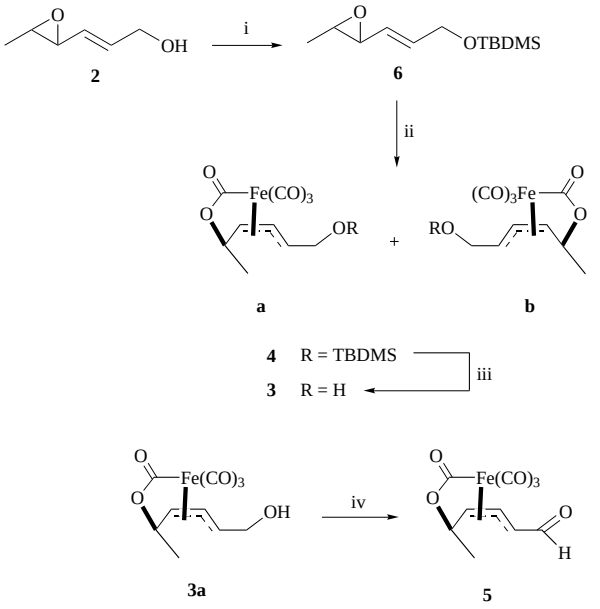
Table 1 Diastereoselective additions of organoaluminium reagents to π-allyltricarbonyliron lactone complex **5**



5 **7**, **8a - 10a** **8b - 10b**

Entry	$RAlX_2$	Product ratio [a]	Combined yield (%)
1	$AlMe_3$	**7** only	76
2	$PhAlMe_2$	**8a** only	26 [c]
3		**9a** : **9b** 9 : 1	70
4		**10a** : **10b** 5 : 1	65 [d]
5		**9a** : **9b** 2 : 1	56
6	$AlPh_3$	**8a** : **8b** 1 : 4 [b]	71

[a] Determined by ^{1}H NMR spectroscopy on the mixture unless otherwise indicated. [b] Based on isolated material. [c] 36% of **7** was also isolated as a single diastereoisomer. [d] 10% of the reduction product **3a** was also isolated.



Scheme 3 *Reagents and conditions*: i, TBDMSCl (1.1 equiv.), imidazole (1.4 equiv.), DMF, 10 min, 99%; ii, $Fe_2(CO)_9$ (2.1 equiv.), THF, 3 h, 74% (**4a** : **4b**; 5 : 1); iii, HF·pyridine, THF, 3 h, 76% (**3a**), or 5 h, 67% (**3b**); iv, Dess–Martin periodinane (1.7 equiv.), DCM, 0 °C, 1 h, 98%, or PDC (1.5 equiv.), 4 Å molecular sieves, DCM, 2 h, 77%

isomers, silyl deprotection with HF–pyridine followed by oxidation as before afforded the *endo* aldehyde complex **5**.

With a more convenient route to quantities of *endo* compound **5**, the reaction with organoaluminium reagents was investigated. The results are summarised in Table 1. From previous work,[1a] X-ray crystallographic data and extensive NOE studies on the related ketone complexes indicate the carbonyl group in the side-chain preferentially adopts an s-*cis* conformation. The stereochemical outcome of addition reactions is predictable by assuming the s-*cis* is also the reactive conformation. With an aldehyde group however, such a preferred conformation might not necessarily be expected on account of diminished steric differentiation on replacing an alkyl group with a proton when changing from a ketone to an aldehyde. Indeed NOE experiments on the aldehyde **5** indicated that both s-*cis* and s-*trans* conformations were populated in the ground state (Fig. 1). Thus at the outset we anticipated the stereochemical outcome of addition reactions to aldehyde groups would be less easy to predict using our model and perhaps

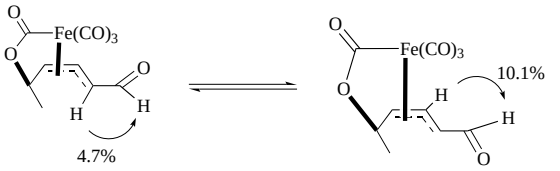


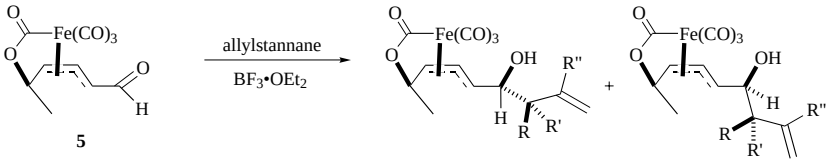
Fig. 1 Selected NOE data showing the aldehyde adopts both s-*cis* and s-*trans* conformations in the side-chain of π-allyltricarbonyliron lactone complexes

stereoselectivity would be lower. Reaction with trimethylaluminium ($AlMe_3$) however proceeded smoothly affording a single product **7** in good yield. Similarly with phenyldimethylaluminium ($PhAlMe_2$), only two products were observed (**7** and **8**); those resulting from methyl group transfer and phenyl group transfer respectively. In both cases single diastereoisomeric products were obtained. The relative stereochemistry of the addition products was readily determined by comparison with their diastereoisomeric counterparts obtained in earlier work from reduction of the respective ketones with triisobutylaluminium ($AlBu^i_3$).[1a] Large differences in the ^{1}H NMR spectra of the diastereoisomeric pairs permitted unequivocal assignment of the relative stereochemistry of the addition products **7** and **8**. Both compounds also proved to be significantly more polar than their diastereoisomeric partners. This relatively large difference in retention factor (R_f) value has been observed in related η^4-dienetricarbonyliron complexes,[7] and in our case proved a quick and reliable aid to stereochemical assignment of the addition products (*vide infra*). Thus in the cases of $AlMe_3$ and $PhAlMe_2$, addition to the aldehyde proceeds with complete control according to our proposed model for additions to the analogous ketone complexes. In spite of the fact that both s-*cis* and s-*trans* conformations of the aldehyde are populated in the ground state, with $AlMe_3$ and $PhAlMe_2$ an apparent single reactive conformation, the s-*cis*, is adopted leading to single diastereoisomeric products resulting from addition *anti* to the bulky tricarbonyliron moiety.

Unfortunately reduced levels of stereocontrol in the addition reaction were uncovered upon extending the work to other organoaluminium reagents (see Table 1). Thus with hex-1-ynyldimethylaluminium and (*E*)-hex-1-enyldiisobutylaluminium, good to moderate levels of stereocontrol were maintained with the major product conforming to our proposed model (entries 3 and 4). Levels of stereoselectivity dropped appreciably, however, upon trying trihex-1-ynylaluminium (entry 5) and were completely reversed when triphenylaluminium was used (entry 6).

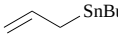
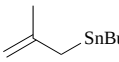
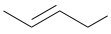
A simple explanation for the observed results is not immediately forthcoming although several points may be made: if steric effects in the transition state were controlling the addition, it might be expected that reaction of the s-*trans* conformer of the aldehyde would be more facile with the sterically encumbered aluminium reagents more distant from the bulky tricarbonyliron moiety. However, in all but one case and even with large isobutyl groups as the dummy ligands, there remains a propensity for addition to the s-*cis* conformer of the aldehyde. Clearly there exists an inherent preference for the aldehyde to adopt an s-*cis* conformation at least in the reactive state. In both cases where selectivity was low or reversed, the dummy ligands are alkynyl or aryl groups, not alkyl groups as is more usual. This change to unsaturation may have profound consequences on the nucleophilicity and reactivity of the reagent in addition to its aggregation state in solution. These factors may effect a different preferred reactive conformation for the aldehyde, which is offset by the inherent preference for the aldehyde itself to react in the s-*cis* conformation, resulting in reduced or reversed levels of stereoselectivity. Whatever the reasons for this decrease, the results still compare favourably with reactions of similar formyl substituted η^4-dienetricarbonyliron complexes with organometallic reagents.[8] These typically proceed with

Table 2 Diastereoselective additions of allylstannanes to π-allyltricarbonyliron lactone complex **5**



5 **11a–13a** **11b–13b, 13c**

11a R = R' = R" = H
11b R = R' = R" = H
12a R = R' = H, R" = Me
12b R = R' = H, R" = Me
13a R = R" = H, R' = Me
13b R = Me, R' = R" = H
13c R = R" = H, R' = Me

Entry	Allylstannane	Temperature (°C)	Product ratio[a]	Combined yield (%)
1		25	**11a**:**11b** 1:6.2	quantitative
2	"	0	**11a**:**11b** 1:8.2	quantitative
3	"	−20	**11a**:**11b** 1:8.3	quantitative
4	"	−40	**11a**:**11b** 1:8.3	quantitative
5	"	−60	**11a**:**11b** 1:2.5	quantitative
6	"	−78	**11a**:**11b** 1:1.0	quantitative
7		0	**12a**:**12b** 1:4.1	quantitative
8	"	−78	**12a**:**12b** 1:1.2	quantitative
9		0	**13a**:**13b**:**13c** 1:32.8:8.6	quantitative
10	"	−78	**13a**:**13b**:**13c** 2.8:3.6:1	quantitative

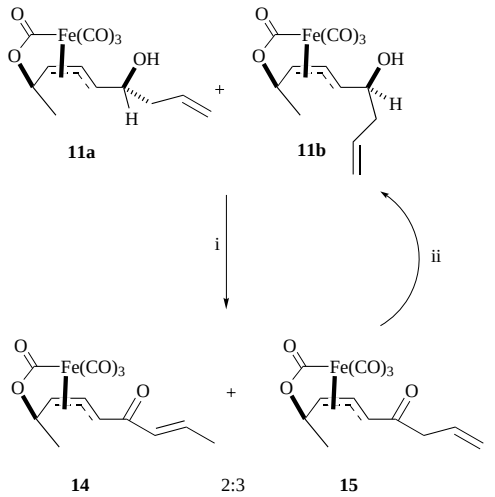
[a] Determined by ^{1}H NMR spectroscopy on the mixture.

diastereoisomeric excesses in the range 0–50% indicating that the presence of the lactone tether in our related complexes has a favourable effect on stereoselection in addition reactions to aldehyde groups in the side-chain.

