Organoiron Complexes in Organic Synthesis. Part 24.[1] Studies in the Synthesis and Reactivity of 6-*exo*-Substituted Cyclohexadienylium(tricarbonyl)iron Salts

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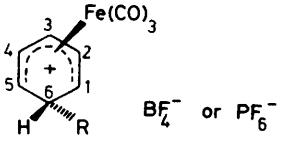
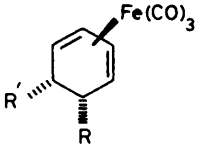
Tricarbonyliron derivatives of 5-substituted cyclohexa-1, 3-dienes bearing a β-hydroxy-group in the substituent undergo thallium(III)-promoted oxidative cyclisation to give tetrahydrobenzofuran(tricarbonyl)iron complexes. The metal can be removed to give the corresponding tetrahydrobenzofuran derivatives, or the complexes may be treated with tetrafluoroboric acid in acetic anhydride to give 6-*exo*-substituted cyclohexadienylium(tricarbonyl)iron complexes. Reactions of these cationic derivatives with nucleophiles is reported.

WHILST a large number of cyclohexadienylium(tricarbonyl)iron complexes have been prepared bearing substituents attached to C-1 to C-5 of the dienyl system [see structure (1)], very little progress has been made towards preparing complexes in which substituents are attached at C-6, either with *endo*- or *exo*-orientation with



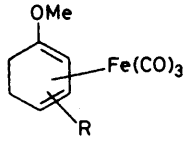
(1) a; R = H
b; R = $CH_2CH(OH)CH_3$
c; R = $CH_2CH(OAc)CH_3$
d; R = $CH(CH_2OAc)CH_2OTs$
e; R = $CH(CH_2OAc)CH_2CH(CO_2Me)_2$
f; R = $CH(CH_2OAc)CH_2OCO{\cdot}CH_2CO_2Me$

respect to the metal.† This mainly arises since most of the available precursors, of general structure (2), are prepared by nucleophile addition to, *e.g.* (1a) and so the substituent is *exo*- to the $Fe(CO)_3$. This presents a considerable degree of steric hindrance to the approach of the triphenylmethylium cation, the usual reagent for



(2) a; R = R′ = H
b; R = OEt, R′ = H
c; R = $CH_2CH(OH)CH_3$, R′ = H
d; R = $CH_2CO{\cdot}CH_3$, R′ = H
e; R = $CH_2CH(OAc)CH_3$, R′ = SPh
f; R = $CH_2CH(OAc)CH_3$, R′ = $CH(CN)_2$
g; R = $CH_2CH(OAc)CH_3$, R′ = $CH(CO_2Me)_2$
h; R = $CH(CO_2Me)_2$, R′ = H
i; R = $CH(CH_2OH)_2$, R′ = H

effecting hydride abstraction, with the result that this reaction will not proceed under the usual conditions.[2,3] An alternative method of forming dienylium complexes, treatment of methoxycyclohexadiene(tricarbonyl)iron derivatives such as (3) with strong acid, has been reported by Birch and Haas,[4] but we would anticipate that this method would not lead satisfactorily to 6-substituted dienylium complexes, since the reaction of necessity involves rearrangement of the diene-$Fe(CO)_3$ group, and also the conditions are too harsh to allow use of a wide range of functionalised substituents. Consequently, we turned our attention to two observations made by Birch *et al.*,[5] and Lewis's group.[6] The former obtained products of oxidative cyclisation on treatment of ketoester or β-diketone-substituted complexes, *e.g.* (4) ⟶ (5), whilst the latter observed that treatment of (2a) with thallium(III) trifluoroacetate in ethanol gave (2b), apparently resulting from oxidative addition of ethanol. The precise mechanisms of these



(3)

reactions are not known. We decided to investigate an intramolecular version of the thallium(III)-promoted reaction with a view to obtaining cyclic ethers which could be converted into complexes (1a) whose reactivity towards nucleophiles could be assessed.

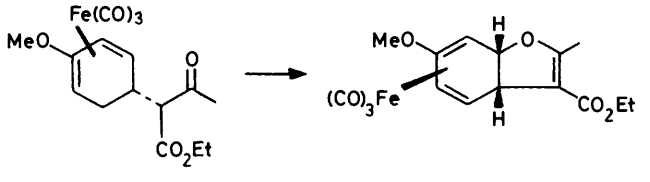
We have previously reported the application of this concept to preparation of very highly substituted analogues of (1), such as (6) which did not show satisfactory reaction with simple nucleophiles.[7] We report herein the preparation of less hindered complexes and the results of both inter- and intra-molecular nucleophile reactions.[8]

RESULTS AND DISCUSSION

The first complex we chose to study was the secondary alcohol (2c) which was readily prepared as an inseparable mixture of diastereoisomers by sodium borohydride reduction of the ketone (2d), available by literature methods.[3] Whilst the methyl group occurred as only one doublet, in the n.m.r. spectrum of (2c), the presence of an equimolar mixture of diastereoisomers was assumed

† The use of *endo*- (same side of ring to that occupied by metal) and *exo*- (opposite side of ring) to denote stereochemistry of these complexes will be used throughout this paper.

because the remoteness of the unsymmetrical diene-$Fe(CO)_3$ unit is not expected to exert any control over the stereochemistry of borohydride reduction. Treatment of (2c) with thallium(III) trifluoroacetate in ethanol followed by addition of sodium hydrogencarbonate gave the cyclised product (7) in 79—84% yield. The n.m.r. spectrum of this compound indicated the presence of two



