Organoiron Complexes in Organic Synthesis. Part 18.[1,2] Spiroannelation Reactions of some Bifunctional Tricarbonyl(cyclohexadienyl)iron Hexafluorophosphate Salts

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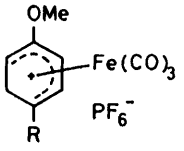
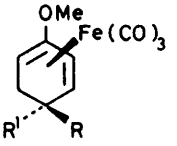
The synthesis of tricarbonyl(cyclohexadienylium)iron salts containing tosyloxy-substituents in the lateral chain, and their reactions with nucleophiles to give spirocyclic compounds, is described. The synthesis and spiroannelation reactions of complexes with *gem*-dinitrile and cyanoester groups in the lateral chain are presented.

We have previously reported synthetic approaches to spiro[4.5]decane and spiro[5.5]undecane derivatives using the reaction of tricarbonyl(cyclohexadienyl)iron complexes (1) and (2) with dimethyl sodiomalonate, followed



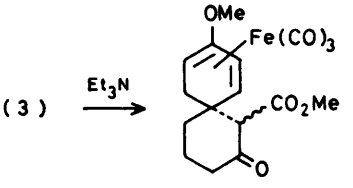
(1) R = $[CH_2]_2 \cdot CO_2Me$
(2) R = $[CH_2]_3 \cdot CO_2Me$
(3) R = $[CH_2]_3 \cdot CO \cdot CH_2 \cdot CO_2Me$
(4) R = $[CH_2]_2 \cdot CH_2OTs$
(5) R = $[CH_2]_3 \cdot CH_2OTs$
(6) R = $[CH_2]_3 \cdot CH(CN)_2$
(7) R = $[CH_2]_3 \cdot CH(CN) \cdot CO_2Me$
(8) R = $[CH_2]_3 \cdot CH(CO_2Me)_2$
(9) R = $[CH_2]_4 \cdot CH(CN)_2$
(10) R = $[CH_2]_4 \cdot CH(CN) \cdot CO_2Me$
(11) R = $[CH_2]_4 \cdot CH(CO_2Me)_2$
(12) R = $[CH_2]_2 \cdot O \cdot CO \cdot CH_2COMe$



(13) R = $[CH_2]_2 \cdot CO_2Me$, R^1 = $CH(CO_2Me)_2$
(14) R = $[CH_2]_3 \cdot CO_2Me$, R^1 = $CH(CO_2Me)_2$

by subsequent elaboration of the products (13) and (14),[3] and we have also reported an alternative approach by means of *intramolecular* carbon nucleophile addition of the keto-ester dienyl complex (3) which gave good yields of spiro[5.5]undecane derivative [equation (1)].[4] This constituted the first recorded example of intramolecular nucleophile addition to these complexes, but our attempts at that time to obtain spiro[4.5]decane derivatives by this means were unsuccessful, owing to (*a*) the propensity of the appropriate keto-ester to cyclise on oxygen rather than on carbon, and (*b*) the insufficient acidity of a substituted *gem* diester methine proton compared with the lateral chain methylene protons α to the dienyl terminus [4] (see later).

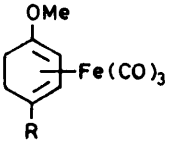
With these results in mind we considered it worthwhile to investigate the synthesis and chemistry of dienyl complexes possessing a wider range of functionality in the 1-substituent in order to develop new methods of ring formation. Whilst the studies reported herein all lead to the formation of spirocyclic ring systems, it is our belief that the knowledge gained from such investigations will be useful in planning a wide range of annelation reactions.



Equation (1)

RESULTS AND DISCUSSION

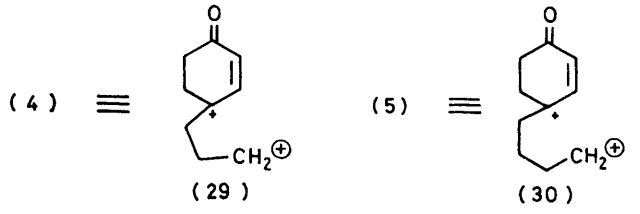
Our starting points were the ester derivatives (15) and (16). Since these were originally prepared in only moderate yield by our previously reported method [3] we



(15) R = $[CH_2]_2 \cdot CO_2Me$
(16) R = $[CH_2]_3 \cdot CO_2Me$
(17) R = $[CH_2]_2 \cdot CH_2 \cdot OH$
(18) R = $[CH_2]_3 \cdot CH_2 \cdot OH$
(19) R = $[CH_2]_2 \cdot CH_2 \cdot OTs$
(20) R = $[CH_2]_3 \cdot CH_2 \cdot OTs$
(21) R = $[CH_2]_3 \cdot CH(CN)_2$
(22) R = $[CH_2]_3 \cdot CH(CN) \cdot CO_2Me$
(23) R = $[CH_2]_3 \cdot CH(CO_2Me)_2$
(24) R = $[CH_2]_4 \cdot CH(CN)_2$
(25) R = $[CH_2]_4 \cdot CH(CN)CO_2Me$
(26) R = $[CH_2]_4 \cdot CH \cdot (CO_2Me)_2$
(27) R = $[CH_2]_2 \cdot OH$
(28) R = $[CH_2]_2 O \cdot CO \cdot CH_2COMe$

have developed an improved synthesis, described in the Experimental section. Whilst the $Fe(CO)_3$ group is generally unstable to lithium aluminium hydride treatment,[5] the ester group in these complexes can be

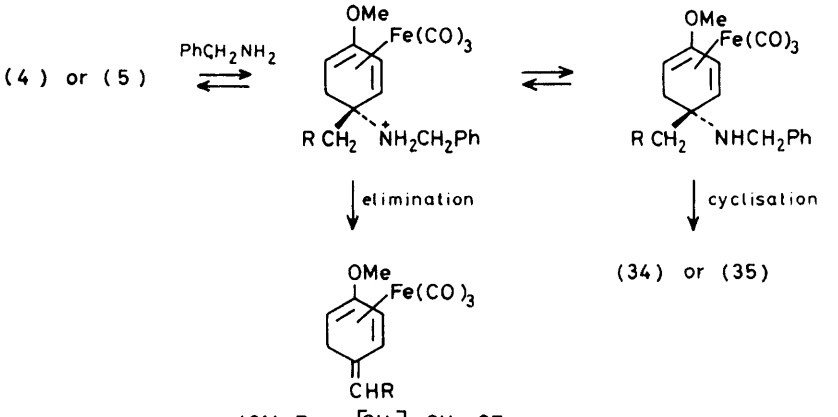
reduced smoothly with di-isobutylaluminium hydride (DIBAL) giving the primary alcohol derivatives (17) and (18) in high yield. These were smoothly converted into the corresponding toluene-*p*-sulphonates (19) and (20) in the usual way, and treatment of these complexes with triphenylmethyl tetrafluoroborate, followed by anion exchange using ammonium hexafluorophosphate gave the dienylium complexes (4), obtained as a solid, and (5), obtained as a gum. Considerable difficulty was encountered in obtaining microanalysis of the latter compound, so a sample was converted into the crystalline Reineckate.



In fact, it was found unnecessary to isolate hexafluorophosphates, since the reactions studied could also be effected with crude tetrafluoroborate salts (Experimental section).