^{1}H NMR analysis on the addition products revealed a consistency in the magnitude of the coupling constant between the carbinol proton and the terminal allyl proton, lying in all cases in the range 3–4 Hz. This implies the addition products adopt well defined and similar solution conformations. Work conducted by Lillya[7] on related η^4-dienetricarbonyliron complexes illustrated a relationship between the relative stereochemistry of the carbinol centre and the relative polarity of the product. Using this principle, comparison of the relative polarity of the adducts **9**–**10** with **7** and **8** allowed the relative stereochemistry of all the addition products to be tentatively assigned.

We next turned our attention to the Lewis acid-mediated addition of allylstannanes into the aldehyde complex **5**. In spite of the plethora of elegant methods already available for stereoselective allylation of aldehydes[9] we believed that the stereoselective addition of an allyl group into an aldehyde in the side-chain of a π-allyltricarbonyliron lactone complex would further extend the utility of these complexes and perhaps offer an insight into the factors controlling the levels of stereoselection. The results are outlined in Table 2. In the first instance the addition reaction was carried out in an analogous fashion to that used with the ketone complexes;[1b] in dichloromethane (DCM) at 0 °C with sequential addition of slight excesses of both Lewis acid [boron trifluoride–diethyl ether (BF_3·OEt_2)] and allylstannane. Under these conditions, the reaction was not surprisingly rapid, and moderate levels of stereocontrol were obtained in the case of allyltributylstannane.† On account of the rapidity of the reaction, we postulated that cooling to lower temperatures might increase the levels of diastereoselectivity. However on conducting the reaction at −78 °C we were rather surprised to find the level of stereocontrol had plummeted and a 1:1 mixture of diastereoisomers was obtained albeit in the usual excellent yield. These results were mirrored when methallyltributylstannane[10] was used: moderate levels of diastereoisomeric excess (de) were obtained at 0 °C dropping again to effectively 0% at −78 °C.

Under the reaction conditions employed, the Lewis acid and stannane are added in rapid succession. If precomplexation of the Lewis acid to the aldehyde was important in affecting the equilibrium of s-*cis* and s-*trans* conformers then at higher temperature this should be achieved more rapidly, potentially increasing the selectivity. However this hypothesis was discounted when BF_3·OEt_2 was added to the aldehyde at 0 °C and left for 15 minutes prior to cooling to −78 °C and adding the allylstannane. In this case the ratio of the addition products remained 1:1. A brief survey of the temperature dependence on the level of diastereoselectivity was conducted using allyltributylstannane as the nucleophile. This revealed that maximum levels of diastereocontrol are achieved between −20 and −40 °C falling slowly as the temperature is increased and more rapidly upon decreasing the temperature further. Several factors are operating in the addition reaction which may affect the outcome of the reaction. Equilibria between s-*cis* and s-*trans* conformations of the aldehyde in complexed and non-complexed forms will be established. If the difference in free energy between the s-*cis* and s-*trans* BF_3–aldehyde complexes is small, then both conformations of the complexed aldehyde will be populated to a similar extent. At low temperature, and if the rate of addition is more rapid than the rate of equilibration between reactive conformers, then a 1:1 mixture of products might be anticipated. At increased temperature the rate of addition will increase but so will the rate of equilibration between reactive conformers. If the temperature dependency of equilibration between reactive conformers is greater than that of the addition reaction, then increased diastereoselection might be expected. Thus at −20 to −40 °C we presume that the rate of equilibration is more rapid than the rate of addition allowing the product ratio to simply reflect the difference in activation energies between the two transition states. At increased tem-



Scheme 4 *Reagents and conditions*: i, PDC (1.5 equiv.), 4 Å molecular sieves, DCM, 2 h, 78% (**14**:**15**; 2:3); ii, $AlBu^{i}_{3}$ (2.2 equiv.), 0 °C, DCM, 0.5 h, 59% (**11b** only)

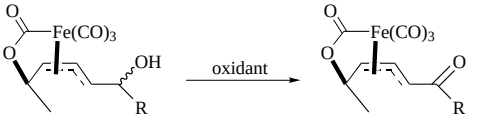
perature, addition becomes less discriminatory and the diastereoselectivity of the reaction falls off once more.

In the case of crotyltributylstannane,[11] the reaction is further complicated by the addition of a second chiral centre producing the possibility of *syn* and *anti* products. At 0 °C three products **13a**–**c**, two of which (**13b** and **c**) were inseparable by flash column chromatography, were observed in a ratio 1:32.8:8.6 whereas at −78 °C the ratio changed to 2.8:3.6:1. By analogy with related systems,[12] crotyltributylstannane additions to aldehydes usually give the *syn* product under $BF_3{\cdot}OEt_2$ activation. Furthermore by comparison with the previous data on allyl and methallyl addition compounds, products **13b** and **13c**, obtained as the major products at 0 °C could be tentatively assigned to be the *syn* and *anti* products respectively derived from one conformation (the s-*trans*; *vide infra*) and the third product **13a** as the *syn* product derived from the other conformation.

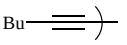
By comparison with the R_f data from the diastereoisomers obtained from the aluminium addition reactions, the less polar products are derived from addition in the s-*trans* conformation. Conclusive evidence was later obtained which indeed showed that the major diastereoisomer was derived from addition to the s-*trans* conformation of the aldehyde (Scheme 4). Oxidation of the allyl addition products **11a** and **b** with pyridinium dichromate (PDC) yielded two ketone products, **15** and enone **14** in which the allylic double bond had isomerised into conjugation with the ketone group. Reaction of the mixture of ketones with triisobutylaluminium afforded two products both as single diastereoisomers resulting from reduction of the s-*cis* conformation of the ketones.[1a] The reformed homoallylic alcohol product proved to be the major product **11b** from the stannane addition into the aldehyde. Thus in complete contrast to all results obtained for additions into ketones and organoaluminium reagents into aldehydes, allylstannanes react preferentially with the aldehyde in an s-*trans* conformation. The balance between stereoelectronic effects in the transition state and the inherent preference for one conformation to be adopted is clearly a fine one. Judicious choice of nucleophile and reaction conditions seem to be important if good levels of stereocontrol are to be realised in reactions of aldehyde-bearing π-allyltricarbonyliron lactone complexes.

Oxidation of the addition products was also briefly investigated. The results are outlined in Table 3. Although π-allyltricarbonyliron lactone complexes are susceptible to oxidative decomplexation,[13] we were pleased to find that barium manganate[14] and PDC both cleanly transformed the secondary alcohol addition complexes **7**, **8** and **9** to the respective ketones **16**, **17** and **18** in high yield. This result could provide a flexible route to

Table 3 Oxidation of alcohol functionality in addition products



7–9 **16–18**

Complex	R	Oxidant	Yield (%)
16	Me	PDC	80
17	Ph	$BaMnO_4$	80
18		$BaMnO_4$	94

tertiary alcohols. By selecting the order of addition of nucleophiles into an aldehyde and then into the ketone produced after oxidation of the resultant secondary alcohol, the tertiary alcohol of choice will be obtained with high diastereoisomeric purity.

In summary, the addition of organoaluminium reagents and allylstannanes into aldehyde groups in the side-chain of π-allyltricarbonyliron lactone complexes is less stereoselective than their ketone congeners. However, the tricarbonyliron unit and lactone tether do still effect a good degree of 1,5-asymmetric induction of chirality. Careful choice of nucleophile and reaction conditions are crucial to ensure moderate to excellent levels of stereocontrol are achieved.

Experimental

^{1}H NMR spectra were recorded in $CDCl_3$ 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 $CDCl_3$, at 150 MHz, 100 MHz, 62.5 MHz or 50 MHz on Bruker DRX-600, 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 or a Bruker BIOAPEX 4.7 T FTICR 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 were obtained on the mixture. Where considerable assignment of ^{1}H and ^{13}C NMR spectra of individual compounds in mixtures is possible, the interpretation is for each component; in other cases, ^{1}H and ^{13}C NMR spectra are interpreted for the mixture.

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 petroleum ether 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 THF. Solvents were degassed by successively evacuating and purging the solvent three times with argon whilst simul-

taneously subjecting the solvent to sonication using an 80 W 55 kHz cleaning bath. Et_2O and THF were distilled from sodium benzophenone ketyl; DCM from calcium hydride. Other reagents and solvents were purified using standard procedures.[15] 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 also extremely toxic. Further, 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*R,5*R**)-Ethyl 4,5-epoxyhex-2-enoate 1**

Trifluoroacetic anhydride (35.7 cm^3, 255 mmol) was slowly added to a suspension of (2*E*,4*E*)-ethyl hexa-2,4-dienoate (3.57 g, 25.5 mmol), urea–hydrogen peroxide addition compound (96.0 g, 1020 mmol) and disodium hydrogenphosphate (72.0 g, 510 mmol) in DCM (400 cm^3) at 0 °C. After removing from the ice bath, the reaction mixture was stirred at room temperature for 20 min and then poured cautiously into vigorously stirred aqueous $NaHCO_3$ (1000 cm^3) at 0 °C. After effervescence had ceased, the phases were separated and the organic fraction washed sequentially with $NaHCO_3$ solution (3 × 300 cm^3) and brine (300 cm^3). The organic phase was then dried ($MgSO_4$) and concentrated *in vacuo*. Purification of the residue by flash column chromatography (eluent: Et_2O–petrol 1:7) provided *epoxide* **1** as a colourless oil (2.57 g, 65%) (Found: C, 61.68; H, 7.80. $C_8H_{12}O_3$ requires C, 61.51; H, 7.75%); ν_{max}(film)/cm^{-1} 3020, 2932, 2897, 1719 (C=O), 1564 (C=C), 1446, 1422, 1378, 1367, 1340, 1303, 1260, 1187, 1141, 1096, 1034, 1006, 977; δ_H(200 MHz) 1.16 (3H, t, *J* 7.1, OCH_2CH_3), 1.24 (3H, d, *J* 5.2, 6-H × 3), 2.84 (1H, qd, *J* 5.2, 2.0, 5-H), 3.05 (1H, dd, *J* 7.0, 2.0, 4-H), 4.07 (2H, q, *J* 7.1, OCH_2CH_3), 5.99 (1H, dd, *J* 15.7, 0.6, 2-H), 6.54 (1H, dd, *J* 15.7, 7.0, 3-H); δ_C(50 MHz) 13.9, 17.2, 56.8, 57.0, 60.1, 123.3, 144.4, 165.2; *m*/*z* (EI) 140 [(M − O)$^+$, 3%], 112 (22, MH − OEt), 84 (100, MH − CO_2Et), 73 (12), 67 (5), 45 [18, M − MeCH(O)CH-$(CH)_2$CO] {Found [(M − O)$^+$] 140.0832. $C_8H_{12}O_2$ requires *M* − O, 140.0837}.