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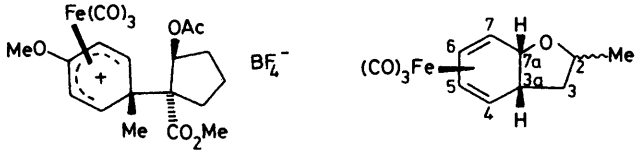
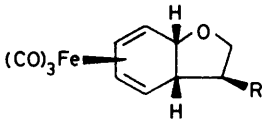


(6) (7) a; β -Me
b; α -Me

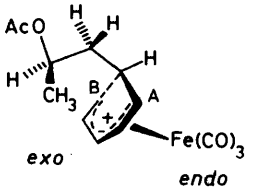


(8) a; R = CH_2OH
b; R = CH_2OAc
c; R = CH_2OTs
d; R = $CH_2CH(CO_2Me)$
e; R = $CH_2OCO \cdot CH_2CO_2Me$

isomers (7a) and (7b) in a ratio of *ca.* 4 : 1, the major isomer being assigned structure (7a) on the basis that the methyl group would prefer to occupy the less substituted face of the tetrahydrofuran ring. The disproportionate mixture of isomers probably arises by equilibration during the reaction or because of the direct intermediacy of the dienyl cation (1b) during the reaction. No attempts were made to determine the mechanism of the reaction, though we did observe that when addition of sodium hydrogencarbonate was omitted the cyclised product was obtained in very much lower yields, suggesting that the acid generated during the reaction causes opening of the tetrahydrofuran ring to give salts which are not extracted by organic solvents. The two isomers (7) were only partially resolved on t.l.c., multiple development allowing only marginal improvement in the purity of the major isomer. Treatment of the mixture with tetrafluoroboric acid in acetic anhydride gave the ether-insoluble tetrafluoroborate salt (1c) in 92% yield which, having a symmetrical dienyl—$Fe(CO)_3$ group, was obtained as a single racemate, showing typical proton n.m.r. spectrum.

We were now in a position to study the reactions of (1c) with nucleophiles. Treatment of the salt in tetrahydrofuran (THF) suspension with thiophenoxide gave the adduct (2e), in excellent yield (94%).

Examination of the n.m.r. spectrum of the crude compound showed the presence of two diastereoisomers in a ratio of *ca.* 2 : 1. The spectrum also indicated that both arose by addition of PhS at the *exo*-face of the dienylium ligand, since a doublet of doublets was obtained for the 6-H of each isomer showing an identical coupling constant; this was also consistent with the values obtained for 5-H of the cyclised complex (7). Thus the preponderance of one diastereoisomer is due to preferential attack at one of the dienyl termini owing to the presence of the remote secondary acetate group which exerts some degree of stereocontrol on the reaction. This may be explained by considering the most likely preferred conformation of the molecule shown in the Figure, when it can be seen that *exo*-approach to the



FIGURE

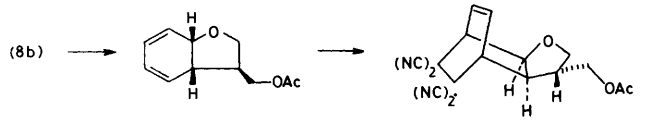
terminal carbon A is rather more hindered than approach to B. Recrystallisation of the mixture (2e) allowed the isolation of a pure single isomer.

Reaction of (1c) with sodiomalononitrile, synthetically a more useful nucleophile which we have previously shown [9] to react satisfactorily with substituted dienylium complexes, gave the expected adduct (2f) but in only moderate yield (45—50%).

A mixture of diastereoisomers, this time in a ratio *ca.* 3 : 1, was also observed for this compound. Dimethyl sodiomalonate also reacted rapidly with (1c) to give (2g), again in rather disappointing yield. The n.m.r. spectrum showed a preponderance of one diastereoisomer, but the ratio could not be estimated owing to obscuring and overlapping of peaks.

In view of the rather low yields of adducts (2f) and (2g) we decided to investigate the preparation of more highly functionalised molecules with a view to examining intramolecular nucleophile additions which might overcome the steric problems and, possibly, by providing novel methods of annulation, extend our previously reported spirocyclisation reactions.[10] To this end the diester complex (2h), obtained by addition of dimethyl sodiomalonate to tricarbonylcyclohexadienyliumiron tetrafluoroborate,[11] was subjected to reduction with di-isobutylaluminium hydride (DIBAL) to give the diol (2i). Treatment of this complex with thallium(III)

trifluoroacetate, as described above, gave the cyclised product (8a), obtained as a crystalline single isomer in 60% yield. Stereochemical assignment of (8a) is based on similar arguments as for complex (7). Acetylation of (8a) under the usual conditions afforded the crystalline acetate (8b) in 86% yield. The tricarbonyliron group was readily removed from this compound under mild conditions using trimethylamine *N*-oxide [12] to give the cyclohexadiene (9) in 98% yield which was readily converted into the crystalline cycloadduct (10) by reaction with tetracyanoethylene.