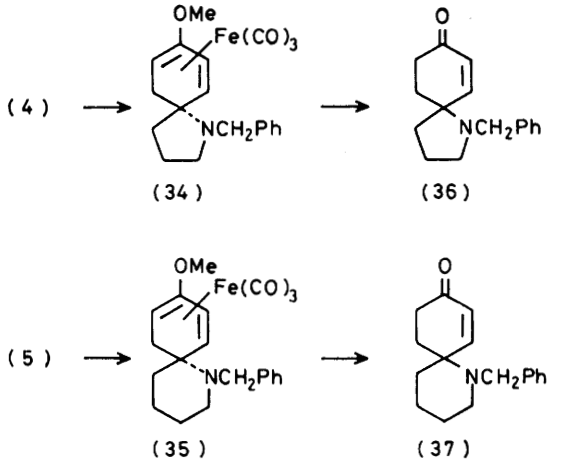
The tosyloxy-substituted dienyl complexes (4) and (5) are interesting in that there are two electrophilic centres in the molecule and, consequently, they might be reactive towards a divalent nucleophile so as to lead to homologation and annelation in one step. Furthermore, as we have previously shown,[3-6] the effect of the 4-methoxy-substituent in these complexes is to electronically deactivate the 5-position, so that nucleophile addition occurs predominantly at C-1. Consequently, the tosyloxy-complexes (4) and (5) may be regarded as synthetic equivalents of the dications (29) and (30), respectively. These are also noteworthy as being cyclohexenones showing umpolung at the γ-carbon atom. To test this hypothesis, and to demonstrate the synthetic usefulness of our complexes, we investigated their reaction with benzylamine, a suitable divalent nucleophile which would hopefully give rise to azaspirocyclic derivatives. The complex (4) reacted smoothly with the amine to give very high yields of the desired azaspirocyclic complex (34) which was readily converted into the enone (36). Our initial attempts to repeat this success with complex (5) resulted in only poor yields of the desired azaspirocycle (35), the main product being the unstable η^4-triene complex (31), which was not fully characterised. Since this problem was not encountered in the reaction of the lower homologue we decided that the initial addition of amine to the dienyl system must occur successfully in both cases, but an equilibrium was established between protonated and unprotonated amino-derivatives, as shown in the Scheme. The unprotonated form can cyclise by tosylate displacement, kinetically favourable in the formation of five-membered rings, whilst the protonated form readily undergoes elimination.

Thus, we reasoned that this problem could be overcome by employing a large excess of amine which would also act as base and possibly shift the equilibrium to favour the unprotonated amine adducts, and therefore the cyclisation product. We were pleased to find that slow addition of an acetonitrile solution of the hexafluorophosphate (5) to a ten-fold excess of benzylamine in acetonitrile resulted in a 90—95% yield of the desired azaspirocycle (35) which was readily converted into the azaspirocyclic enone (37). An interesting observation is that quenching of the reaction of (5) with benzylamine after a short time allowed isolation of appreciable quantities of a product whose spectroscopic data were consistent with the structure (38), the product of amine addition to the electronically deactivated C-5 position of (5). When the reaction was allowed to proceed for extended times, this compound disappeared (t.l.c.) and only traces were obtained in the final solution. Thus, the reaction is reversible, the unexpected product (38)

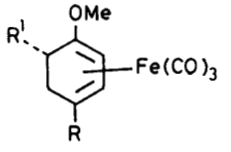


SCHEME

readily re-protonating and eliminating amine to form the salt (5), which eventually gives the stable spirocyclic complex. This was verified when the reactions of (4) and (5) with irreversible nucleophiles were studied.



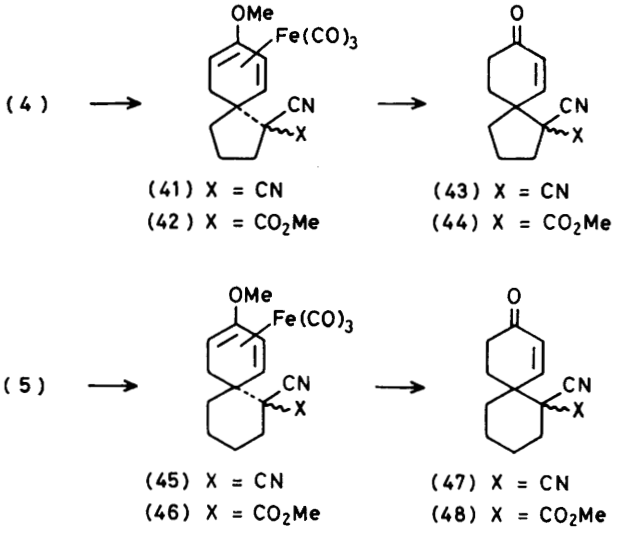
Treatment of the tosylate complexes (4) and (5) with an excess of sodiomalononitrile or methyl sodiocyanoacetate resulted in the direct formation of the spirocyclic complexes (41), (42), (45), and (46), which were converted into the enones (43), (44), (47), and (48). Interestingly, use of cyanoacetic ester did not give an equimolar



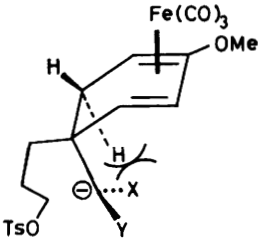
(38) R = $[CH_2]_4$·OTs, R^1 = $PhCH_2NH$
(39) R = $[CH_2]_3$·OTs, R^1 = CH(X)(Y)
(40) R = $[CH_2]_4$·OTs, R^1 = CH(X)(Y)

X, Y = CN, CO_2Me

mixture of diastereoisomers. Examination of the n.m.r. spectra revealed diastereoisomer mixtures of 2 : 1 for (42) and >9 : 1 for (46). We have not yet derived the relative stereochemistries of these compounds, but it seems likely that the most favourable arrangement of the cyanoester anion during cyclisation for formation of (42) is that in which there is least steric interaction between the C-6 methylene group of the ring and the ester group, *i.e.* (B) is more favourable than (A) (see Figure). From our own *X*-ray data,[6c,d] the shape of the complexed cyclohexadiene resembles the boat form of a cyclohexene. The representation given in the Figure is probably more useful in considering the formation of five-membered than six-membered rings, since more complex conformational effects are expected to contribute to the latter. In these reactions only moderate yields of spirocycles were obtained, as a result of the irreversible addition of the carbanion to C-5 of complexes (4) and (5) giving products (39) and (40) in yields usually *ca.* 15%. We envisaged that this major side-reaction, which is expected to become more important in complexes with branched 1-substituents,[5] might be overcome if intramolecular reaction of malononitrile, *etc.*, could be achieved.



With the tosylate diene complexes (19) and (20) now in hand we were in a position to examine the synthesis of complexes suitable for these studies. Successful displacement of toluene-*p*-sulphonate with sodiomalononitrile, methyl sodiocyanoacetate, and dimethyl sodiomalonate, to give the cyclohexadiene complexes (21)—(26), was achieved by heating in either tetrahydrofuran or dioxan under nitrogen. These solvents were found



(A) X = CO_2Me, Y = CN
(B) X = CN, Y = CO_2Me

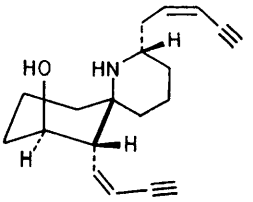
FIGURE

to give least decomposition of the complex compared with, for example, dimethylformamide. The keto-ester complex (28) was also prepared, by reaction of the primary alcohol derivative (27) [5] with keten dimer in the presence of acid catalyst. Thus contains a keto-ester in the 1-substituent and its derived dienyl complex (12) was expected to show similar behaviour to the earlier reported complex (3). The next step was the conversion of these complexes into the corresponding dienyl salts. Treatment of (21) and (22) with triphenylmethyl tetra-

fluoroborate in refluxing dichloromethane, followed by addition of ether gave no ether-insoluble material (dienyl complexes). Evaporation of solvent, followed by chromatography allowed the isolation of the spiro-[4.5]decane derivatives (41) and (42) in moderate yield. Thus, cyclisation of the dienyl complexes (6) and (7) occurs spontaneously, again reflecting the facility of five-membered ring formation. Also, n.m.r. examination of the cyano-ester (42) revealed that it was an equimolar mixture of diastereoisomers, in contrast to the mixture obtained earlier. Apparently, the greater reactivity (lower activation energy) of the dienyl system towards nucleophiles, compared to tosylate esters, leads to (intramolecular) reaction of the nucleophile indiscriminately, whichever orientation it adopts. We have previously shown that the *gem* diester dienyl complex (8) does not cyclise on treatment with base, but instead undergoes deprotonation α- to the dienyl terminus [4] (see later), so the present results indicate that a relatively acidic methine proton is necessary for the cyclisation reaction to occur.