(2*E*,4*R,5*R**)-4,5-Epoxyhex-2-en-1-ol 2**

Diisobutylaluminium hydride (9.45 cm^3 of a 1.0 mol dm^{-3} solution in hexanes, 9.45 mmol) was slowly added to the ester **1** (0.641 g, 4.10 mmol) in THF (10 cm^3) at −78 °C. After stirring at this temperature for 1 h, MeOH (10 cm^3) was slowly added and the resultant solution allowed to warm to room temperature. Triethanolamine (4 cm^3) was then added and the mixture stirred at room temperature for a further 13 h. Filtration through a pad of Celite washing with Et_2O (100 cm^3) and concentration *in vacuo* provided the crude product which was purified by flash column chromatography (eluent: Et_2O–petrol 1:4→2:1; gradient) to give *alcohol* **2** as a colourless oil (0.420 g, 89%) (Found: C, 63.19; H, 8.96. $C_6H_{10}O_2$ requires C, 63.12; H, 8.84%); ν_{max}(film)/cm^{-1} 3404 (OH), 2988, 2927, 2862, 1673, 1447, 1429, 1379, 1336, 1296, 1245, 1145, 1127, 1092, 1060, 1009; δ_H(200 MHz) 1.31 (3H, d, *J* 5.2, 6-H × 3), 1.62 (1H, s, OH), 2.89 (1H, qd, *J* 5.2, 2.1, 5-H), 3.06 (1H, dd, *J* 7.9, 2.1, 4-H), 4.11 (2H, d, *J* 5.2, 1-H × 2), 5.41 (1H, dd, *J* 15.6, 7.9, 3-H), 6.02 (1H, dt, *J* 15.6, 5.2, 2-H); δ_C(100 MHz) 17.5 (CH_3, 6-C), 56.5 (CH, 4-C or 5-C), 58.9 (CH, 5-C or 4-C), 62.7 (CH_2, 1-C), 128.8 (CH, 2-C or 3-C), 134.2 (CH, 3-C or 2-C); *m*/*z* (EI) 114 (M^+, 11%), 97 (12, M − OH), 83 (81, M − CH_2OH), 70 (100, M − $CHCH_2OH$).

[(4*E*,2*R,3*S**)-2-(Carbonyloxy-κ*C*)-6-hydroxy-(3,4,5-η)-hex-4-en-3-yl]tricarbonyliron 3a, [(4*E*,2*R**,3*R**)-2-(carbonyloxy-κ*C*)-6-hydroxy-(3,4,5-η)-hex-4-en-3-yl]tricarbonyliron 3b and [(3*E*,2*R**,5*R**)-1-(carbonyloxy-κ*C*)-5-hydroxy-(2,3,4-η)-hex-3-en-2-yl]tricarbonyliron 3c**

THF (degassed, 90 cm^3) was added to $Fe_2(CO)_9$ (3.80 g, 10.5 mmol) and the suspension was vigorously stirred in the absence of light for 15 min. Epoxy alkene **2** (0.57 g, 5.0 mmol) was then added and the reaction mixture was stirred for a further 1 h after which time the mixture was filtered through a pad of Celite washing the residue with Et_2O (150 cm^3). Removal of the volatiles *in vacuo* provided the crude products which were immediately subjected to partial purification by flash column chromatography (eluent: Et_2O–petrol 1:24→3:2; gradient) to afford a mixture of three isomeric complexes **3a**, **3b** and **3c** (1.17 g, 83%) in a ratio 10:1:3.5 as determined by 600 MHz NMR spectroscopic analysis. Full characterisation of the complexes was best achieved after a silyl protection/separation/deprotection sequence (*vide infra*).

[(4*E*,2*R,3*S**)-6-*tert*-Butyldimethylsilyloxy-2-(carbonyloxy-κ*C*)-(3,4,5-η)-hex-4-en-3-yl]tricarbonyliron 4a, [(4*E*,2*R**,3*R**)-6-*tert*-butyldimethylsilyloxy-2-(carbonyloxy-κ*C*)-(3,4,5-η)-hex-4-en-3-yl]tricarbonyliron 4b and [(3*E*,2*S**,5*R**)-5-*tert*-butyldimethylsilyloxy-1-(carbonyloxy-κ*C*)-(2,3,4-η)-hex-3-en-2-yl]tricarbonyliron 4c**

tert-Butyldimethylsilyl chloride (0.688 g, 4.6 mmol) was added to a stirred solution of a mixture of alcohol complexes **4a**, **4b** and **4c** (partially purified by flash column chromatography; 1.170 g, 4.1 mmol) and imidazole (0.396 g, 5.8 mmol) in dimethylformamide (1 cm^3) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 10 min after which time the solution was poured into H_2O (2 cm^3) and Et_2O (3 cm^3). The layers were separated and the aqueous phase extracted with Et_2O (2 × 5 cm^3). The combined organic fractions were washed with brine (5 cm^3), dried ($MgSO_4$) and then concentrated *in vacuo*. Purification of the residue by flash column chromatography (eluent: Et_2O–petrol 1:19→3:7; gradient) afforded the silyl protected complexes **4a**, **4b** and **4c** as whitish grey solids: in order of elution *endo alcohol* **4a** (0.769 g, 45% from the epoxy alkene **2**); ν_{max}(film)/cm^{-1} 2930, 2857, 2071 (CO), 1998 (CO), 1657 (C=O), 1470, 1255, 1129, 1100, 1043, 993, 838; δ_H(500 MHz) 0.08 (3H, s, $SiCH_3$), 0.10 (3H, s, $SiCH_3$), 0.90 [9H, s, $SiC(CH_3)_3$], 1.35 (3H, d, *J* 6.4, 1-H × 3), 4.15 (1H, dt, *J* 11.9, 2.8, 5-H), 4.20 (1H, dd, *J* 14.4, 2.8, 6-H × 1), 4.38–4.47 (2H, m, 2-H, 6-H × 1), 4.63 (1H, dd, *J* 8.2, 4.7, 3-H), 4.83 (1H, dd, *J* 11.9, 8.2, 4-H); δ_C(62.5 MHz) −5.6 (CH_3, $SiCH_3$), 18.5 [quat. C, $SiC(CH_3)_3$], 22.0 (CH_3, 1-C), 25.9 [CH_3, $SiC(CH_3)_3$], 62.4 (CH_2, 6-C), 73.5 (CH), 77.3 (CH), 82.5 (CH), 85.9 (CH), 204.1 (CO), 206.2 (CO), 206.4 (CO), 209.3 (CO); *m*/*z* (FAB) 397 (MH^+, 100%), 369 (7, MH − CO), 340 (8, M − 2CO), 313 (11, MH − 3CO), 285 (46, MH − 4CO), 268 (8, M − 4CO − O), 211 (14, M − 4CO − O − Bu′), 165 (12), 140 (33), 131 (20) [Found (MH^+) 397.0790. $C_{16}H_{25}FeO_6Si$ requires *M*H, 397.0770]; and then *exo complex* **4b** (0.068 g, 4% from epoxy alkene **2**); ν_{max}(film)/cm^{-1} 2932, 2860, 2075 (CO), 2015 (CO), 1652 (C=O), 1471, 1334, 1308, 1257, 1132, 1050, 1000, 838; δ_H(500 MHz) 0.07 (3H, s, $SiCH_3$), 0.09 (3H, s, $SiCH_3$), 1.35 (3H, d, *J* 6.2, 1-H × 3), 4.01 (1H, dt, *J* 11.7, 2.7, 5-H), 4.16 (1H, dd, *J* 14.5, 2.7, 6-H × 1), 4.25 (1H, q, *J* 6.2, 2-H), 4.33–4.44 (2H, m, 3-H, 6-H × 1), 4.98 (1H, dd, *J* 11.7, 8.1, 4-H); δ_C(62.5 MHz) −5.6 (CH_3, $SiCH_3$), 18.5 [quat. C, $SiC(CH_3)_3$], 23.9 (CH_3, 1-C), 25.9 [CH_3, $SiC(CH_3)_3$], 62.2 (CH_2, 6-C), 71.3 (CH), 76.5 (CH), 81.8 (CH), 87.2 (CH), 204.3 (CO), 206.0 (CO), 206.4 (CO), 209.6 (CO); *m*/*z* (FAB) 397 (MH^+, 66%), 369 (11, MH − CO), 340 (15, M − 2CO), 313 (39, MH − 3CO), 285 (61, MH − 4CO), 268 (26, M − 4CO − O), 211 (39, M − 4CO − O − Bu′), 187 (30), 165 (29), 145 (100), 131 (58), 107 (28) [Found (MH^+) 397.0767. $C_{16}H_{25}FeO_6Si$ requires *M*H, 397.0770]; and then *silyl protected alcohol* **4c** (0.258 g, 15% from epoxy alkene **2**); ν_{max}(film)/cm^{-1} 2929, 2067 (CO), 1991 (CO), 1658 (C=O), 1465, 1369, 1312, 1257, 1148, 1047, 972, 831; δ_H(500 MHz) 0.11 [6H, s, $Si(CH_3)_2$], 0.90 [9H, s, $SiC(CH_3)_3$],