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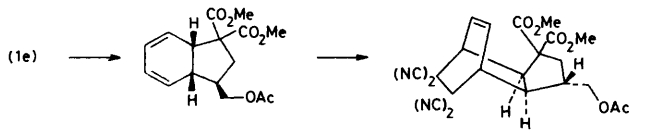

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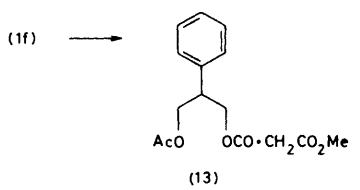
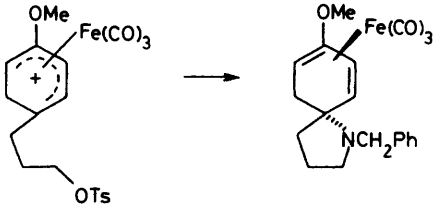


(13)

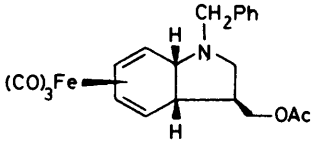
In order to test the possibility of carrying out annulation reactions of dienylium complexes derived from (8a), it was necessary to convert the primary alcohol group into a latent nucleophile. For these purposes, two possibilities were investigated. The first, designed to achieve formation of a hydrindane derivative, required that the alcohol be replaced by, *e.g.*, a malonate group. To this end (8a) was converted into the tosylate (8c) (97% yield) and the tosylate was displaced in excellent yield using dimethyl potassiomalonate to give the required gem-diester derivative (8d), which now contained an enolisable and therefore a nucleophilic group. The second mode of cyclisation we considered was simply an intramolecular delivery of carbon nucleophile which was attached as an ester of the already existent primary alcohol. Such a grouping was readily introduced by esterification of the hydroxy-function with methoxycarbonylpropionyl chloride to give the mixed malonate derivative (8e).

Formation of cyclohexadienylium complexes was straightforward, involving treatment with tetrafluoroboric acid–acetic anhydride as above. Since these compounds did not give such readily crystallised tetrafluoroborate salts they were converted into the hexafluorophosphate derivatives by anion exchange. Thus we were able to convert the complexes (8c), (8d), and (8e) in good yield into the hexafluorophosphates (1d), (1e), and (1f), respectively. Treatment of the dimethyl malonate derivative (1e) with base under mild conditions caused cyclisation, as evidenced by replacement of the dienylium–$Fe(CO)_3$ i.r. bands at 2 130, 2 090, and 2 070 cm^{-1} by those due to a neutral diene species at 2 050 and 1 975 cm^{-1}. Examination by t.l.c. showed the formation of a single product whose instability precluded its complete characterisation apart from i.r. and n.m.r. spectra of the crude material. Accordingly, the crude complex was treated directly with trimethylamine *N*-oxide to give the *cis*-hydrindane derivative (11), but in a disappointing yield of 16—20%. Treatment of this compound with tetracyano-ethylene gave the crystalline Diels-Alder adduct (12). The stereochemical assignments of these compounds is based upon similar arguments to those presented for complexes (7) and (8).

Attempts to effect cyclisation of the mixed malonate derivative (1f) using a range of bases and reaction conditions resulted in complex mixtures. Preparative t.l.c. allowed isolation only of the aromatic compound



(14) (15)



(16)

(13), which could also be prepared by treatment of (1f) with ceric ammonium nitrate.

The complex (1c) contains two electrophilic centres in the molecule, *viz.* the dienylium ligand and the tosylate (by virtue of its leaving-group character). We have recently shown [13] that the related complex (14) undergoes facile reaction with benzylamine, in a reversible reaction, to produce the azaspirocyclic derivative (15) in high yield. Reaction of the compound (1c) with benzylamine under a wide range of conditions led only to complex mixtures and we were unable to obtain evidence for formation of the tetrahydroindole complex (16).

EXPERIMENTAL

N.m.r. spectra were recorded using a Varian EM 390, i.r. spectra with a Perkin-Elmer 577, and mass spectra with A.E.I. MS12 or MS30 spectrometers. M.p.s are uncorrected.

All reactions and chromatographic operations were conducted under an atmosphere of dry nitrogen or argon. Tetrahydrofuran was freshly distilled from sodium–benzophenone, dichloromethane from calcium hydride, and pyridine from barium oxide. Rigorous assignments of n.m.r. spectra, where presented, were made on the basis of spin decoupling experiments.

Tricarbonyl{1—4-η-[5-(2-hydroxypropyl)cyclohexadiene]}iron (2c).—To the ketone derivative (2d) (1.1 g) in ethanol (15 ml) was added sodium borohydride (0.30 g) and the mixture was stirred at room temperature for 1 h. The ethanolic solution was poured into water (150 ml) and the product was extracted with ether in the usual way to afford, after purification by column chromatography (silica gel, 10% ethyl acetate in benzene), the alcohol (2c) as a golden yellow syrup (0.9 g, 82%). An analytical sample was obtained by bulb-to-bulb distillation, $\nu_{max.}$ ($CHCl_3$) 3 600, 3 430, 2 040, and 1 960 cm^{-1}; δ ($CDCl_3$) 5.33 (2 H, m), 3.77 (1 H, m), 3.15 (2 H, m), 2.4—1.2 (5 H and 1 H exch. D_2O), and 1.15 (3 H, d, *J* 7 Hz) (Found: C, 51.45; H, 5.35%; M^+, 278. Calc. for $C_{12}H_{14}FeO_4$: C, 51.83; H, 5.07%; M^+, 278).

Tricarbonyl[4—7-η-(2-methyl-2,3,3aβ,7aβ-tetrahydrobenzofuran)] iron (7).—The alcohol complex (2c) (0.49 g) was dissolved in dry ethanol (8 ml) and the stirred solution was cooled to −10 °C. Thallium(III) trifluoroacetate (1.7 g) was added and the mixture was stirred for 10 min, after which time solid sodium hydrogen carbonate (0.8 g) was added.