Treatment of the homologous diene complexes (23)—(26), and of the keto-ester (28), with triphenylmethyl tetrafluoroborate as above resulted in the formation of the dienyl complexes (9)—(12), isolated as their hexafluorophosphates, in moderate to good yields. Since lower yields were obtained for the bisnitrile and cyano-ester complexes (9) and (10) the liquors from the reaction were examined for the presence of spirocyclic complexes. Small amounts of these were found, indicating minor spontaneous cyclisation. Treatment of the isolated hexafluorophosphates (9) and (10) with mild base resulted in their conversion into spiro[5.5]undecane complexes (45) and (46) in high yield. Again, the cyano-ester (46) was produced as an equimolar mixture of diastereoisomers. A slight improvement in yield of spirocycles was obtained by using a one-pot procedure, *i.e.* direct treatment of the trityl tetrafluoroborate reaction mixture with triethylamine. The *gem*-diester complex (11) could not be induced to cyclise by base treatment, and gave only the unstable η^4-triene complex (32), as expected from our previous studies.[4] Similarly, no cyclisation of the keto-ester (12) could be achieved, treatment of this with base giving rise to considerable decomposition to give aromatic material presumably *via* the η^4-triene complex (33). Some i.r. and n.m.r. evidence for the formation of this complex was obtained, but its instability prohibited purification and proper characterisation. This result is puzzling in view of the facility with which the similar keto-ester complex (3) cyclises.[4] It appears that the heterocyclic transition state for six-membered ring formation is disfavoured in some way, which may partly account for Trost's recent observation that eight-membered lactones are formed in preference to six-membered lactones by cyclisation of allylpalladium derivatives.[7] We have not further investigated this problem.

Concluding Remarks.—We have developed new methods for the synthesis of aza- and carbo-spirocyclic compounds using organoiron complexes, which we envisage may be usefully applied to the synthesis of a wide range of natural products. In this respect, we are currently studying the conversion of the azaspirocyclic enone (39) into derivatives of histrionicotoxin (49), which have recently been the subject of much synthetic work.[8]



(49)

EXPERIMENTAL

I.r. spectra were determined with a Perkin-Elmer 577, mass spectra with A.E.I. MS12 (organometallics) or MS30 (organic compounds), and ^{1}H n.m.r. spectra with Varian EM390 instruments. M.p.s are uncorrected. All preparative and chromatographic operations involving iron complexes were conducted under a nitrogen atmosphere.

Tricarbonyl[methyl 3-(4-methoxycyclohexa-1,3-dienyl)propanoate]iron (15).—This compound was prepared by a similar route to that previously reported,[3] however, pure 1,4-diene was isolated after the Birch reduction and esterification stage, and conjugated before treatment with Fe(CO)$_5$. This modification gave an improved overall yield. Birch reduction of *p*-methoxycinnamic acid (98%) followed by esterification with dimethyl sulphate (93%) gave methyl 3-(4-methoxycyclohexa-1,4-dienyl)propanoate as white flakes from hexane, m.p. 46—48 °C, $\nu_{max.}$ ($CHCl_3$) 1 735, 1 700, and 1 660 cm^{-1}; δ(CCl_4) 5.36br (1 H, s, vinyl-H), 4.56br (1 H, s, vinyl-H), 3.64 (3 H, s, CO_2Me), 3.51 (3 H, s, OMe), and 2.2—2.8 (8 H) (Found: C, 67.1; H, 8.02%; *M*, 196.1087. $C_{11}H_{16}O_3$ requires C, 67.3; H, 8.22%; *M*, 196.1100), *m/e* (%) 196 (30) and 123 (100).

This cyclohexa-1,4-diene (22.5 g) was conjugated with toluene-*p*-sulphonic acid (13 mg) at 80 °C under nitrogen for 25 min, poured into aqueous potassium carbonate at 0 °C and extracted with ether in the usual way to give a pale yellow oil (22.3 g, 99%) which contained the equilibrium mixture of the 1,3- and 1,4-cyclohexadienes in a 4 : 1 ratio. Treatment of this mixture with pentacarbonyliron as before [3] gave (15) (55%).

Tricarbonyl[3-(4-methoxycyclohexa-1,3-dienyl)propanol]iron (17).—Di-isobutylaluminium hydride (DIBAL) (107 ml of a 1M-solution in hexane, 107 mmol) was transferred dropwise under nitrogen to a solution of the above complex (15) (14.96 g, 44.5 mmol) in THF (40 ml) at −78 °C. The stirred mixture was allowed to reach room temperature during 15 h, after which time a little sodium borohydride was added; stirring was continued for a further 1 h. Deoxygenated methanol (40 ml) was added during 30 min with ice cooling followed by deoxygenated water. The solution was filtered free from the white granular precipitate and the solvent removed under reduced pressure. The oil was extracted into ether, washed with water, dried ($MgSO_4$), and evaporated to give the *alcohol* (17) (13.33 g, 43.27 mmol, 97%) as an oil, chromatographically and spectroscopically pure, $\nu_{max.}$ ($CHCl_3$) 3 260—3 560, 3 615, 2 035, and 1 958

cm^{-1}; δ($CDCl_3$) 5.14 (1 H, d, *J* 5 Hz, 3-H), 4.95 (1 H, d, *J* 5 Hz, 2-H), 3.60br (2 H, t, CH_2OH), 3.44 (3 H, s, OMe), and 1.3—2.4 (9 H) [Found: (*M* − CO) 280.0421. Calc. for $C_{13}H_{16}FeO_5$ (M-CO); 280.0389], *m/e* (%), 252 (35), 224 (2), 222 (100), and 166 (28).

Tricarbonyl[3-(4-*methoxycyclohexa*-1,3-*dienyl*)*propyl toluene*-p-*sulphonate*]*iron* (19).—Toluene-*p*-sulphonyl chloride (5.76 g) in pyridine (15 ml) at −10 °C was added to a solution of the alcohol (17) (5.24 g) in pyridine during 10 min at −10 °C. After 11 h at 0 °C the reaction was complete and poured into ice–water. The product was extracted with ether, washed with dilute aqueous hydrochloric acid and water at 0 °C, and isolated in the usual way to give the tosylate (19) (7.84 g, 100%), $\nu_{max.}$ ($CHCl_3$) 2 065, 1 965, 1 602, 1 363, and 1 178 cm^{-1}; δ($CDCl_3$) 7.79 (2 H, d, *J* 9 Hz, 2 × ArH), 7.33 (2 H, d, *J* 9 Hz, 2 × ArH), 5.15 (1 H, d, *J* 5 Hz, 3-H), 4.88 (1 H, d, *J* 5 Hz, 2-H), 4.02br (2 H, s, CH_2OTs), 3.52 (3 H, s, OMe), 2.57 (3 H, s, Ar-CH_3), and 1.4—2.3 (8 H); *m/e* (%) 462 (*M*, 0.2), 434 (0.3), 406 (20), 378 (25), 322 (20), and 221 (100).

Tricarbonyl[3-(4-*methoxycyclohexa*-2,4-*dienylium*)*propyl toluene*-p-*sulphonate*]*iron Hexafluorophosphate* (4).—Triphenylmethylium tetrafluoroborate (396 mg) was added to a solution of the above complex (19) (330 mg) in dichloromethane (11 ml) and the mixture was heated under reflux for 55 min; it was then poured into ether. The resulting oil was washed with ether, dissolved in dichloromethane and shaken with an excess of aqueous ammonium hexafluorophosphate (20 min). The organic solution was washed with water and the yellow, crystalline hexafluorophosphate salt (4) (390 mg, 90%) was crystallised by addition of ether and cooling, $\nu_{max.}$ (CH_2Cl_2) 2 108, 2 055, 1 600, 1 500, 1 360, 1 176, 845, and 555 cm^{-1}; δ(CD_3CN) 7.81 (2 H, d, *J* 8 Hz, 2 × ArH), 7.47 (2 H, d, *J* 8 Hz, 2 × ArH), 6.78 (1 H, dd, *J* 6, 2 Hz, 3-H), 5.55 (1 H, d, *J* 6 Hz, 2-H), 4.02 (2 H, t, *J* 6 Hz, CH_2OTs), 3.87 (1 H, m, 5-H), 3.78 (3 H, s, 4-OMe), 2.93 (1 H, dd, *J* 6, 15 Hz, *endo*-5-H), 2.47 (3 H, s, Ar-CH_3), 2.25 (1 H, d, *J* 15 Hz, *exo*-5-H), and 1.5—2.1 (4 H) (Found: C, 39.9; H, 3.5. Calc. for $C_{20}H_{21}FeO_7PS$; C, 39.6; H, 3.49%).