1.45 (3H, d, *J* 6.3, 6-H × 3), 3.94–4.07 (3H, m, 1-H × 2, 4-H), 4.56–4.65 (2H, m, 2-H, 5-H), 4.94 (1H, dd, *J* 11.9, 8.1, 3-H); δ_C(62.5 MHz) −4.7 (CH_3, SiCH_3), −4.5 (CH_3, SiCH_3), 18.2 [quat. C, Si$C(CH_3)_3$], 25.9 [CH_3, SiC$(CH_3)_3$], 26.3 (CH_3, 6-C), 64.7 (CH_2, 1-C), 67.5 (CH), 69.5 (CH), 88.4 (CH), 90.2 (CH), 203.9 (CO), 206.8 (CO × 2), 209.0 (CO); *m*/*z* (FAB) 397 (MH^+, 100%), 357 (7), 335 (13), 285 (75, MH − 4CO), 268 (9, M − 4CO − O), 227 (13), 211 (24, M − 4CO − O − Bu^t), 145 (39), 131 (27) [Found (MH^+) 397.0767. $C_{16}H_{25}FeO_6Si$ requires *M*H, 397.0770].

Preparation of a stock solution of HF·pyridine in pyridine–THF

Pyridine–hydrogen fluoride (*ex* Fluka, 11.4 cm^3) was added to a stirred solution of pyridine (42 cm^3) in THF (120 cm^3) in a polyvinylchloride bottle under argon. The resulting colourless solution was stored under argon at 4 °C and was used as the stock solution in all the following silyl deprotection reactions.

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

HF–pyridine stock solution (50 cm^3) was added to a solution of **4a** (0.868 g, 2.20 mmol) in THF (5 cm^3) and the reaction mixture was stirred for 3 h at room temperature. The reaction mixture was then diluted with Et_2O (400 cm^3) and added to aqueous $NaHCO_3$ (400 cm^3). After effervescence had ceased, the phases were separated and the aqueous phase extracted with Et_2O (3 × 100 cm^3). The organic phases were washed with aqueous $CuSO_4$ (100 cm^3), H_2O (100 cm^3) and brine (100 cm^3) and then dried ($MgSO_4$). Concentration *in vacuo* followed by purification by flash column chromatography (eluent: Et_2O–petrol 1:1→neat Et_2O; gradient) afforded *alcohol* **3a** as a whitish solid (0.470 g, 76%); ν_{max}(film)/cm^{-1} 3389 (OH), 2981, 2080 (CO), 2008 (CO), 1635 (C=O), 1452, 1374, 1113, 1089, 1046, 945; δ_H(500 MHz) 1.37 (3H, d, *J* 6.3, 1-H × 3), 1.97–2.11 (1H, m, OH), 4.08–4.18 (2H, m, 5-H or 6-H × 1, 6-H × 1), 4.35–4.48 (2H, m, 2-H, 6-H or 5-H × 1), 4.68 (1H, dd, *J* 8.2, 4.7, 3-H), 4.86 (1H, dd, *J* 11.7, 8.2, 4-H); δ_C(62.5 MHz) 21.9, 62.2, 73.6, 77.9, 81.6, 87.6, 203.6, 206.2, 207.2, 209.1; *m*/*z* (FAB) 283 (MH^+, 100%), 255 (8, MH − CO), 226 (10, M − 2CO), 209 (8, M − 2CO − OH), 199 (14, MH − 3CO), 171 (14, MH − 4CO), 152 (15), 120 (24), 107 (35) [Found (MH^+) 282.9901. $C_{10}H_{11}FeO_6$ requires *M*H, 282.9905].

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

HF–pyridine stock solution (20 cm^3) was added to a solution of **4b** (0.156 g, 0.42 mmol) in THF (3 cm^3) and the reaction mixture was stirred for 5 h at room temperature. The reaction mixture was then diluted with Et_2O (200 cm^3) and added to $NaHCO_3$ solution (200 cm^3). After effervescence had ceased, the phases were separated and the aqueous phase extracted with Et_2O (3 × 50 cm^3). The organic phases were washed with aqueous $CuSO_4$ (50 cm^3), H_2O (50 cm^3) and brine (50 cm^3) and then dried ($MgSO_4$). Concentration *in vacuo* followed by purification by flash column chromatography (eluent: Et_2O–petrol 1:1→neat Et_2O; gradient) afforded *alcohol* **3b** as a whitish solid (0.080 g, 67%); ν_{max}(film)/cm^{-1} 3347 (OH), 2986, 2925, 2865, 2082 (CO), 2022 (CO), 1991 (CO), 1614 (C=O), 1464, 1443, 1373, 1333, 1308, 1112, 1047, 1032, 951, 941; δ_H(500 MHz) 1.36 (3H, d, *J* 6.5, 1-H × 3), 2.09 (1H, s, OH), 3.98 (1H, dt, *J* 11.9, 3.5, 5-H), 4.11 (1H, br d, *J* 14.0, 6-H × 1), 4.27 (1H, q, *J* 6.4, 2-H), 4.37 (1H, br d, *J* 14.0, 6-H × 1), 4.44 (1H, d, *J* 8.0, 3-H), 5.01 (1H, dd, *J* 11.9, 8.0, 4-H); δ_C(50 MHz) 24.3 (CH_3, 1-C), 62.3 (CH_2, 6-C), 71.7 (CH), 77.6 (CH), 80.8 (CH), 89.2 (CH), 204.2 (CO), 206.5 (CO), 206.9 (CO), 209.8 (CO); *m*/*z* (FAB) 283 (MH^+, 58%), 255 (12, MH − CO), 249 (29), 227 (31, MH − 2CO), 221 (33), 207 (35), 199 (26, MH − 3CO), 193 (42), 171 (24, MH − 4CO), 147 (69), 133 (100), 107 (42) [Found (MH^+) 282.9899. $C_{10}H_{11}FeO_6$ requires *M*H, 282.9905].

[(3*E*,2*R**,5*R**)-1-(Carbonyloxy-κ*C*)-5-hydroxy-(2,3,4-η)-hex-3-en-2-yl]tricarbonyliron 3c

HF–pyridine stock solution (20 cm^3) was added to a solution of **4c** (0.158 g, 0.40 mmol) in THF (3 cm^3) and the reaction mixture was stirred for 72 h at room temperature. The reaction mixture was then diluted with Et_2O (200 cm^3) and added to aqueous $NaHCO_3$ (200 cm^3). After effervescence had ceased, the phases were separated and the aqueous phase extracted with Et_2O (3 × 50 cm^3). The organic phases were washed with aqueous $CuSO_4$ (50 cm^3), H_2O (50 cm^3) and brine (50 cm^3) and then dried ($MgSO_4$). Concentration *in vacuo* followed by purification by flash column chromatography (eluent: Et_2O–petrol 1:1→neat Et_2O; gradient) afforded *alcohol* **3c** as a whitish solid (0.029 g, 26%); ν_{max}(film)/cm^{-1} 3401 (OH), 2978, 2931, 2884, 2085 (CO), 2003 (CO), 1637 (C=O), 1472, 1455, 1373, 1320, 1243, 1167, 1143, 1061, 997, 914, 867, 832; δ_H(500 MHz) 1.50 (3H, d, *J* 6.4, 6-H × 3), 2.06 (1H, br s, OH), 3.90 (1H, dd, *J* 12.1, 3.3, 4-H), 3.99 (1H, dd, *J* 12.1, 5.3, 1-H_{endo}), 4.03 (1H, apparent t, *J* 11.7, 1-H_{exo}), 4.35–4.40 (1H, m, 5-H), 4.58–4.68 (1H, m, 2-H), 4.98 (1H, dd, *J* 12.1, 8.0, 3-H); δ_C(100 MHz) 25.6 (CH_3, 6-C), 64.7 (CH_2, 1-C), 67.4 (CH), 70.5 (CH), 88.0 (CH), 89.8 (CH), 203.7 (CO), 206.6 (CO), 207.5 (CO), 208.8 (CO); *m*/*z* (FAB) 283 (MH^+, 93%), 255 (23, MH − CO), 227 (16, MH − 2CO), 199 (20, MH − 3CO), 154 (100, M − 4CO − O), 136 (100, M − 4CO − O − H_2O), 109 (64) [Found ($MH)^+$ 282.9894. $C_{10}H_{11}FeO_6$ requires *M*H, 282.9905].