After being stirred for a further 5 min, the mixture was poured into ethyl acetate (10 ml) and filtered through a short column of alumina. The filtrate and washings were evaporated and subjected to preparative t.l.c. to give the mixture of diastereoisomers (7) as a yellow oil (0.41 g, 84%). Multiple development t.l.c. gave only partial separation of isomers. The compound was not sufficiently stable thermally to allow distillation. When this procedure was repeated on larger scale (1.9 g of alcohol complex) a yield of 79% was recorded. $\nu_{max.}$ ($CHCl_3$) 2 055 and 1 975 cm^{-1}; δ ($CDCl_3$) major isomer: 5.5 (2 H, m), 4.55 (1 H, dd, *J* 9, 4 Hz, 7a-H), 3.95 (1 H, m, 2-H), 3.0 (3 H, m), 1.5 (2 H, m), 1.14 (3 H, d, *J* 6 Hz); minor isomer: 4.36 (1 H, dd, *J* 9, 4 Hz, 7a-H), 1.18 (3 H, d, *J* 6 Hz); M^+ 276.

Tricarbonyl{1—5-η-[6-(2-acetoxypropyl)cyclohexadienylium]}iron Tetrafluoroborate (1c).—The cyclised complex (7) (1.5 g) was stirred in acetic anhydride (20 ml) at 0 °C whilst 40% aqueous tetrafluoroboric acid (1.5 ml) was added dropwise. Stirring was continued at 0 °C for 20 min, after which time an excess of ether was added. Filtration, followed by thorough washing with ether and drying *in vacuo* gave the pure tetrafluoroborate (1c) (2.0 g, 92%), $\nu_{max.}$ (Nujol) 2 130, 2 075, and 1 737 cm^{-1}; δ (CD_3CN) 7.10 (1 H, t, *J* 5.5 Hz, 3-H), 5.83 (2 H, dd, *J* 6, 5.5 Hz, 2-H, 4-H), 4.7 (1 H, hext, *J* 6 Hz), 4.50 (2 H, t, br, *J* 6 Hz, 1-H, 5-H), 2.97 (1 H, quint., *J* 6.5 Hz, 6-H), 1.98 (3 H, s), 1.17 (2 H, m, obscured), and 1.06 (3 H, d, *J* 6 Hz) (Found: C, 41.55; H, 3.65. Calc. for $C_{14}H_{15}FeO_5BF_4$: C, 41.43; H, 3 72%).

Tricarbonyl{1—4-η-[5-(2-acetoxypropyl)-6-phenylthiocyclohexa-1,3-diene]}iron (2e).—A suspension of the tetrafluoroborate salt (1c) (300 mg) was stirred in THF (6 ml) at 0 °C whilst thiophenol (90 μl), followed by triethylamine (90 μl) were added. Dissolution of the complex occurred instantaneously, and the mixture was poured into water, extracted with ether in the usual way, and chromatographed on grade III neutral alumina to give the crystalline mixture of diastereoisomers (2e) (296 mg, 94%). Recrystallisation from pentane to constant m.p. gave a single (major) isomer, m.p. 77—78 °C, $\nu_{max.}$ ($CHCl_3$) 2 050, 1 970, 1 720, 1 580w cm^{-1}; δ ($CDCl_3$) 7.28 (5 H), 5.34 (2 H, m), 3.80 (1 H, dd, *J* 10, 3.5 Hz, 6-H), 3.27 (2 H, m), 2.6—1.4 (3 H, m), 2.05 (3 H, s) 1.21 (3H, d, *J* 6 Hz) (Found: C, 56.2; H, 4.55; Calc. for $C_{20}H_{18}FeO_5S$: C, 56.35; H, 4.26%). The minor isomer gave (from mixed spectrum): δ 3.75 (1 H, dd, *J* 10, 3.5 Hz), 2.02 (3 H, s), and 1.18 (3 H, d, *J* 6 Hz).

Tricarbonyl{2—5-η-[6-(2-acetoxypropyl)cyclohexa-2,4-dienylmalonitrile]}iron (2f).—A suspension of sodiomalononitrile, prepared from NaH (12 mg) and malononitrile (36 mg) in THF (3 ml) was stirred and cooled to −10 °C whilst the solid hexafluorophosphate (1c) (200 mg, prepared by anion exchange) was added. Stirring was continued for 15 min after which the mixture was poured into water and the product extracted in the usual way with ether to give the crude complex (2f) as an orange gum (98 mg, 59%). Preparative t.l.c. afforded the unstable mixture of diastereoisomers (2f) as a yellow foam (75 mg, 45%), $\nu_{max.}$ ($CHCl_3$) 2 265w, 2 065, 1 990, and 1 730 cm^{-1}; δ ($CDCl_3$) major isomer: 5.53 (2 H, m), 5.05 (1 H, hext, *J* 6 Hz), 3.93 (1 H, d, *J* 4 Hz), 3.18 (2 H, m), 2.85 (1 H, m), 2.4 (1 H, m), 2.05 (3 H, s), 1.6 (2 H, m), and 1.25 (3 H, d, *J* 6 Hz); minor isomer: 5.00 (1 H, hext., *J* 6 Hz) and 3.77 (1 H, d, *J* 4.5 Hz) (Found: C, 53.25; H, 4.5; *M*, 384. Calc. for $C_{17}H_{16}FeN_2O_5$: C, 53.15; H, 4.20%; *M*, 384).