Tricarbonyl{6—9-η-(8-*methoxy*-1-*benzyl*-1-*azaspiro*[4.5]-*deca*-6,8-*diene*}*iron* (34). A solution of the above complex (4) (24.2 mg) in nitromethane (1 ml) was treated with benzylamine (8.7 μl) at room temperature and stirred for 10 min. The reaction mixture was poured into aqueous potassium carbonate and extracted with ethyl acetate; the extract was dried (K_2CO_3) to give the product (34) as an oil (15.4 mg, 98%), $\nu_{max.}$ (Nujol mull, KBr disc), 2 795, 2 050, 1 940, 1 608, and 1 488 cm^{-1}; δ($CDCl_3$) 7.26 (5 H, s, ArH), 5.25 (1 H, dd, *J* 6.5, 2.4 Hz, 7-H), 3.66 (3 H, s, OMe), 3.35 (2 H, ABq, CH_2Ph), 3.3 (1 H, m, 9-H), 2.45 (3 H, m, 6-H and CH_2N), and 1.97—1.57 (6 H); *m/e* (%) 395 (M^+, 23), 367 (40), 339 (1), 311 (82), 255 (6), 240 (8), 220 (100), and 91 (97).

1-*Benzyl*-1-*azaspiro*[4.5]*dec*-6-*en*-8-*one* (36).—The above complex (34) (227.6 mg) was treated with anhydrous trimethylamine *N*-oxide (2.6 g) in benzene (30 ml) and stirred at 37 °C for 2 h and then 35 °C for 13.5 h. The reaction mixture was filtered through Celite and evaporated under reduced pressure. The residue was extracted into ether and the extract washed with water, dried (K_2CO_3), and the solvent removed under reduced pressure to give 8-methoxy-1-benzyl-1-azaspiro[4.5]deca-6,8-diene (130.5 mg, 89%); $\nu_{max.}$ ($CHCl_3$) 2 835 and 1 655 cm^{-1}; δ(CCl_4) 7.1 (5 H, m, ArH), 5.8 (1 H, dd, *J* 10, 2 Hz, 6-H), 5.5 (1 H, d, *J* 10 Hz, 7-H), 4.4 (1 H, m, 9-H), 3.49 (2 H, s, $PhCH_2N$), 3.30 (3 H, s, 8-OMe), and 1.0—2.7 (8 H) (Found: *M*, 255.1618. Calc. for $C_{17}H_{21}NO$: 255.1623).

A solution of the dienol ether (12.8 mg) in methanol (2 ml) was treated with a solution of oxalic acid (91 mg) in water (0.5 ml) at room temperature for 40 min. Basification with potassium carbonate and extraction with ether yielded the enone (36) (5.4 mg, 54%, not optimised); $\nu_{max.}$ (CCl_4) 2 805, 1 685, and 1 608 cm^{-1}; δ(CCl_4) 7.09 (5 H, s, ArH), 6.50 (1 H, dd, *J* 10, 2 Hz, 6-H), 5.73 (1 H, d, *J* 10 Hz, 7-H), 3.40 (2 H, s, $PhCH_2N$), and 1.5—2.6 (10 H) (Found: *M*, 241.1479. Calc. for $C_{16}H_{19}NO$: 241.1467).

Tricarbonyl[*methyl* 4-(4-*methoxycyclohexa*-1,3-*dienyl*)*butyrate*]*iron* (16).—4-(*p*-Methoxyphenyl)butyric acid was subjected to Birch reduction and immediate esterification as described above. The crude dienol ether (25.9 g) was stirred at 80 °C with toluene-*p*-sulphonic acid (0.05 g) under an atmosphere of nitrogen. After 0.5 h the mixture was cooled, diluted with an equal volume of diethyl ether, and filtered through neutral alumina (activity 1). Removal of solvent gave an equilibrium mixture of conjugated and unconjugated dienes (24.8 g, 96%) in approximate proportions 3 : 1 (n.m.r.). The mixture was heated at reflux in di-n-butyl ether with an excess of pentacarbonyliron (20 h) [3] and gave, after chromatography on silica gel (hexane–dichloromethane, gradient elution) the complex (16) (59%).

Tricarbonyl[4-(4-*methoxycyclohexa*-1,3-*dienyl*)*butanol*]*iron* (18). The ester complex (16) (1.99 g) in dry THF (45 ml) was treated with di-isobutylaluminium hydride (12.6 ml of a 1M solution in hexane, 2.2 equiv.) as described for compound (17), to give the alcohol (18) as a yellow oil (1.79 g, 98%), which could not be crystallised. Preparative layer chromatography on silica gel, (10% ethyl acetate in benzene) gave no significant purification, so the crude complex was used for further reactions; $\nu_{max.}$ ($CHCl_3$) 3 640, 2 040, and 1 970 cm^{-1}; δ($CDCl_3$) 5.15 (1 H, d, *J* 5 Hz, 3-H), 4.90 (1 H, d, *J* 5 Hz, 2-H), 3.63 (2 H, m, CH_2OH), 3.43 (3 H, s, OMe), and 2.5—1.2 (11 H, changes on D_2O shake, methylenes and OH); *m/e* (%) 322 (1), 294 (4), 266 (11), 238 (5), 236 (44), and 118 (100).

Tricarbonyl[4-(4-*methoxycyclohexa*-1,3-*dienyl*)*butyl toluene*-p-*sulphonate*]*iron* (20). The alcohol complex (18) (0.865 g) was treated with toluene-*p*-sulphonyl chloride (0.87 g, 1.7 equiv.) in dry pyridine (7 ml), as described for compound (19). After 23 h at 0 °C the usual work-up gave the tosylate (20) as a yellow oil (1.251 g, 98%), which was purified by preparative t.l.c. on silica (10% ethyl acetate in benzene), $\nu_{max.}$ ($CHCl_3$) 2 040, 1 965, 1 375, and 1 350 cm^{-1}; δ($CDCl_3$) 7.84 (2 H, d, *J* 8.5 Hz) and 7.37 (2 H, d, *J* 8.5 Hz) (aromatics), 5.18 (1 H, d, *J* 4.5 Hz, 3-H), 4.90 (1 H, d, *J* 4.5 Hz, 2-H), 4.07 (2 H, m, CH_2OTs), 3.48 (3 H, s, OMe), 2.49 (3 H, s, Ar-*Me*), and 2.4—1.3 (10 H, methylenes); *m/e* (%) 476 (1), 448 (1), 420 (15), 392 (34), and 235 (100).

Tricarbonyl[4-(4-*methoxycyclohexa*-2,4-*dienylium*)*butyl toluene*-p-*sulphonate*]*iron Hexafluorophosphate* (5).—The diene complex (20) (2.223 g) and triphenylmethylium tetrafluoroborate (2.3 g, 1.5 equiv.) were stirred at reflux in dichloromethane (30 ml) under nitrogen for 1 h. Solvent was removed, and the residue was washed by decantation with hexane and ether; it was then dissolved in dichloromethane (20 ml) and stirred with ammonium hexafluorophosphate (1.6 g) in water (10 ml), under nitrogen, for 0.5 h. The layers were separated, and the aqueous portion repeatedly extracted with dichloromethane. The combined organic portions were washed with water and dried ($MgSO_4$).