(2*E*,4*R**,5*R**)-1-*tert*-Butyldimethylsilyloxy-4,5-epoxyhex-2-ene 6

tert-Butyldimethylsilyl chloride (1.54 g, 10.2 mmol) was added to a solution of the alcohol **2** (1.06 g, 9.3 mmol) and imidazole (0.89 g, 13.0 mmol) in dimethylformamide (1 cm^3) at 0 °C and then allowed to warm to room temperature. After 10 min the reaction mixture was concentrated *in vacuo* and the residue subjected to purification by flash column chromatography (eluent: Et_2O–petrol 1:1) affording *silyl protected alcohol* **6** as a light yellow liquid (2.10 g, 99%); ν_{max}(film)/cm^{-1} 2946, 2925, 2855, 1469, 1378, 1253, 1122, 1067, 1007, 961, 931, 836; δ_H(200 MHz) 0.31 [6H, s, Si$(CH_3)_2$], 0.87 [9H, s, SiC$(CH_3)_3$], 1.30 (3H, d, *J* 5.2, 6-H × 3), 2.87 (1H, qd, *J* 5.2, 2.1, 5-H), 3.04 (1H, dd, *J* 7.8, 2.1, 4-H), 4.15 (2H, dd, *J* 4.6, 1.8, 1-H × 2), 5.41 (1H, ddt, *J* 15.4, 7.8, 1.8, 3-H), 5.94 (1H, dt, *J* 15.4, 4.5, 2-H); δ_C(50 MHz) −5.5 [CH_3, Si$(CH_3)_2$], 17.1 (CH_3, 6-C), 18.1 [quat. C, Si$C(CH_3)_3$], 25.7 [CH_3, SiC$(CH_3)_3$], 56.0 (CH, 4-C or 5-C), 58.7 (CH, 5-C or 4-C), 62.6 (CH_2, 1-C), 126.9 (CH, 2-C or 3-C), 134.0 (CH, 3-C or 2-C); *m*/*z* (CI) 229 (MH^+, 26%), 213 (6, MH − O), 211 (11, MH − H_2O), 171 (13, M − Bu^t), 132 (13), 114 (14, MH − Bu^{t}Me$_2$Si), 98 (64, MH − Bu^{t}Me$_2$SiO), 97 (52, M − Bu^{t}Me$_2$SiO), 81 (100, M − O − Bu^{t}Me$_2$SiO) [Found (MH^+) 229.1624. $C_{12}H_{25}O_2Si$ requires *M*H, 229.1624].

[(4*E*,2*R**,3*S**)-6-*tert*-Butyldimethylsilyloxy-2-(carbonyloxy-κ*C*)-(3,4,5-η)-hex-4-en-3-yl]tricarbonyliron 4a, [(4*E*,2*R**,3*R**)-6-*tert*-butyldimethylsilyloxy-2-(carbonyloxy-κ*C*)-(3,4,5-η)-hex-4-en-3-yl]tricarbonyliron 4b

THF (degassed, 70 cm^3) was added to $Fe_2(CO)_9$ (3.82 g, 10.5 mmol) and the suspension was vigorously stirred in the absence of light for 15 min. Epoxy alkene **6** (1.14 g, 5.0 mmol) was then added and the reaction mixture was stirred for a further 3 h after which time the mixture was filtered through a pad of Celite washing the residue with Et_2O (120 cm^3). Removal of the volatiles *in vacuo* provided the crude products which were immediately subjected to purification by flash column chromatography (eluent: Et_2O–petrol 1:24→3:7; gradient) affording *endo* and *exo* complexes **4a** and **4b** (1.36 g, 74%, **4a**:**4b** 5:1) which were both spectroscopically identical to material prepared earlier (*vide supra*).

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

Method A. A solution of Dess–Martin periodinane (0.627 g, 1.5 mmol) in DCM (5 cm^3) was added dropwise over 5 min to a solution of alcohol **3a** (0.252 g, 0.9 mmol) in DCM (10 cm^3) at 0 °C. After 1 h, aqueous $Na_2S_2O_3$ (6 cm^3) was added and the mixture was stirred for a further 10 min before partitioning the reaction mixture between H_2O (5 cm^3) and Et_2O (5 cm^3). The layers were separated and the aqueous phase extracted with Et_2O (2 × 5 cm^3). The combined organic fractions were washed with brine (10 cm^3) and then dried ($MgSO_4$). After concentration *in vacuo*, purification by flash column chromatography (eluent: Et_2O–petrol 1 : 1→neat Et_2O; gradient) afforded *aldehyde* **5** as a yellowish green solid (0.245 g, 98%) (Found: C, 42.80; H, 2.82. $C_{10}H_8FeO_6$ requires C, 42.86; H, 2.88%); ν_{max}(film)/cm^{-1} 3019, 2975, 2925, 2810, 2095 (CO), 2020 (CO), 1674 (C=O), 1448, 1372, 1216, 1047; δ_H(500 MHz) 1.40 (3H, d, *J* 6.4, 1-H × 3), 4.02 (1H, dd, *J* 11.4, 2.9, 5-H), 4.57 (1H, apparent quintet, *J* 6.0, 2-H), 5.09 (1H, dd, *J* 8.6, 4.6, 3-H), 5.44 (1H, dd, *J* 11.4, 8.6, 4-H), 9.73 (1H, d, *J* 2.9, 6-H); δ_C(100 MHz) 21.8 (CH_3, 1-C), 66.7 (CH), 72.8 (CH), 86.8 (CH), 92.2 (CH), 193.9 (CO), 199.8 (CO), 201.0 (CO), 203.5 (CO), 207.4 (CO); *m*/*z* (FAB) 281 (MH^+, 24%), 279 (17, M − H), 253 (16, MH − CO), 197 (17, MH − 3CO), 153 (100, MH − 4CO − O) [Found (MH^+) 280.9752. $C_{10}H_9FeO_6$ requires *M*H, 280.9748].

Method B. Alcohol **3a** (0.053 g, 0.21 mmol) was added to a suspension of pyridinium dichromate (0.117 g, 0.31 mmol) and 4 Å molecular sieves (*ca.* 0.060 g) in DCM (4 cm^3) which had been previously vigorously stirred for 10 min. After 2 h, Et_2O (30 cm^3) was added and the resultant solution was stirred vigorously for a further 15 min. Filtration of the reaction mixture through a pad of $MgSO_4$/silica/$MgSO_4$, washing the residue with Et_2O (100 cm^3) followed by concentration of the filtrate *in vacuo* provided aldehyde **5** (0.045 g, 77%) which was spectroscopically identical to material prepared according to method A.

General procedure for the addition of organoaluminium reagents into ketone complexes: synthesis of complexes 7–10

The organoaluminium reagent was prepared as described[1a] (0.30 mmol) and added dropwise to a cooled (0 °C unless stated otherwise) solution of aldehyde **5** in DCM (unless stated otherwise) (2 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 (*ca.* 0.7 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 to 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*R**)-2-(Carbonyloxy-κ*C*)-6-hydroxy-(3,4,5-η)-hept-4-en-3-yl]tricarbonyliron 7**

Complex **7** was prepared according to the general procedure from $AlMe_3$ (0.150 cm^3 of a 2.0 mol dm^{-3} solution in toluene, 0.30 mmol) and aldehyde **5** (0.036 g, 0.13 mmol) using benzene–toluene (2 cm^3, 4 : 1) as solvent. After 10 min, work-up as described followed by purification by flash column chromatography (eluent: Et_2O–petrol 1 : 1→3 : 1; gradient) afforded *alcohol* **7** as a cream-coloured solid (0.029 g, 76%) (Found: C, 44.31; H, 3.91. $C_{11}H_{12}FeO_6$ requires C, 44.59; H, 4.09%); ν_{max}(film)/cm^{-1} 3409 (OH), 3018, 2980, 2930, 2084 (CO), 2012 (CO), 1644 (C=O), 1452, 1375, 1216, 1141, 1087, 1048, 999, 946, 851; δ_H(200 MHz) 1.33 (3H, d, *J* 6.4, 1-H × 3), 1.53 (3H, d, *J* 6.3, 7-H × 3), 2.26 (1H, br s, OH), 4.05 (1H, dd, *J* 12.0, 3.1, 5-H), 4.38–4.46 (2H, m, 2-H, 6-H), 4.67 (1H, dd, *J* 8.2, 4.7, 3-H), 4.90 (1H, dd, *J* 12.0, 8.2, 4-H); δ_C(100 MHz) 21.9 (CH_3), 26.3 (CH_3), 66.8 (CH), 73.6 (CH), 78.4 (CH), 85.7 (CH), 87.2 (CH), 203.4 (CO), 206.6 (CO), 207.3 (CO), 209.9 (CO); *m*/*z* (FAB) 297 (MH^+, 100%), 281 (7, M − Me), 269 (9, MH − CO), 241 (7, MH − 2CO), 226 (7, M − Me − 2CO), 213 (12, MH − 3CO), 208 (8, M − Me − 2CO − OH), 195 (6, M − 3CO − OH), 168 (11, M − 4CO − O) [Found (MH^+) 297.0066. $C_{11}H_{13}FeO_6$ requires *M*H, 297.0061].

[(4*E*,2*R,3*S**,6*S**)-2-(Carbonyloxy-κ*C*)-6-hydroxy-6-phenyl-(3,4,5-η)-hex-4-en-3-yl]tricarbonyliron 8a**

Complex **8a** was prepared according to the general procedure from $PhAlMe_2$ [prepared from Me_2AlCl (0.325 cm^3 of a 1.0 mol dm^{-3} solution in hexanes, 0.325 mmol) and PhLi (0.181 cm^3 of a 1.8 mol dm^{-3} solution in cyclohexane–Et_2O, 0.325 mmol) in toluene (1 cm^3)][1a] and aldehyde **5** (0.030 g, 0.11 mmol) using DCM (1 cm^3) as solvent. After 20 min, work-up as described followed by purification by flash column chromatography (eluent: Et_2O–petrol 1 : 1→2 : 1; gradient) afforded *alcohol* **8a** as a cream-coloured solid (0.010 g, 26%); ν_{max}(film)/cm^{-1} 3407 (OH), 3015, 2981, 2930, 2082 (CO), 2012 (CO), 1642 (C=O), 1492, 1453, 1375, 1357, 1312, 1217, 1187, 1086; δ_H(200 MHz) 1.24 (3H, d, *J* 6.3, 1-H × 3), 2.25 (1H, d, *J* 3.0, OH), 4.17 (1H, dd, *J* 12.0, 3.0, 5-H), 4.41 (1H, qd, *J* 6.3, 4.6, 2-H), 4.69 (1H, dd, *J* 8.2, 4.6, 3-H), 5.09 (1H, dd, *J* 12.0, 8.2, 4-H), 5.32 (1H, apparent t, *J* 3.0, 6-H), 7.31–7.50 (5H, m, Ph-*H*); δ_C(100 MHz) 22.0 (CH_3), 73.4 (CH × 2), 77.7 (CH), 84.8 (CH), 85.5 (CH), 125.9 (CH), 128.7 (CH), 129.2 (CH), 142.7 (quat. C), 203.4 (CO), 206.3 (CO × 2), 209.2 (CO); *m*/*z* (FAB) 359 (MH^+, 57%), 341 (4, M − OH), 330 (42, M − CO), 281 (9, M − Ph), 274 (16, M − 3CO), 229 (13, M − H − 4CO − O), 175 (22, MH − 4CO − O − Fe), 157 (100, MH − 4CO − Fe − O − OH) [Found (MH^+) 359.0212. $C_{16}H_{15}FeO_6$ requires *M*H, 359.0218]; and then alcohol **7** (0.012 g, 38%) which was spectroscopically identical to material prepared earlier (*vide supra*).