Tricarbonyl{2—5-η-[dimethyl 6-(2-acetoxypropyl)cyclohexa-2,4-dienylmalonate]}iron (2g).—The hexafluorophosphate (1c) (190 mg) was treated as above with an excess of dimethyl sodiomalonate in THF (3 ml) at −10 °C for 15 min. Preparative t.l.c. afforded the inseparable mixture of diastereoisomers (2g) as a yellow gum (90 mg, 49%), $\nu_{max.}$ ($CHCl_3$) 2 060, 1 980, 1 755, and 1 732 cm^{-1}; δ ($CDCl_3$) major isomer: 5.30 (2 H, m), 5.1 (1 H, m), 3.73 (3 H, s), 3.70 (3 H, s), 3.7 (1 H, obscured), 3.2 (2 H, m), 2.8 (1 H, m), 2.3 (1 H, m), 2.03 (3 H, s), 1.30 (2 H, m, obscured), and 1.17 (3 H, d, *J* 6 Hz); minor isomer: 2.01 (3 H, s, OAc); M^+ 450.

Tricarbonyl [2—5-η-(dimethyl cyclohexa-2,4-dienylmalonate)]iron (2h).—To a stirred suspension of sodium hydride (1.73 g of 50% dispersion in mineral oil, washed under N_2 with pentane) in THF (90 ml) at 0 °C was added dropwise a solution of dimethyl malonate (4.7 g) in THF (10 ml), to give a suspension of dimethyl sodiomalonate. Tricarbonylcyclohexadienyliumiron tetrafluoroborate (1a) (10.0 g) was added as a solid in one portion, with back flushing of nitrogen, and stirring was continued until a clear solution was obtained (15 min). The solution was concentrated, poured into ether (250 ml), washed with water (3 × 100 ml), dried ($MgSO_4$), and evaporated to give the diester (2h) (11.0 g, 100%) which was sufficiently pure for the next step. An analytical sample was obtained by recrystallisation from 5% ether in pentane; $\nu_{max.}$ ($CHCl_3$) 2 050, 1 975, 1 750sh, and 1730 cm^{-1}; δ ($CDCl_3$) 5.25 (2 H, m), 3.69 (3 H, s), 3.66 (1 H, obscured), 3.64 (3 H, s), 2.95 (3 H, m), 2.04 (1 H, ddd, *J* 15.3, 9.8, 3.8 Hz), 1.36 (1 H, dt, *J* 15.3, 2.6 Hz) (Found: C, 47.8; H, 3.8; *M*, 350. Calc. for $C_{14}H_{14}FeO_7$: C, 48.03; H, 4.03%; *M*, 350).

Tricarbonyl [2—5-η-(cyclohexa-2,4-dienylpropane-1,3-diol)]-iron (2i).—To a stirred solution of the crude diester (2h) (7.3 g) in THF (250 ml) at 0 °C was added dropwise di-isobutylaluminium hydride (100 ml of a 1.0M-solution in hexane) over 15 min. The solution was stirred overnight at room temperature, and worked up by the dropwise addition of ethanol (20 ml) and then water (20 ml). Small amounts of aldehyde produced in the reaction (t.l.c.) were reduced by addition of sodium borohydride (50 mg). The mixture

was filtered through Celite and the white filter cake was washed with ethanol (50 ml) and ether (100 ml).

Evaporation of the filtrate to *ca.* 100 ml, followed by partitioning between ether (200 ml) and water (200 ml), drying of the organic layer ($MgSO_4$), and evaporation gave a yellow oil which was crystallised from 10% ether in pentane to afford the diol (2i) as pale yellow crystals (5.9 g, 96%), m.p. 110—111 °C, $\nu_{max.}$ ($CHCl_3$) 3 620, 3 500, 2 050, and 1 980 cm^{-1}; δ [$(CD_3)_2SO$] 5.55 (2 H, m), 4.26 (2 H, t, *J* 6 Hz, exch. D_2O, 2 × OH), 3.45—3.09 (6 H, m 2-H, 5-H, and 2 × CH_2O), 2.49 (1 H, m), 2.22 (1 H, m, 1-H), 1.88 (1 H, m, *endo*-6-H), and 1.3 (1 H, m, *exo*-6-H); *m/z* 294, 266 [294 ⟶ 266 *m** 240.67], 238 [266 ⟶ 238 *m** 212.95], and 210 [238 ⟶ 210 *m** 185.29] (Found: C, 48.9; H, 4.8. Calc for $C_{12}H_{14}FeO_5$: C, 49.0; H, 4.80%).

Tricarbonyl[4—7-η-(3β-*hydroxymethyl*-2,3,3aβ,7aβ-*tetrahydrobenzofuran*)]*iron* (8a).—The diol (2i) (2.5 g) was dissolved in ethanol (100 ml) and the stirred solution was cooled to —10 °C whilst sodium hydrogen carbonate (3.0 g), followed by thallium(III) trifluoroacetate (7.8 g) were added. After 15 min the reaction mixture was poured into ethyl acetate (500 ml), treated with ether (5 ml), and the thallium salts thus precipitated were removed by filtration through Celite. The filtrate was washed with aqueous $NaHCO_3$, dried ($MgSO_4$), and evaporated to give the product which was recrystallised from 50% ether in pentane to give pure compound (8a) as pale yellow crystals, m.p. 121—122 °C (1.5 g, 60%), $\nu_{max.}$ ($CHCl_3$) 3 620, 3 430, 2 060, and 1 985 cm^{-1}; δ ($CDCl_3$) 5.63 (2 H, m 5-H, 6-H), 4.56 (1 H, dd, $J_{7,7a}$ 4.2, $J_{3a,7a}$ 9 Hz, 7a-H), 3.71 (2 H, ABX, J_{AB} 9.3, J_{AX} 5.4, J_{BX} 3 Hz, 2-H_2), 3.41 (2 H, d, *J* 6.9 Hz, CH_2OH), 3.15—2.83 (2 H, m, 4-H, 7-H), 2.59 (1 H, m, 3a-H), 1.95 (1 H, s, exch. D_2O), and 1.90 (1 H, m, 3-H); *m/z* 292, 264, 236, 208 (Found: C, 49.6; H, 4.35. Calc. for $C_{12}H_{12}FeO_5$: C, 49.35; H, 4.14%).