The solution was concentrated under reduced pressure and the product (5) was precipitated with ether; the supernatant liquid was decanted and the residual yellow gum (2.542 g, 88%) washed well with ether and dried under high vacuum, $\nu_{max.}$ (CH_2Cl_2) 2 115, 2 060, 1 600, 1 500, and 1 360 cm^{-1}; δ(CD_3CN) 7.73 (2 H, d, *J* 8 Hz) and 7.40 (2 H, d, *J* 8 Hz) (aromatics), 6.76 (1 H, dd, *J* 6, 3 Hz, 3-H), 5.41 (1 H, d, *J* 6 Hz, 2-H), 3.99 (2 H, t, *J* 6 Hz, CH_2OTs), 3.9 (1 H, s, obscured, 5-H), 3.76 (3 H, s, OMe), 2.90 (1 H, dd, *J* 14, 5.5 Hz, *endo*-6-H), 2.43 (3 H, s, Ar-Me), and 2.3—1.3 (methylenes, *exo*-6-H) (Found: C, 41.5; H, 3.85; Calc. for $C_{21}H_{23}F_6FeO_7PS$: C, 40.66; H, 3.74%). The Reineckate derivative was formed by anion exchange between compound (5) (0.050 g) and ammonium Reineckate (0.1 g), proceeding as for the conversion of tetrafluoroborate into hexafluorophosphate salt (above), to give purple crystals on trituration with pentane (Found: C, 38.4; H, 4.1; N, 10.45. Calc. for $C_{25}H_{29}CrFeN_6O_7S_5$: C, 37.83; H, 3.68; N, 10.59%).

Tricarbonyl(7—10-η-1-*benzyl*-9-*methoxy*-1-*azaspiro*[5.5]-*undeca*-7,9-*diene*)*iron* (35).—To a rapidly stirred solution of benzylamine (0.90 ml) in acetonitrile (10 ml) under nitrogen was added dropwise compound (5) (0.508 g) in acetonitrile (20 ml) over 1 h. The mixture was stirred for a further 0.5 h, and washed through neutral alumina (activity 1) with ether. Removal of solvent, followed by preparative t.l.c. on silica gel (ethyl acetate), gave pure compound (35) (0.301 g, 90%). Similar results were found using nitromethane as solvent for the reaction, and/or with the tetrafluoroborate salt; $\nu_{max.}$ ($CHCl_3$) 2 050, 1 975, and 1 485 cm^{-1}; δ($CDCl_3$) 7.25 (5 H, m, aromatics), 5.27 (1 H, dd, *J* 6.5, 2.5 Hz, 8-H), 3.67 (3 H, s, OMe), 3.35 (1 H, d) and 3.13 (1 H, d) (ABq, *J* 15 Hz, NCH_2Ph), 3.25 (1 H, m, 10-H), 2.70 (1 H, d, *J* 6.5 Hz, 7-H), 2.31 (2 H, m, CH_2NCH_2Ph), and 2.0—1.2 (8 H, methylenes); *m/e* (%) 409 (11), 381 (23), 353 (1), and 325 (100).

1-*Benzyl*-1-*azaspiro*[5.5]*undec*-7-*en*-9-*one* (37).—A mixture of anhydrous trimethylamine *N*-oxide (3.10 g) and the complex (35) (1.14 g) in *N*,*N*-dimethylacetamide (30 ml) were stirred under nitrogen for 5 h. The mixture was poured into brine and extracted with ethyl acetate; the extract was washed well with brine and water and dried ($MgSO_4$). This crude dienol ether was stirred under nitrogen for 2 h in 10% aqueous sulphuric acid–THF (1 : 3) (10 ml) after which the mixture was poured into aqueous sodium carbonate, and extracted with ether; the extract was then dried (Na_2CO_3). Flash chromatography [9] on silica gel (230—400 mesh, dichloromethane) under nitrogen pressure, gave the enone (37) (0.531 g, 75%), as a pale yellow oil, chromatographically homogeneous, which darkened with time; $\nu_{max.}$ ($CHCl_3$) 1 680 and 1 605 cm^{-1}; δ($CDCl_3$) 7.30 (5 H, m, aromatic), 6.88 (1 H, d, *J* 10 Hz, 7-H), 5.95, 1 H, d, *J* 10 Hz, 8-H), 3.81 (1 H, d) and 3.30 (1 H, d) (ABq, *J* 14 Hz, NCH_2Ph), 3.30 (2 H, m, CH_2N), and 2.7—1.0 (10 H, methylenes); *m/e* (%) 255 (12), 164 (26), and 91 (100) (Found: *M*, 255.1605; Calc. for $C_{17}H_{21}NO$: 255.1623).

Reactions of the Tosylate Salts (4) *and* (5) *with Anions, with Spontaneous Cyclisation.*—Reactions were carried out as follows. To a stirred solution or suspension of the salt in dry THF under nitrogen at −78 °C was added dropwise a suspension of 3 equiv. of sodiomalononitrile or methyl sodiocyanoacetate in THF (from 3 equiv. of sodium hydride and a slight excess of malononitrile or methyl cyanoacetate in THF). The mixture was then allowed to warm to ambient temperature after which it was stirred for 0.5—1 h, poured into brine, extracted with ether, and dried ($MgSO_4$). The products were then separated and purified by preparative t.l.c. on silica gel (10% ethyl acetate in benzene). The spirocycles (41), (42), (45), and (46) were isolated as crystalline products, but the products of addition to the C-5 position of the dienyl system [*i.e.* (39) and (40)] were isolated as yellow oils which could not be crystallised.

Tricarbonyl{6—9-η-(1,1-*di-cyano*-8-*methoxyspiro*[4.5]*deca*-6,8-*diene*}*iron* (41).—The tetrafluoroborate salt (4) (0.304 g) in THF (4 ml), and 3 equiv. of sodiomalononitrile in THF (4 ml) gave, after chromatography, the spirocycle (41) (0.110 g) (55%) and compound (39; R^1 — $CH(CN)_2$)] (0.070 g, 26%). Recrystallisation from hexane gave pure compound (41), m.p. 90—92 °C; $\nu_{max.}$ ($CHCl_3$) 2 250, 2 060, 1 980, and 1 487 cm^{-1}; δ($CDCl_3$) 5.26 (1 H, dd, *J* 6, 2.5 Hz, 7-H), 3.72 (3 H, s, OMe), 3.34 (1 H, m, 9-H), 2.57 (1 H, d, *J* 6 Hz, 6-H), and 2.5—1.6 (8 H, methylenes); *m/e* (%) 354 (7), 326 (15), 298 (12), and 270 (100) (Found: C, 54.35; H, 4.1; N, 7.9. Calc. for $C_{16}H_{14}FeN_2O_4$: C, 54.26; H, 3.98; N, 7.91%).

Tricarbonyl{6—9-η-(1-*cyano*-1-*methoxycarbonyl*-8-*methoxyspiro*[4.5]*deca*-6,8-*diene*}*iron* (42).—The tetrafluoroborate salt (4) (0.299 g) in THF (6 ml) and methyl sodiocyanoacetate (3 equiv.) in T HF (3 ml) gave, after chromatography, the spirocycle (42) (0.102 g, 47%) and [39; R^1 = $CH(CN)CO_2Me$] (0.036 g, 12%). Recrystallisation of the product from hexane gave (42), as a 2 : 1 mixture of diastereoisomers (see text), $\nu_{max.}$ ($CHCl_3$) 2 235, 2 045, 1 980, 1 738, and 1 490 cm^{-1}; δ($CDCl_3$) 5.25 and 4.99 (1 H, dd, each, *J* 6, 2.5 Hz, 7-H), 3.79 and 3.77 (3 H, s, each, OMe), 3.62 and 3.60 (3 H, s, each, CO_2Me), 3.35 and 3.23 (1 H, dd, each, *J* 6, 2.5 Hz, 9-H), and 2.75—1.4 (methylenes and 6-H); *m/e* (%) 387 (5), 359 (18), 331 (1), and 303 (100) (Found: C, 52.95; H, 4.45; N, 3.7. Calc. for $C_{17}H_{17}FeNO_6$: C, 52.74; H, 4.43; N, 3.62%).

Tricarbonyl{7—10-η-(1,1-*di-cyano*-9-*methoxyspiro*[5.5]*undeca*-7,9-*diene*}*iron* (45).—The hexafluorophosphate salt (5) (0.156 g) in THF (4 ml) and sodiomalononitrile (3 equiv.) in THF (2 ml) gave, after chromatography, the spirocycle (45) (0.058 g, 53%) and compound [40; R^1 = $CH(CN)_2$] (0.033 g, 20%). Recrystallisation of the product from hexane gave pure compound (45), m.p. 116—117 °C; $\nu_{max.}$ ($CHCl_3$) 2 250, 2 060, 1 985, and 1 490 cm^{-1}; δ($CDCl_3$) 5.20 (1 H, dd, *J* 6.5, 2 Hz, 8-H), 3.71 (3 H, s, OMe), 3.26 (1 H, m, 10-H), 2.52 (1 H, d, *J* 6.5 Hz, 7-H), and 2.45—1.1 (10 H, methylenes); *m/e* (%), 368 (6), 340 (10), 312 (12), and 284 (100) (Found: C, 55.35; H, 4.4; N, 7.5. Calc. for $C_{17}H_{16}FeN_2O_4$: C, 55.46; H, 4.15; N, 7.61%).