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

Complexes **8a** and **8b** were prepared according to the general procedure from $AlPh_3$ [prepared from $AlCl_3$ (0.049 g, 0.37 mmol; dried over P_2O_5 *in vacuo* overnight) and PhLi (0.615 cm^3 of a 1.8 mol dm^3 solution in cyclohexane–Et_2O, 1.10 mmol) in toluene (1.5 cm^3)][16] and aldehyde **5** (0.046 g, 0.16 mmol) using DCM (1.5 cm^3) as solvent. After 90 min, work-up as described followed by purification by flash column chromatography (eluent: Et_2O–petrol 1 : 1→2 : 1; gradient) afforded in order of elution, alcohol **8b** (0.032 g, 58%)[1a] and then alcohol **8a** (0.008 g, 14%) which was spectroscopically identical to material prepared earlier (*vide supra*).

[(4*E*,2*R,3*S**,6*S**)-2-(Carbonyloxy-κ*C*)-6-hydroxy-(3,4,5-η)-dodec-4-en-7-yn-3-yl]tricarbonyliron 9a and [(4*E*,2*R**,3*S**,6*R**)-2-(carbonyloxy-κ*C*)-6-hydroxy-(3,4,5-η)-dodec-4-en-7-yn-3-yl]tricarbonyliron 9b**

Method A. Complexes **9a** and **9b** were prepared according to the general procedure from hex-1-ynyldimethylaluminium [prepared from Me_2AlCl (0.210 cm^3 of a 1.0 mol dm^{-3} solution in hexanes, 0.21 mmol), Bu^{n}Li (0.130 cm^3 of a 1.6 mol dm^{-3} solution in hexanes, 0.21 mmol) and hex-1-yne (0.024 cm^3, 0.08 mmol) in toluene (1.4 cm^3)][1a] and aldehyde **5** (0.023 g, 0.08 mmol) using DCM (1.4 cm^3) as solvent. After 20 min, work-up as described followed by purification by flash column chromatography (eluent: Et_2O–petrol 1 : 1) afforded *alcohols* **9a** and **9b** as a yellow oil (0.019 g, 70%; **9a** : **9b**, 9 : 1); ν_{max}(film)/cm^{-1} 3381 (OH), 3013, 2960, 2983, 2873, 2227 (C≡C), 2085 (CO), 2011 (CO), 1645 (C=O), 1513, 1450, 1356, 1328, 1217, 1184, 1145, 1113, 1085, 1043, 1005; δ_H(500 MHz; major diastereoisomer) 0.89 (3H, t, *J* 7.3, 12-H × 3), 1.36 (3H, d, *J* 6.4, 1-H × 3), 1.38

(2H, sextet, *J* 7.3, 11-H × 2), 1.48 (2H, q, *J* 7.3, 10-H × 2), 2.20 (2H, t, *J* 7.3, 9-H × 2), 2.60 (1H, d, *J* 4.0, OH), 4.14 (1H, dd, *J* 12.0, 3.9, 5-H), 4.42–4.46 (1H, m, 2-H), 4.67 (1H, dd, *J* 8.3, 4.7, 3-H), 4.93 (1H, dd, *J* 12.0, 8.3, 4-H), 5.02–5.07 (1H, m, 6-H); peaks for minor diastereoisomer observed at 2.64 (1H, d, *J* 4.0, OH), 4.07 (1H, dd, *J* 12.0, 3.9, 5-H), 4.97 (1H, dd, *J* 12.0, 8.2, 4-H), 5.10–5.13 (1H, m, 6-H); δ_C(100 MHz; major diastereoisomer) 13.6 (CH_3), 18.4 (CH_2), 21.9 (CH_3), 22.0 (CH_2), 30.3 (CH_2), 62.5 (CH), 73.4 (CH), 78.0 (CH), 78.5 (quat. C), 83.1 (CH), 88.2 (CH), 88.7 (quat. C), 203.3 (CO), 205.7 (CO), 205.9 (CO), 209.1 (CO); *m*/*z* (FAB) 363 (MH^+, 100%), 335 (4, MH − CO), 306 (7, M − 2CO), 290 (5, MH − 2CO − OH), 282 [6, MH − $Me(CH_2)_3CC$], 279 (22, MH − 3CO), 261 (13, M − 3CO − OH), 233 (12, M − H − 4CO − O), 216 (17), 161 (71, M − 4CO − O − Fe − OH) [Found (MH^+) 363.0529. $C_{16}H_{19}FeO_6$ requires *M*H, 363.0531].

Method B. Complexes **9a** and **9b** were prepared according to the general procedure from tris(hex-1-ynyl)aluminium [prepared from hex-1-yne (0.086 cm^3, 0.75 mmol), Bu^{n}Li (0.464 cm^3 of a 1.6 mol dm^{-3} solution in hexanes, 0.75 mmol) and $AlCl_3$ (0.033 g, 0.25 mmol; dried over P_2O_5 *in vacuo* overnight) in toluene (1.4 cm^3)][16] and aldehyde **5** (0.030 g, 0.11 mmol) using DCM (1.4 cm^3) as solvent. After 1 h, work-up as described followed by purification by flash column chromatography (eluent: Et_2O–petrol 1 : 1) afforded *alcohols* **9a** and **9b** as a yellow oil (0.022 g, 56%; **9a** : **9b**, 2 : 1). The spectroscopic properties were in agreement with material prepared earlier.

[(4*E*,7*E*,2*R**,3*S**,6*R**)-2-(Carbonyloxy-κ*C*)-6-hydroxy-(3,4,5-η)-dodeca-4,7-dien-3-yl]tricarbonyliron 10a and [(4*E*,7*E*,2*R**,3*S**,6*S**)-2-(carbonyloxy-κ*C*)-6-hydroxy-(3,4,5-η)-dodeca-4,7-dien-3-yl]tricarbonyliron 10b

Complexes **10a** and **10b** were prepared according to the general procedure from hex-1-enyldiisobutylaluminium [prepared from diisobutylaluminium hydride (0.167 cm^3 of a 1.5 mol dm^{-3} solution in toluene, 0.25 mmol) and hex-1-yne (0.029 cm^3, 0.25 mmol) in hexane (3 cm^3)][1a] and aldehyde **5** (0.030 g, 0.11 mmol) using DCM (3 cm^3) as solvent. After 20 min, work-up as described followed by purification by flash column chromatography (eluent: Et_2O–petrol 1 : 1→neat Et_2O; gradient) afforded in order of elution, *alcohols* **10a** and **10b** as a light yellow oil (0.026 g, 65%; **10a** : **10b**; 5 : 1); ν_{max}(film)/cm^{-1} 3402 (OH), 3019, 2927, 2855, 2093 (CO), 2028 (CO), 1654 (C=O), 1643 (C=C), 1215, 1052; δ_H(500 MHz; major diastereoisomer) 0.90 (3H, t, *J* 7.1, 12-H × 3), 1.10–1.64 (7H, m, 1-H × 3, 10-H × 2, 11-H × 2), 1.88 (1H, s, OH), 2.08 (2H, apparent q, *J* 6.9, 9-H × 2), 4.04 (1H, dd, *J* 12.1, 3.3, 5-H), 4.43 (1H, apparent quintet, *J* 6.0, 2-H), 4.63–4.68 (2H, m, 3-H, 6-H), 4.86 (1H, dd, *J* 12.1, 8.3, 4-H), 5.57 (1H, dd, *J* 15.2, 7.5, 7-H), 5.81 (1H, dt, *J* 15.2, 6.9, 8-H); peaks for minor diastereoisomer observed at 4.17 (1H, dd, *J* 12.0, 3.3, 5-H), 4.92 (1H, dd, *J* 12.0, 8.3, 4-H); δ_C(100 MHz; major diasteroisomer) 13.9 (CH_3, 12-C), 22.0 (CH_3, 1-C), 22.2 (CH_2), 31.0 (CH_2), 31.8 (CH_2), 72.3 (CH), 73.4 (CH), 77.8 (CH), 84.5 (CH), 86.0 (CH), 131.5 (CH), 135.0 (CH), 203.6 (CO), 206.4 (CO), 206.5 (CO), 209.3 (CO); *m*/*z* (FAB) 363 [(M − H)$^+$, 100%], 319 (47, M − CO − OH), 307 (22, M − H − 2CO), 235 (21, M − H − 4CO − O) {Found [(M − H)$^+$] 363.0512. $C_{16}H_{19}FeO_6$ requires *M* − H, 363.0531}; and then primary alcohol reduction product **3a** (0.003 g, 10%) which was spectroscopically identical to material prepared earlier (*vide supra*).