Tricarbonyl{4—7-η-[3β-(p-*tolylsulphonyloxymethyl*)-2,3,-3aβ,7aβ-*tetrahydrobenzofuran*]}*iron* (8c).—The alcohol (8a) (627 mg) was stirred in pyridine (7 ml) at 0 °C with toluene-*p*-sulphonyl chloride (820 mg) for 3 h.

Excess of tosyl chloride was destroyed by addition of water (0.5 ml; 15 min) after which the mixture was poured into ether (200 ml); it was then washed with cold 10% acetic acid and then aqueous $NaHCO_3$, and finally dried ($MgSO_4$) and evaporated. Recrystallisation of the product from 10% ether in pentane afforded the pale yellow crystalline tosylate (8c) (929 mg, 97%), m.p. 88—89 °C, $\nu_{max.}$ ($CHCl_3$) 2 050, 1 980, and 1 600 cm^{-1}; δ ($CDCl_3$) 7.32 (2 H, d, *J* 7 Hz), 7.75 (2 H, d, *J* 7 Hz), 5.51 (2 H, m), 4.45 (1 H, dd, *J* 9, 3.9 Hz, 7a-H), 3.76 (2 H, d, *J* 8.3 Hz), 3.7 (1 H, d, J_{gem} 9.8 Hz, 2β-H), 3.43 (1 H, dd, J_{gem} 9.8, $J_{2,3}$ 3.8 Hz, 2α-H), 2.89 (2 H, m), 2.44 (3 H, s), 2.46 (1 H, m, 3a-H), and 2.00 (1 H, m, 3-H); *m/z* 446, 418 [446 ⟶ 418 *m** 391.76], 390 (418 ⟶ 390 *m** 363.88), 362[390 ⟶ 362 *m** 336.01] (Found: C, 50.8; H, 4.15. Calc. for $C_{19}H_{18}FeO_7S$: C, 51.14; H, 4.07%).

Tricarbonyl[4—7-η-(3β-*acetoxymethyl*-2,3,3aβ,7aβ-*tetrahydrobenzofuran*)]*iron* (8b).—The alcohol (8a) (75 mg) was dissolved in pyridine (1 ml) containing acetic anhydride (0.2 ml) and set aside at —10 °C for 24 h. Water (0.5 ml) was then added to the reaction mixture which was set aside at room temperature for 0.5 h and then poured into ether. The ether solution was washed with cold 10% acetic acid and then aqueous sodium hydrogencarbonate, dried ($MgSO_4$), and evaporated to give the acetate (8b) (76 mg, 86%), m.p. 82.5—83.5 °C (ether–pentane), $\nu_{max.}$ ($CHCl_3$) 2 060, 1 985, and 1 735 cm^{-1}; δ ($CDCl_3$) 5.53 (2 H, m), 4.52 (1 H, dd, *J* 9, 4.5 Hz, 7a-H), 4.05 (2 H, m, CH_2OAc), 3.75 (1 H, d, J_{gem} 9 Hz, 2β-H), 2.94 (2 H, m, 4-H, 7-H) 2.65 (1 H, dd, J_{gem} 9 Hz, $J_{2,3}$ 3 Hz, 2α-H), 2.50 (1 H, m), 1.99 (3 H, s), and 1.98 (1 H, m); *m/z* 334, 306 [334 ⟶ 306 *m** 280.35], 278 [306 ⟶ 278 *m** 252.56], 250 [278 ⟶ 250 *m** 224.82], and 193 (Found: C, 50.45; H, 4.35. Calc. for $C_{14}H_{14}FeO_6$: C, 50.33; H, 4.22%).

3β-*Acetoxymethyl*-2,3,3aβ,7aβ-*tetrahydrobenzofuran* (9) *and Diels-Alder Adduct* (10).—To a stirred suspension of anhydrous trimethylamine *N*-oxide (1.5 g) in dry benzene (100 ml) at room temperature was added the above complex (8b) (90 mg) in benzene (1 ml). Stirring was continued for 24 h, after which the mixture was filtered through Celite and the filtrate washed with water, dried ($MgSO_4$), and evaporated to give a colourless oil which was purified by preparative t.l.c. to afford the tetrahydrobenzofuran derivative (9) (51 mg, 98%), $\nu_{max.}$ ($CHCl_3$) 1 735 cm^{-1}; δ ($CDCl_3$) 5.66—6.10 (4 H, m, diene), 4.62 (1 H, dd, $J_{7,7a}$ 3.75, $J_{3a,7a}$ 10.5 Hz, 7a-H), 4.77—4.06 (2 H, m, CH_2OAc), 3.78 (1 H, dd, J_{gem} 8.5, $J_{2,3}$ 6.75 Hz, 2β-H), 3.39 (1 H, dd, J_{gem} 8.5, $J_{2,3}$ 7.5 Hz, 2α-H), 2.66 (1 H, m, 3α-H), 2.48 (1 H, m, 3-H), and 2.06 (3 H, s); *m/z* 134 (*M* − AcOH) and (100%) [Found: *M* − AcOH, 134.0731. Calc. for $C_9H_{10}O$ (*M* − AcOH): 134.0732].