Tricarbonyl{7—10-η-(1-*cyano*-1-*methoxycarbonyl*-9-*methoxyspiro*[5.5]*undeca*-7,9-*diene*}*iron* (46).—The tetrafluoroborate salt (5) (0.282 g) in THF (6 ml) and methyl sodiocyanoacetate (3 equiv.) in THF (2 ml) gave, after chromatography, the spirocycle (46) (0.134 g, 66%) and compound [40; R^1 = $CH(CN)CO_2Me$]; the latter product was contaminated with methyl cyanoacetate, inseparable on t.l.c. Recrystallisation of the former product from hexane gave compound (46), as a 9 : 1 mixture of diastereoisomers (see text); $\nu_{max.}$ ($CHCl_3$) 2 245, 2 055, 1 985, 1 735, and 1 490 cm^{-1}; δ($CDCl_3$) 5.01 (1 H, m, 8-H), 3.81 and 3.79 (3 H, s, each, OMe), 3.61 and 3.58 (3 H, s, each, CO_2Me) 3.26 (1 H, m, 10-H), and 2.7—1.1 (methylenes and 7-H); *m/e* (%) 401 (5), 373 (11), 345 (5), 317 (100), and 315 (8) (Found: C, 53.9; H, 4.95; N, 3.5. Calc. for $C_{18}H_{19}FeNO_6$: C, 53.89; H, 4.77; N, 3.49%).

Removal of Iron, and Hydrolysis of Dienol Ethers.—Reactions were carried out as follows. Solutions of the complexes (41), (42), (45), and (46) in dry benzene or *N*,*N*-dimethylacetamide (DMA) were stirred under nitrogen with anhydrous trimethylamine *N*-oxide. Benzene solutions were decanted, washed with brine and water, dried ($MgSO_4$), and solvent was removed under reduced pressure. DMA solutions were poured into brine, extracted with ethyl acetate, washed well with water, dried ($MgSO_4$), and solvent was removed under reduced pressure. The crude dienol ethers were dissolved in 80% aqueous methanol and stirred with oxalic acid for 0.5—1 h; the mixtures were then poured into dilute aqueous sodium hydrogen carbonate, extracted with ether in the usual way and the extracts dried ($MgSO_4$), and evaporated under reduced pressure. Preparative t.l.c. (silica gel–ether) gave the enones (43), (44), (47), and (48).

1,1-*Dicyanospiro*[4.5]*dec*-6-*en*-8-*one* (43).—The complex (41) (0.104 g) and anhydrous trimethylamine *N*-oxide (0.22 g, 10 equiv.) were stirred in DMA (3 ml) under nitrogen for 2 h. The crude dienol ether was stirred with oxalic acid (0.1 g) in 80% aqueous methanol (5 ml) for 40 min, giving, after extraction and purification as described above, the enone (43) (0.020 g, 34%). Recrystallisation from dichloromethane–hexane gave the spirocycle (43), m.p. 86—87.5 °C; $\nu_{max.}$ (CCl_4) 2 260, 1 697, and 1 615 cm^{-1}; $\delta(CDCl_3)$ 6.83 (1 H, d, *J* 10.5 Hz, 6-H), 6.18 (1 H, d, *J* 10.5 Hz, 7-H), and 3.0—1.9 (10 H, methylenes); *m/e* (%), 200 (34) and 107 (100) (Found: C, 71.80; H, 6.22; N, 14.15%; *M*, 200.0948. Calc. for $C_{12}H_{12}N_2O$: C, 71.98; H, 6.04; N, 13.99%; *M*, 200.0949).

1-*Cyano*-1-(*methoxycarbonyl*)*spiro*[4.5]*dec*-6-*en*-8-*one* (44).—The complex (42) (0.058 g) and anhydrous trimethylamine *N*-oxide (0.10 g, 10 equiv.) were stirred in DMA (3 ml) under nitrogen for 3 h. Isolation of the crude dienol ether, hydrolysis, and purification as for compound (43) gave a diastereoisomeric mixture of the enones (44) (0.011 g, 32%) as a colourless oil which could not be crystallised; $\nu_{max.}$ (CCl_4) 2 250, 1 750, 1 693, and 1 619 cm^{-1}; $\delta(CDCl_3)$ 7.02 and 6.68 (1 H, d, each, *J* 10 Hz, 6-H), 6.05 and 5.92 (1 H, d, each, *J* 10 Hz, 7-H), 3.78 (3 H, s, CO_2Me), and 2.9—1.7 (methylenes); *m/e* (%) 233 (19), and 122 (100) (Found: *M*, 233.1063. Calc. for $C_{13}H_{15}NO_3$: 233.1074).

1,1-*Dicyanospiro*[5.5]*undec*-7-*en*-9-*one* (47). The complex (45) (0.102 g) and anhydrous trimethylamine *N*-oxide (10 equiv.) were stirred at room temperature in dry benzene (35 ml) under nitrogen for 5.5 h. Extraction as above gave crude dienol ether (0.062 g). A portion of this (0.051 g) was stirred with oxalic acid (0.06 g) in 80% aqueous methanol (4 ml) for 50 min, to give the enone (47) (0.028 g, 57%). Recrystallisation of the product from dichloromethane–hexane gave pure compound (47), m.p. 74—76 °C; $\nu_{max.}$ (CCl_4) 2 255, 1 695, and 1 605 cm^{-1}; $\delta(CDCl_3)$ 6.94 (1 H, d, *J* 10.5 Hz, 7-H), 6.15 (1 H, d, *J* 10.5 Hz, 8-H), and 2.6—1.5 (12 H, methylenes); *m/e* (%) 214 (69) and 68 (100) (Found: C, 73.00; H, 6.45; N, 12.93%; *M*, 214.1106. Calc. for $C_{13}H_{14}N_2O$: C, 72.87; H, 6.59; N, 13.07; *M*, 214.1105).

1-*Cyano*-1-*methoxycarbonylspiro*[5.5]*undec*-7-*en*-9-*one* (48).—The complex (46) (0.031 g) and anhydrous trimethylamine *N*-oxide (10 equiv.) were stirred in DMA (3 ml) for 4 h. The crude dienol ether was stirred with oxalic acid (0.05 g) in 80% aqueous methanol (2.5 ml) for 40 min yielding, after extraction and purification, the enone (48) (0.012 g, 60%). Recrystallisation of the product from ether–pentane gave compound (48) as a colourless crystalline mixture of diastereoisomers, $\nu_{max.}$ (CCl_4) 2 240, 1 750, 1 695, and 1 620 cm^{-1}; $\delta(CDCl_3)$ 7.3—7.1 (1 H, m, 7-H), 5.99 (1 H, d, *J* 10.5 Hz, 8-H), 3.78 and 3.76 (3 H, s, each, CO_2Me), and 2.6—1.2 (methylenes); *m/e* (%) 247 (47), and 108 (100) (Found: C, 67.75; H, 7.05; N, 5.8. Calc. for $C_{14}H_{17}NO_2$: C, 68.00; H, 6.93; N, 5.66%).

Tosylate Displacement Reactions.—The complexes (21), (22), and (24)—(26) were prepared according to the following general method. A suspension of the appropriate sodio-derivative was prepared from sodium hydride (50% dispersion in mineral oil, washed under nitrogen with pentane) and a slight excess of the active methylene compound in dioxan or THF (2—3 ml). After effervescence had subsided, the tosylate (19) or (20) was added in the appropriate solvent (6—10 ml) and the mixture was then stirred at reflux under an atmosphere of dry nitrogen for 4—24 h. The reaction mixtures were poured into brine and extracted with ether in the usual way; the extracts were then washed with water and dried ($MgSO_4$). Preparative t.l.c. (silica gel/10% ethyl acetate in benzene) gave the complexes, in some cases as oils which could not be crystallised.