General procedure for the addition of allylstannanes into aldehyde complex 5: synthesis of complexes 11–13

BF_3·OEt_2 (0.030 cm^3, 0.24 mmol) and allylstannane (0.094 cm^3, 0.30 mmol) were added sequentially to a cooled (see text) solution of aldehyde **5** (0.156 g, 0.20 mmol) in DCM (5 cm^3). Upon consumption of starting material, H_2O (5 cm^3) and KF (excess) were added and the reaction mixture was stirred vigorously. After 15 min, the solution was filtered through a pad of cotton wool washing the residue with DCM (5 cm^3). The layers were separated and the aqueous phase extracted with DCM (2 × 5 cm^3). The combined organic fractions were dried ($MgSO_4$). Concentration of the filtrate *in vacuo* afforded the crude products which were subjected to purification by flash column chromatography (eluent: Et_2O–petrol).

[(4*E*,2*R**,3*S**,6*R**)-2-(Carbonyloxy-κ*C*)-6-hydroxy-(3,4,5-η)-nona-4,8-dien-3-yl]tricarbonyliron 11a and [(4*E*,2*R**,3*S**,6*S**)-2-(carbonyloxy-κ*C*)-6-hydroxy-(3,4,5-η)-nona-4,8-dien-3-yl]-tricarbonyliron 11b

Complexes **11a** and **11b** were synthesised according to the general procedure from allyltributylstannane (0.094 cm^3, 0.30 mmol), BF_3·OEt_2 (0.030 cm^3, 0.24 mmol) and aldehyde **5** (0.056 g, 0.20 mmol) in DCM (5 cm^3) at −78 °C. After 5 min, work-up as described and purification by column chromatography (eluent: Et_2O–petrol 1 : 3→neat Et_2O; gradient) afforded, in order of elution, *alcohol* **11b** as a whitish solid (0.032 g, 50%) (Found: C, 48.38; H, 4.50. $C_{13}H_{14}FeO_6$ requires C, 48.48; H, 4.38%); ν_{max}(film)/cm^{-1} 3379 (OH), 3079, 2980, 2931, 2083 (CO), 2008 (CO), 1642 (C=O), 1450, 1375, 1357, 1338, 1266, 1183, 1087, 1047, 1001, 945, 911, 733, 664; δ_H(250 MHz) 1.34 (3H, d, *J* 6.3, 1-H × 3), 2.05 (1H, d, *J* 2.5, OH), 2.33–2.45 (1H, m, 7-H × 1), 2.65–2.74 (1H, m, 7-H × 1), 4.02 (1H, dd, *J* 12.0, 2.6, 5-H), 4.32–4.48 (2H, m, 2-H, 6-H), 4.68 (1H, dd, *J* 8.2, 4.7, 3-H), 4.89 (1H, dd, *J* 12.0, 8.2, 4-H), 5.21–5.28 (2H, m, 9-H × 2), 5.82–5.97 (1H, m, 8-H); δ_C(100 MHz) 22.0, 44.6, 68.9, 73.4, 77.6, 84.2, 85.6, 120.1, 133.2, 203.5, 206.6, 206.8, 209.3; *m*/*z* (FAB) 345 [(M + Na)$^+$, 10%] (100, MH), 295 (4, MH − CO), 267 (12, MH − 2CO), 239 (21, MH − 3CO), 226 (8), 210 (27, M − 4CO), 193 (14, M − 4CO − O), 165 (15), 151 (9), 134 (13), 121 (37) [Found (MH^+) 323.0188. $C_{13}H_{15}FeO_6$ requires *M*H, 323.0218]; and then *alcohol* **11a** as a whitish solid (0.032 g, 50%); ν_{max}(film)/cm^{-1} 3397 (OH), 2976, 2925, 2082 (CO), 2002 (CO), 1639 (C=O), 1443, 1373, 1358, 1338, 1253, 1182, 1082, 1047, 997, 946, 916; δ_H(600 MHz) 1.34 (3H, d, *J* 6.4, 1-H × 3), 2.35 (1H, d, *J* 3.9, OH), 2.44–2.51 (1H, m, 7-H × 1), 2.63–2.57 (1H, m, 7-H × 1), 4.03 (1H, dd, *J* 12.2, 3.8, 5-H), 4.13–4.18 (1H, m, 6-H), 4.41–4.48 (1H, m, 2-H), 4.64 (1H, dd, *J* 8.3, 4.7, 3-H), 4.79 (1H, dd, *J* 12.2, 8.3, 4-H), 5.21–5.29 (2H, m, 9-H × 2), 5.82–5.91 (1H, m, 8-H); δ_C(150 MHz) 21.8 (CH_3, 1-C), 44.2 (CH_2, 7-H), 70.8 (CH), 73.3 (CH), 77.2 (CH), 86.4 (CH), 88.3 (CH), 119.9 (CH_2, 9-C), 133.3 (CH, 8-C), [203.3, 206.6, 209.4 (CO × 4)]; *m*/*z* (FAB) 323 (MH^+, 77%), 295 (10, MH − CO), 267 (32, MH − 2CO), 239 (49, MH − 3CO), 221 (20, M − 3CO − OH), 193 (33, M − 4CO − OH), 191 (15), 149 (100), 136 (46), 121 (81) [Found (MH)$^+$ 323.0207. $C_{13}H_{15}FeO_6$ requires *M*H, 323.0218].

[(4*E*,2*R**,3*S**,6*R**)-2-(Carbonyloxy-κ*C*)-6-hydroxy-8-methyl-(3,4,5-η)-nona-4,8-dien-3-yl]tricarbonyliron 12a and [(4*E*,2*R**,3*S**,6*S**)-2-(carbonyloxy-κ*C*)-6-hydroxy-8-methyl-(3,4,5-η)-nona-4,8-dien-3-yl]tricarbonyliron 12b

Complexes **12a** and **12b** were synthesised according to the general procedure from methallyltributylstannane (0.100 cm^3, *ca.* 0.30 mmol), BF_3·OEt_2 (0.030 cm^3, 0.24 mmol) and aldehyde **5** (0.056 g, 0.20 mol) in DCM (5 cm^3) at 0 °C. After 5 min, work-up as described and purification by column chromatography (eluent: Et_2O–petrol 1 : 3→neat Et_2O; gradient) afforded, in order of elution, *alcohol* **12b** as a whitish solid (0.053 g, 79%); ν_{max}(film)/cm^{-1} 3385 (OH), 3074, 2973, 2929, 2076 (CO), 2005 (CO), 1641 (C=O), 1451, 1374, 1087, 1047, 1010, 943, 894, 661, 609, 578; δ_H(600 MHz) 1.33 (3H, d, *J* 6.3, 1-H × 3), 1.82 (3H, s, 8-Me), 2.17 (1H, br s, OH), 2.31 (1H, dd, *J* 13.4, 9.5, 7-H × 1), 2.60 (1H, dd, *J* 13.4, 2.8, 7-H × 1), 4.03 (1H, dd, *J* 12.0, 2.1, 5-H), 4.34 (1H, br d, 9.5, 6-H), 4.40–4.47 (1H, m, 2-H), 4.68 (1H, dd, *J* 8.3, 4.7, 3-H), 4.91 (1H, s, 9-H × 1), 4.93 (1H, dd, 12.0, 8.3, 4-H), 4.97 (1H, s, 9-H × 1); δ_C(150 MHz) 22.1 (CH_3, 1-C or 8-Me), 22.3 (CH_3, 8-Me or 1-C), 49.4 (CH_2, 7-C), 67.5 (CH),

73.9 (CH), 78.2 (CH), 85.2 (CH), 85.9 (CH), 115.7 (CH_2, 9-C), 142.6 (quat. C, 8-C), [204.7, 207.9, 210.6 (CO × 4)]; *m/z* (FAB) 337 (MH^+, 100%), 297 (32), 281 (26, MH − 2CO), 253 (71, MH − 3CO), 224 (41, M − 4CO), 207 (55, MH − 4CO − H_2O), 154 (36), 135 (93), 109 (59) [Found $(MH)^+$ 337.0349. $C_{14}H_{17}FeO_6$ requires *M*H, 337.0375]; and then *alcohol* **12a** as a whitish solid (0.014 g, 21%); 3401 (OH), 3074, 2976, 2932, 2856, 2082 (CO), 1997 (CO), 1643 (C=O), 1447, 1375, 1355, 1085, 1046, 998, 945, 897, 658, 602; δ_H(600 MHz) 1.36 (3H, d, *J* 6.3, 1-H × 3), 1.81 (3H, s, 8-Me), 2.18 (1H, d, *J* 2.4, OH), 2.42 (1H, dd, *J* 13.6, 9.7, 7-H × 1), 2.53 (1H, dd, *J* 13.6, 3.7, 7-H × 1), 4.03 (1H, dd, *J* 12.2, 3.3, 5-H), 4.27–4.32 (1H, m, 6-H), 4.42–4.48 (1H, m, 2-H), 4.64 (1H, dd, *J* 8.3, 4.6, 3-H), 4.82 (1H, dd, *J* 12.2, 8.3, 4-H), 4.90 (1H, s, 9-H × 1), 4.98 (1H, s, 9-H × 1); δ_C(150 MHz) 21.8 (CH_3, 1-C or 8-Me), 22.4 (CH_3, 8-Me or 1-C), 48.1 (CH_2, 7-C), 68.4 (CH), 73.3 (CH), 77.2 (CH), 86.7 (CH), 88.2 (CH), 115.1 (CH_2, 9-C), 141.2 (quat. C, 8-C), 203.4 (CO), 205.9 (CO), 206.7 (CO), 209.4 (CO); *m/z* (FAB) 337 (MH^+, 31%), 327 (10), 289 (6), 281 (25, MH − 2CO), 253 (15, MH − 3CO), 221 (16), 207 (47, MH − 4CO − H_2O), 173 (12), 149 (93), 136 (84), 109 (100) [Found $(MH)^+$ 337.0370. $C_{14}H_{17}FeO_6$ requires *M*H, 337.0375].