The product (9) (200 mg) was dissolved in benzene (5 ml) containing an excess of tetracyanoethylene (528 mg). After 2 h at room temperature the solvent was removed from the mixture which was then subjected to column chromatography (silica gel, 20% ethyl acetate in benzene), to give the Diels-Alder adduct (10) (200 mg, 60%), m.p. 185—186.5 °C (from $CHCl_3$), $\nu_{max.}$ ($CHCl_3$) 2 240 and 1 745 cm^{-1}; δ (CD_2Cl_2) 6.61 (2 H, m), 4.64 (1 H, dd, *J* 9, 3 Hz), 4.13 (2 H, d, *J* 7 Hz), 4.20—3.26 (4 H, m), 2.70 (1 H, m), 2.29 (1 H, m), and 2.05 (3 H, s). (Irradiation at δ 6.61 caused partial collapse of signal at 4.20—3.26 and irradiation 4.64 caused partial collapse of the signal at 2.70); *m/z* 262 (*M*-AcOH) (Found: C, 63.35; H, 4.1; N, 17.5. Calc. for $C_{17}H_{14}N_4O_3$: C, 63.35; H, 4.38; N, 17.38%).

Tricarbonyl[4—7-η-(3β-*methoxycarbonylpropionyloxymethyl*-2,3,3aβ,7aβ-*tetrahydrobenzofuran*)]*iron* (8e).—The alcohol (8a) (770 mg) was dissolved in 1 : 1 pyridine–benzene (4 ml) and the stirred solution was cooled to 0 °C whilst a solution of methoxycarbonylpropionyl chloride (0.7 ml) in benzene (2 ml) was added dropwise. After 2 h at 0 °C the reaction mixture was poured into ether (50 ml) and washed with cold 10% acetic acid and then aqueous sodium hydrogencarbonate, dried ($MgSO_4$), and evaporated. The residue was chromatographed on neutral alumina to give the ester (8e), as a yellow oil eluted with chloroform (552 mg, 54%), $\nu_{max.}$ ($CHCl_3$) 2 060, 1 985, 1 755, and 1 740 cm^{-1}; δ ($CDCl_3$) 5.68—5.42 (2 H, m), 4.57 (1 H, dd, $J_{7,7a}$ 4.5, $J_{3a,7a}$ 9 Hz, 7a-H), 4.10—3.72 (2 H, m, obscured), 3.73 (3 H, s), 3.91—3.43 (2 H, m, obscured, 2-H_2), 3.33 (2 H, s), 2.95 (2 H, m, 4-H, 7-H), 2.55 (1 H, m, 3a-H), 2.03 (1 H, m, 3-H); *m/z* 336 (*M* − 2CO), 308 [336 ⟶ 308 *m** 282.33].

Tricarbonyl{4—7-η-[3β-(2-*bismethoxycarbonylethyl*)-2,3,3aβ,7aβ-*tetrahydrobenzofuran*]}*iron* (8d).—The tosylate (8c) (1.0 g) was added to a suspension of dimethyl potassiomalonate [from $KOBu^t$ (1.0 g) and dimethyl malonate (1.19 g)] in dry dioxan (50 ml). The mixture was heated under reflux for 24 h, cooled, and poured into ether. The ether solution was washed with water, dried ($MgSO_4$), and evaporated. The residue was separated by column chromatography (silica gel, ethyl acetate in light petroleum) to give the faster-running fraction of unchanged tosylate (56 mg, 6%) followed by the diester (8d) (0.90 g, 93%) obtained as a yellow syrup, whose thermal instability pre-

cluded further purification by short path distillation; $\nu_{max.}$ ($CHCl_3$) 2 060, 1 985, 1 750, and 1 735 cm^{-1}; δ ($CDCl_3$) 5.56 (2 H, m), 4.55 (1 H, dd, *J* 9, 3.75 Hz), 3.76 (6 H, s), 4.10—3.23 (5 H, m, 2-H_2, and diester side-chain, 3 H), 3.13—2.82 (2 H, m) 2.44 (1 H, m), and 1.89 (1 H, m); *m/z* 406 (M^+), 378 [406 ⟶ 378 *m** 351.93], 350 [378 ⟶ 350 *m** 324.07], 322 [350 ⟶ 322 *m** 324.07].

Tricarbonyl(2—6η-{6-[1-*acetoxy*-4,4-*bis*(*methoxycarbonyl*)-*propan*-2-*yl*]*cyclohexa*-2,4-*dienylium*}])*iron* (1e).—To a stirred solution of the above diester complex (8d) (0.96 g) in acetic anhydride (10 ml) at 0 °C was added dropwise 40% aqeuous tetrafluoroboric acid (1.69 ml). Stirring was continued at 0 °C for 15 min and the solution was poured into ether. The ether was decanted and the gummy residue was washed by decantation with ether and dissolved in water (100 ml). Ammonium hexafluorophosphate (0.5 g) was added and the insoluble salt was extracted into dichloromethane (2 × 100 ml). The organic layer was dried ($MgSO_4$) and evaporated to dryness, and the residue was triturated with ether to give the pure salt (1e); this was filtered off (360 mg, 61%), $\nu_{max.}$ (CH_2Cl_2) 2 130, 2 090, 2 070, 1 740, and 850 cm^{-1} (PF_6^-); δ (CD_3CN) 7.00 (1 H, t, *J* 5.5 Hz, 4-H), 5.86 (2 H, m, 3-H and 5-H), 4.51 (2 H, t, *J* 6.0 Hz, 2-H and 6-H), 3.85 (2 H, m, CH_2OAc), 3.66 (3 H, s), 3.65 (3 H, s), 3.38 (1 H, dd, *J* 9, 5.5 Hz malonate CH), 2.85 (1 H, dt, *J* 9.0, 6.0 Hz, 1-H), 1.99 (3 H, s), 2.06—1.33 (2 H, m), and 0.95 (1 H, m). (Irradiation at δ 2.85 caused partial collapse of the signals at 4.51 and 0.95. Irradiation at δ 4.50 caused the signal at 2.85 to collapse to a doublet.) (Found: C, 38.3; H, 3.35. Calc. for $C_{19}H_{21}F_6FeO_9$: C, 38.4; H, 3.5%).