In two cases, (24) and (25), some aromatic contamination was found, due to decomposition during the reaction. This co-chromatographed with the complexes, and instability of the complexes at elevated temperatures prevented distillation. The crude compounds could be used in the later hydride-abstraction steps, since the dienyl salts thus formed are ether-insoluble.

Tricarbonyl[3-(4-*methoxycyclohexa*-1,3-*dienyl*)*propylmalononitrile*]*iron* (21).—The tosylate (19) (0.633 g) and sodiomalononitrile (3 equiv.) gave after 7.5 h in refluxing dioxan (6 ml), extraction, and purification, the complex (21) (0.334 g, 70.5%), which was recrystallised from ether–hexane, to give pale yellow needles, m.p. 97.5—99 °C; $\nu_{max.}$ ($CHCl_3$) 2 260, 2 045, and 1 970 cm^{-1}; $\delta(CDCl_3)$ 5.23 (1 H, d, *J* 5 Hz, 3-H), 4.97 (1 H, d, *J* 5 Hz, 2-H), 3.76 (1 H, t, *J* 6 Hz, $CH(CN)_2$), 3.49 (3 H, s, OMe), and 2.6—1.3 (10 H, methylenes); *m/e* (%) 356 (1), 328 (5), 300 (16), 272 (23), and 270 (100) (Found: C, 53.95; H, 4.6; N, 7.8. Calc. for $C_{16}H_{16}FeN_2O_4$: 3, 53.96; H, 4.53; N, 7.87%).

Tricarbonyl{*methyl* [3-(4-*methoxycyclohexa*-1,3-*dienyl*)-*propyl*]*cyanoacetate*}*iron* (22). The tosylate (19) (0.096 g) and methyl sodiocyanoacetate (3 equiv.), in the presence of sodium iodide (0.031 g, 1 equiv.) gave, after 5 h at reflux in THF (4 ml), extraction and purification, a diastereoisomeric mixture of the cyanoesters (22) (0.055 g, 66%), as a yellow oil which could not be crystallised; $\nu_{max.}$ ($CHCl_3$) 2 250, 2 035, 1 965, and 1 750 cm^{-1}; $\delta(CDCl_3)$ 5.19 (1 H, d, *J* 4.5 Hz, 3-H), 4.92 (1 H, d, *J* 4.5 Hz, 2-H), 3.83 (3 H, s, CO_2Me), 3.5 [1 H, m, obscured, $CH(CN)CO_2Me$], 3.46 (3 H, s, OMe), and 2.6—1.2 (10 H, methylenes); *m/e* (%) 389 (0.5), 361 (2), 333 (16), 305 (28), and 303 (100).

Tricarbonyl[4-(4-*methoxycyclohexa*-1,3-*dienyl*)*butylmalononitrile*]*iron* (24).—The tosylate (20) (0.404 g) and sodiomalononitrile (3 equiv.) gave, after 8 h at reflux in dioxan (10 ml), extraction and purification, the product (24) (0.197 g, 63%), as a yellow–green oil, containing *ca.* 15% aromatic material (n.m.r.), inseparable by repeated chromatography; $\nu_{max.}$ ($CHCl_3$) 2 265, 2 045, and 1 965 cm^{-1}; $\delta(CDCl_3)$ 5.17 (1 H, d, *J* 5 Hz, 3-H), 4.91 (1 H, d, *J* 5 Hz, 2-H), 3.70 (1 H, t, *J* 6.5 Hz, $CH(CN)_2$), 3.44 (3 H, s, OMe), and 2.7—1.3 (12 H, methylenes); *m/e* (%) 370 (0.5), 342 (1), 314 (19), 286 (15), and 284 (100).

Tricarbonyl{methyl [4-(4-methoxycyclohexa-1,3-dienyl)-butyl]cyanoacetate}iron (25).—The tosylate (20) (0.398 g) and methyl sodiocyanoacetate (3 equiv.) gave, after 23.5 h at reflux in dioxan (10 ml), extraction, and purification, the cyanoester (25) (0.176 g, 52%, not optimised), as a green oil which could not be crystallised, and which contained *ca.* 15% aromatic material (n.m.r.); $\nu_{max.}$ ($CHCl_3$) 2 260, 2 040, 1 965, and 1 750 cm^{-1}; δ($CDCl_3$) 5.16 (1 H, d, *J* 5 Hz, 3-H), 4.90 (1 H, d, *J* 5 Hz, 2-H), 3.80 (3 H, s, CO_2Me), 3.6—3.4 [4 H, m, OMe and C*H*(CN)CO_2Me], and 2.5—1.3 (12 H, methylenes); *m/e* (%) 403 (0.5), 375 (2), 347 (30), 319 (27), and 317 (100).

Tricarbonyl{dimethyl [4-(4-methoxycyclohexa-1,3-dienyl)-butyl]malonate}iron (26). The tosylate (20) (0.105 g) and dimethyl sodiomalonate (4 equiv.) gave, after 4 h at reflux in dioxan (8 ml), extraction, and purification, the diester (26) (0.072 g, 75%), as a pale yellow-green oil which could not be crystallised, but which was free from aromatic material (n.m.r.); $\nu_{max.}$ ($CHCl_3$) 2 040, 1 965, 1 760, and 1 745 cm^{-1}; δ($CDCl_3$) 5.15 (1 H, d, *J* 4.5 Hz, 3-H), 4.88 (1 H, d, *J* 4.5 Hz, 2-H), 3.72 (6 H, s, 2 × CO_2Me), 3.5—3.3 [4 H, m, OMe and C*H*($CO_2Me)_2$], and 2.5—1.2 (12 H, methylenes); *m/e* (%) 436 (0.5), 408 (0.5), 380 (8), 362 (71), and 121 (100).

Hydride Abstraction and Cyclisation of the Complexes (21) *and* (22).—The diene complex (21) (0.334 g) was stirred at reflux under nitrogen with triphenylmethylium (trityl) tetrafluoroborate (0.403 g, 1.3 equiv.) in dry dichloromethane (10 ml) for 1 h. Material not in solution was dissolved by further addition of dichloromethane. Addition of an excess of ether gave no isolable dienylium salts, using the usual procedure.[3] Solvent was removed, and the residues chromatographed with (i) 10% ethyl acetate in benzene and (ii) dichloromethane, to give the spirocycle (41) (0.134 g, 40%), identical (n.m.r., i.r., and t.l.c.) with that obtained above.

The diene complex (22) (0.120 g) was stirred at reflux under nitrogen with trityl tetrafluoroborate (0.203 g, 2 equiv.) in dry dichloromethane (10 ml) for 1 h. Solvent was removed under reduced pressure, and the gum was washed well with hexane to remove triphenylmethane. It was then dissolved in dichloromethane (10 ml) and stirred with water (2 ml) for 2 min, to destroy excess of trityl tetrafluoroborate. The layers were separated, the aqueous layer being extracted with a minimum of dichloromethane; the combined organic portions were dried ($MgSO_4$). In order to ensure complete cyclisation (*cf.* above), triethylamine (47 μl, 1.1 equiv.) was added to the filtered solution, which was then stirred under nitrogen for 45 min, washed with dilute hydrochloric acid, and dried ($MgSO_4$). Solvent was removed *in vacuo*, and the crude spirocycle was purified by preparative t.l.c. on silica (10% ethyl acetate in benzene) to give compound (42) (0.056 g, 47%), identical with the sample prepared above, but with a different proportion of diastereoisomers (n.m.r.).

Hydride Abstraction from the Complexes (24)—(26).—The dienylium complexes (9)—(11) were prepared according to the following general method. The diene complex and trityl tetrafluoroborate were stirred at reflux in dry dichloromethane (3—6 ml) for 1—2 h. The tetrafluoroborate salt was precipitated by addition of ether and extracted into a minimum of water. To this extract was added ammonium hexafluorophosphate (2.5 equiv.) in a minimum of water to give a precipitate which was extracted into dichloromethane, dried ($MgSO_4$), and evaporated under reduced pressure.