[(4*E*,2*R,3*S**,6*S**,7*S**)-2-(Carbonyloxy-κ*C*)-6-hydroxy-7-methyl-(3,4,5-η)-nona-4,8-dien-3-yl]tricarbonyliron 13a and [(4*E*,2*R**,3*S**,6*R**,7*R**)-2-(carbonyloxy-κ*C*)-6-hydroxy-7-methyl-(3,4,5-η)-nona-4,8-dien-3-yl]tricarbonyliron 13b and [(4*E*,2*R**,3*S**,6*R**,7*S**)-2-(carbonyloxy-κ*C*)-6-hydroxy-7-methyl-(3,4,5-η)-nona-4,8-dien-3-yl]tricarbonyliron 13c**

Complexes **13a**, **13b** and **13c** were synthesised according to the general procedure from crotyltributylstannane (0.100 cm^3, *ca.* 0.30 mmol), $BF_3{\cdot}OEt_2$ (0.030 cm^3, 0.24 mmol) and aldehyde **5** (0.056 g, 0.20 mmol) in DCM (5 cm^3) at −78 °C. After 5 min, work-up as described and purification by column chromatography (eluent: Et_2O–petrol 1:3→neat Et_2O; gradient) afforded, in order of elution, *alcohols* **13b** and **13c** as a whitish solid (0.034 g, 50%; **13b**:**13c** 4:1); ν_{max}(film)/cm^{-1} 3378 (OH), 3074, 2977, 2932, 2082 (CO), 2006 (CO), 1638 (C=O), 1453, 1420, 1376, 1355, 1088, 1044, 1000, 946, 913, 728, 663, 608; δ_H(600 MHz) 1.17 (2.4H, d, *J* 6.9, 7-Me), 1.20 (0.6H, d, *J* 6.8, 7-Me), 1.34 (3H, d, *J* 6.3, 1-H × 3), 1.98 (0.8H, br s, OH), 2.11 (0.2H, br s, OH), 2.41–2.48 (0.2H, m, 7-H), 2.54–2.61 (0.8H, m, 7-H), 3.98 (0.8H, dd, *J* 12.1, 1.8, 5-H), 4.03 (0.2H, dd, *J* 12.1, 2.7, 5-H), 4.10–4.14 (0.2H, m, 6-H), 4.31 (0.8H, br d, *J* 2.3, 6-H), 4.40–4.47 (1H, m, 2-H), 4.68 (1H, dd, *J* 8.1, 4.8, 3-H), 4.86 (1H, dd, *J* 12.1, 8.1, 4-H), 5.18–5.26 (2H, m, 9-H × 2), 5.80 (0.2H, ddd, *J* 17.1, 10.3, 8.5, 8-H), 5.91 (0.8H, ddd, *J* 17.4, 10.4, 7.2, 8-H); δ_C(150 MHz) 13.7 (CH_3, 7-Me), [21.96 (CH_3, 1-C), 21.98 (CH_3, 1-C)], [47.4 (CH, 7-C), 45.2 (CH, 7-C)], [72.7 (CH, 7-C), 72.8 (CH, 7-C)], 73.4 (CH, 2-C), [77.1 (CH, 3-C), 77.2 (CH, 3-C)], [83.4 (CH, 5-C), 83.5 (CH, 5-C)], 86.0 (CH, 4-C), [116.9 (CH_2, 9-C), 117.9 (CH_2, 9-C)], [139.2 (CH, 8-C), 139.3 (CH, 8-C)], 203.5 (CO), 206.7 (CO), 207.1 (CO), 209.4 (CO); *m/z* (FAB) 337 (MH^+, 37%), 313 (6), 281 (17, MH − 2CO), 253 (23, MH − 3CO), 225 (13, MH − 4CO), 207 (23, MH − 4CO − H_2O), 171 (10), 147 (32), 123 (51), 109 (100) [Found $(MH)^+$ 337.0388. $C_{14}H_{17}FeO_6$ requires *M*H, 337.0375]; and then *alcohol* **13a** as a whitish solid (0.034 g, 50%); ν_{max}(film)/cm^{-1} 3390 (OH), 3074, 2976, 2932, 2082 (CO), 2006 (CO), 1638 (C=O), 1453, 1420, 1376, 1333, 1082, 1044, 1000, 946, 919, 733, 657, 608; δ_H(600 MHz) 1.20 (3H, d, *J* 6.7, 7-Me), 1.33 (3H, d, *J* 6.3, 1-H × 3), 2.35 (1H, d, *J* 5.7, OH), 2.45–2.54 (1H, m, 7-H), 3.60–3.67 (1H, m, 6-H), 4.08 (1H, dd, *J* 12.0, 5.7, 5-H), 4.40–4.48 (1H, m, 2-H), 4.63 (1H, dd, *J* 8.2, 4.6, 3-H), 4.68 (1H, dd, *J* 12.0, 8.2, 4-H), 5.22 (1H, d, *J* 10.4, 9-H × 1), 5.25 (1H, d, *J* 17.3, 9-H × 1), 5.73–5.82 (1H, m, 8-H); δ_C(150 MHz) 16.2 (CH_3, 7-Me), 21.8 (CH_3, 1-C), 46.3 (CH, 7-C), 73.1 (CH), 76.9 (CH), 77.1 (CH), 85.9 (CH), 89.7 (CH), 117.8 (CH_2, 9-C), 138.8 (CH, 8-C), [203.5, 206.2, 209.3 (CO × 4)]; *m/z* (FAB) 337 (MH^+, 65), 325 (9), 297 (10), 281 (42, MH − 2CO), 253 (45, MH − 3CO), 221 (30), 207 (52, M − 4CO − H_2O), 190.1 (13), 147 (77), 135 (100), 109 (100) [Found $(MH)^+$ 337.0369. $C_{14}H_{17}FeO_6$ requires *M*H, 337.0375].

[(4*E*,2*R,3*S**)-2-(Carbonyloxy-κ*C*)-6-oxo-(3,4,5-η)-hept-4-en-3-yl]tricarbonyliron 16**

Alcohol **7** (0.010 g, 0.03 mmol) in DCM (1 cm^3) was added *via* cannula to a suspension of pyridinium dichromate (0.017 g, 0.05 mmol) and 4 Å molecular sieves (*ca.* 0.020 g) in DCM (1 cm^3) which had been previously stirred for 10 min. After stirring for 20 h, Et_2O (30 cm^3) was added and the resulting solution vigorously stirred for a further 10 min. The solution was then filtered through a pad of $MgSO_4$/silica/$MgSO_4$ and then concentrated *in vacuo* to afford ketone **16** (0.008 g, 80%) which was identical to material prepared previously.[1a]

[(4*E*,2*R,3*S**)-2-(Carbonyloxy-κ*C*)-6-oxo-6-phenyl-(3,4,5-η)-hex-4-en-3-yl]tricarbonyliron 17**

Barium(VI) manganate (0.062 g, 0.240 mmol) was added in two portions to a stirred solution of alcohol **8** (0.009 g, 0.024 mmol) in DCM (1 cm^3) at room temperature and the solution was stirred for 4 h. The reaction mixture was then filtered through a pad of Celite washing the residue with toluene (1 cm^3) and DCM (20 cm^3). Removal of the volatiles *in vacuo* afforded the crude product as a solution in toluene. Purification by flash column chromatography (eluent: Et_2O–petrol 1:1) provided ketone **17** (0.008 g, 94%) which was identical to material prepared earlier.[1a]

[(4*E*,2*R,3*S**)-2-(Carbonyloxy-κ*C*)-6-oxo-(3,4,5-η)-dodec-4-en-7-yn-3-yl]tricarbonyliron 18**

Barium(VI) manganate (0.090 g, 0.35 mmol) was added in one portion to a solution of alcohols **9a** and **9b** (0.024 g, 0.07 mmol; **9a**:**9b**; 9:1) in DCM (3 cm^3). After stirring for 3 h, the mixture was filtered through a pad of Celite and the residue washed with DCM (3 cm^3) to afford *ketone* **18** as a light brown oil (0.019 g, 80%); ν_{max}(film)/cm^{-1} 3016, 2960, 2931, 2873, 2213 (C≡C), 2092 (CO), 2025 (CO), 1670 (C=O), 1644 (C=O), 1498, 1454, 1419, 1309, 1258, 1235, 1180, 1085, 1050, 944; δ_H(200 MHz) 0.93 (3H, t, *J* 7.1, 12-H × 3), 1.38 (3H, d, *J* 6.4, 1-H × 3), 1.41–1.67 (4H, m, 10-H × 2, 11-H × 2), 2.42 (2H, t, *J* 6.9, 9-H × 2), 4.08 (1H, d, *J* 11.4, 5-H), 4.53 (1H, qd, *J* 6.4, 4.6, 2-H), 5.03 (1H, dd, *J* 8.7, 4.6, 3-H), 5.60 (1H, dd, *J* 11.4, 8.7, 4-H); δ_C(100 MHz) 13.4 (CH_3), 18.9 (CH_2), 21.9 (CH_3), 22.0 (CH_2), 29.6 (CH_2), 68.8 (CH), 72.9 (CH), 80.3 (quat. C), 85.4 (CH), 92.1 (CH), 98.4 (quat. C), 180.8 (C=O), 199.9 (CO), 201.8 (CO), 203.9 (CO), 207.7 (CO); *m/z* (FAB) 361 (MH^+, 7%), 327 (12), 249 (43), 193 (23), 165 (31), 147 (52), 109 (100, M − $C_9H_7O_5Fe$) [Found (MH^+) 361.0387. $C_{16}H_{17}FeO_6$ requires *M*H, 361.0374].

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