Tricarbonyl{1—5-η-[(1-*acetoxy*-3-p-*tolylsulphonyloxypropan*-2-*yl*)*cyclohexadienylium*]}*iron Hexafluorophosphate* (1d).—Treatment of the complex (8c) (766 mg) as described above for the preparation of (1e), gave the pure hexafluorophosphate (1d) (900 mg, 92%), $\nu_{max.}$ (Nujol) 2 140, 2 070, and 1 740 cm^{-1}; δ (CD_3CN) 7.85 (2 H, d, *J* 9 Hz), 7.53 (2 H, d, *J* 9 Hz), 7.07 (1 H, t, br, *J* 6.0 Hz), 5.90 (2 H, t, *J* 6.0 Hz), 4.47 (1 H, t, *J* 6.0 Hz) and 4.34 (1 H, t, *J* 6.0 Hz, 1-H and 5-H), 3.90 (2 H, d, *J* 5.5 Hz, CH_2O), 3.79 (2 H, d, *J* 6.0 Hz, CH_2O), 2.97 (1 H, dt, *J* 10, 6 Hz, 6-H), 2.47 (3 H, s), 1.90 (3 H, s, OAc), and 1.30 (1 H, m, methine) (Found: C, 39.4; H, 3.4. Calc. for $C_{21}H_{21}F_6FeO_8SP$: C, 39.76; H, 3.34%).

Tricarbonyl{1—5-η-[6-(1-*acetoxy*-3-*methoxycarbonyl*-*acetoxypropan*-2-*yl*)*cyclohexadienylium*]}*iron Hexafluorophosphate* (1f).—Treatment of the complex (8e) (480 mg) as above gave the hexafluorophosphate (1f) (700 mg, 99%), $\nu_{max.}$ (CH_2Cl_2) 2 130, 2 060, 2 050, 1 745, and 845 cm^{-1}; δ (CD_3CN) 7.07 (1 H, t, *J* 6.0 Hz) 5.92 (2 H, t, *J* 6.0 Hz), 4.49 (2 H, t, br, *J* 6.0 Hz), 3.99 (1 H, dd, J_{AB} 5.0, *J* 1.5 Hz), and 3.92 (1 H, d, J_{AB} 5.0 Hz, CH_2OAc), 3.71 (3 H, s), 3.41 (2 H, s), 3.05 (1 H, dt, br, *J* 9.0, 6.0 Hz), 2.01 (3 H, s), and 1.40 (1 H, m) (Found: C, 36.85; H, 3.45. Calc. for $C_{18}H_{19}FeO_9PF_6$: C, 37.27; H, 3.30%).

Cyclisation of the Diester Complex (1e).—The complex (1e) (250 mg) was stirred in dichloromethane (5 ml) at −78 °C and treated with 1 equiv. of 1,8-diazabicyclo[5.4.0]-undec-7-ene. After 15 min no dienylium complex remained, as judged by i.r. spectral examination. The reaction mixture was poured into ether, washed with water, dried ($MgSO_4$), and evaporated to give an unstable yellow oil, $\nu_{max.}$ ($CHCl_3$) 2 050, 1 975, and 1 735 cm^{-1}. Treatment of the crude product with anhydrous trimethylamine *N*-oxide, as described for the preparation of diene (9), followed by preparative t.l.c. gave the hydrindane derivative (11) (20 mg, 16% overall as a colourless oil, $\nu_{max.}$ ($CHCl_3$) 1 730, and 1 650 cm^{-1}; δ ($CDCl_3$) 5.84—5.47 (4 H, m), 4.02 (2 H close ABq), 3.69 (3 H, s), 3.65 (3 H, s), 2.55 (4 H, m), 2.01 (3 H, s), and 1.94 (1 H, m); *m/z* (%) 248 (15, *M* − AcOH), 188 (18), 145 (30), 129 (40), and 104 (100) (Found: *M* − AcOH, 248.1045. Calc. for $C_{14}H_{15}O_7$: 248.1049).

Treatment of this compound with tetracyanoethylene in benzene as described for the diene (9), gave the crystalline Diels-Alder adduct (12), m.p. 116—119 °C.

Attempted Cyclisation of the Complex (1f).—Attempts to effect the cyclisation of complex (1f) using a wide range of bases and reaction conditions gave the aromatic compound (13) as the major product. This compound was also obtained by direct treatment of (1f) with ceric ammonium nitrate in 85—90% yield; $\nu_{max.}$ ($CHCl_3$) 1 740, and 1 605 cm^{-1}; δ ($CDCl_3$) 7.26 (5 H, m), 4.39 (4 H, m), 3.68 (3 H, s), 3.35 (2 H, s), 3.34 (1 H, m), and 2.0 (3 H, s).

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