Tricarbonyl[{4-(4-methoxycyclohexa-2,4-dienylium)butyl} malononitrile]iron Hexafluorophosphate (9).—Complex (24) (0.170 g) and trityl tetrafluoroborate (0.199 g, 1.3 equiv.) with subsequent ammonium hexafluorophosphate (0.199 g, 2.5 equiv.) treatment, gave the salt (9) (0.103 g, 43%), as a yellow powder, m.p. 139—141 °C (decomp.), $\nu_{max.}$ (Nujol mull) 2 260, 2 110, and 2 050 cm^{-1}; δ(CD_3CN) 6.78 (1 H, dd, *J* 6, 3 Hz, 3-H), 5.56 (1 H, d, *J* 6 Hz, 2-H), 4.06 [1 H, t, *J* 7 Hz, CH($CN)_2$], 3.88 (1 H, m, 5-H), 3.76 (3 H, s, OMe), 2.97 (1 H, dd, *J* 15, 6.5 Hz, *endo*-6-H), and 2.5—1.2 (methylenes, *exo*-6-H at 2.30) (Found: C, 39.45; H, 3.4; N, 5.5. Calc. for $C_{17}H_{18}F_6FeN_2O_4P$: C, 39.71; H, 3.33; N, 5.45%).

Tricarbonyl{methyl [4-(4-methoxycyclohexa-2,4-dienylium)-butyl]cyanoacetate}iron Hexafluorophosphate (10). The complex (25) (0.285 g) and trityl tetrafluoroborate (0.288 g, 1.5 equiv.), with subsequent ammonium hexafluorophosphate (0.237 g, 2.5 equiv.) treatment, gave the salt (10) (0.112 g, 35%) as an orange gum which could not be crystallised, $\nu_{max.}$ (CH_2Cl_2) 2 255, 2 115, 2 060, and 1 750 cm^{-1}; δ(CD_3CN) 6.80 (1 H, dd, *J* 6, 2.5 Hz, 3-H), 5.57 (1 H, d, *J* 6 Hz, 2-H), 4.0—3.6 [8 H, 5-H, OMe, CO_2Me and C*H*(CN)-CO_2Me], 2.98 (1 H, dd, *J* 15.5, 6 Hz, *endo*-6-H), 2.31 (1 H, d, *J* 15.5 Hz, *exo*-6-H), and 2.2—1.1 (methylenes).

Tricarbonyl[dimethyl {4-(4-methoxycyclohexa-2,4-dienylium)butyl}malonate]iron Hexafluorophosphate (11).—The complex (26) (0.322 g) trityl tetrafluoroborate (0.296 g, 1.3 equiv.), with subsequent ammonium hexafluorophosphate (0.314 g) treatment gave the salt (11) (0.295 g, 69%), as an orange gum which could not be crystallised, $\nu_{max.}$ (CH_2Cl_2) 2 115, 2 060, 1 750, and 1 735 cm^{-1}; δ(CD_3CN) 6.80 (1 H, dd, *J* 6, 2.5 Hz, 3-H), 5.57 (1 H, d, *J* 6 Hz, 2-H), 3.90 (1 H, m, 5-H), 3.77 (3 H, s, OMe), 3.68 (6 H, s, 2 × CO_2-Me), 3.38 [1 H, t, *J* 7 Hz, C*H*($CO_2Me)_2$], 2.97 (1 H, dd, *J* 15, 6 Hz, *endo*-6-H), and 2.5—1.2 (methylenes, *exo*-6-H at 2.30).

Spiroannelation Reaction of the Dienylium Complexes (9)—(11).—*Complex* (9). To the salt (9) (0.088 g) in acetonitrile (4 ml) at 0 °C under N_2 was added triethylamine (27 μl, 1.1 equiv.). After being stirred for 20 min, the mixture was poured into dilute hydrochloric acid and extracted with ether in the usual way. The extract was dried ($MgSO_4$) and solvent removed under reduced pressure to give a yellow oil which was purified by preparative t.l.c. on silica gel (10% ethyl acetate in benzene), giving the crystalline spirocycle (45) (0.074 g, quantitative); this was identical (t.l.c., i.r., n.m.r., and m.p.) with the sample prepared above.

Complex (10). To the salt (10) (0.028 g) in dichloromethane (2 ml) at −78 °C under N_2 was added triethylamine (11 μl, 1.1 equiv.). Work-up as for compound (9) gave compound (46) (0.014 g, 80%) as a mixture of diastereoisomers, in a ratio different from that obtained above (n.m.r.), but individually identical (t.l.c. and i.r.).

Complex (11). To the salt (11) (0.121 g) in dichloromethane (5 ml) at −78 °C under nitrogen was added triethylamine (32 μl, 1.1 equiv.). Work-up as for compound (9) gave the complex (32) (0.083, 91%), as an exceedingly unstable green oil, which could not be crystallised. N.m.r. showed the presence of a 1 : 1 mixture of geometric isomers; $\nu_{max.}$ ($CHCl_3$) 2 050, 1 980, 1 753, 1 735, 1 615 (v. weak), and 1 490 cm^{-1}; δ($CDCl_3$) 5.2—5.0 (m) and 4.74 (t) (2 H, 1′-H and 3-H), 3.72 (6 H, s, 2 × CO_2Me), 3.63 (3 H, s, OMe), 3.55—3.1 [3 H, m, 2-H, 5-H, and C*H*($CO_2Me)_2$], and 2.4—1.2 (8 H, methylenes); *m/e* (%) 434 (2), 406 (3), 378 (10), 350 (100).

Cyclisation of the Complex (24): *a One-pot Procedure*.—The complex (24) (0.217 g) and trityl tetrafluoroborate (0.254 g, 1.3 equiv.) were stirred under nitrogen at reflux in dichloromethane (5 ml) for 1 h. Solvent was removed under reduced pressure and the residual orange gum was washed well with hexane and dissolved in wet acetonitrile (destroys excess of trityl tetrafluoroborate); the mixture was then cooled to 0 °C under nitrogen. Triethylamine (0.09 ml, 1.2 equiv.) was added, and the reaction was worked up and chromatographed as above, to give the spirocycle (45) (0.110 g, 51%), identical with that produced by other routes.

Tricarbonyl[2-(4-*methoxycyclohexa*-1,3-*dienyl*)*ethyl acetoacetate*]*iron* (28).—The primary alcohol complex (27) (0.30 g) was heated in benzene (5 ml) under reflux and a nitrogen atmosphere with diketen (0.5 ml, 50% solution in acetone) and a catalytic amount of toluene-*p*-sulphonic acid for 12 h. The mixture was cooled, poured into water, and extracted with ether. Preparative t.l.c. (silica gel, 10% ethyl acetate in benzene) gave the acetoacetate (28) as a yellow oil (0.24 g, 62%), $\nu_{max.}$ ($CHCl_3$) 2 040, 1 970, 1 755, and 1 710 cm^{-1}; δ($CDCl_3$) 5.20 (1 H, d, *J* 4 Hz, 3-H), 4.90 (1 H, d, *J* 4 Hz, 2-H), 4.15 (2 H, t, *J* 6 Hz, CH_2OAcAc), 3.45 (3 H, s, OMe), 3.53 (2 H, s, AcAc CH_2), 2.21 (3 H, s, COMe), and 2.4—1.5 (6 H, m); *M*, 378.

Tricarbonyl[2-(4-*methoxycyclohexa*-2,4-*dienylium*)*ethyl acetoacetate*]*iron Hexafluorophosphate* (12).—The above complex (28) (0.20 g) and trityl tetrafluoroborate (0.25 g) were refluxed in dichloromethane under nitrogen for 1 h. Work-up and anion exchange as for preceding dienylium complexes gave the complex (12) as a yellow solid (0.11 g, 40%), $\nu_{max.}$ (Nujol) 2 115, 2 075, 2 057, 1 754, and 1 710 cm^{-1}; δ(CD_3-CN) 6.83 (1 H, dd, $J_{2,3}$ 6, $J_{3,5}$ 3 Hz, 3-H), 5.70 (1 H, d, *J* 6 Hz, 2-H), 4.14 (2 H, t, *J* 6 Hz, CH_2OAcAc), 3.92 (1 H, m, 5-H), 3.78 (3 H, s, OMe), 3.51 (2 H, s, acetoacetate, CH_2), 3.03 (1 H, dd, J_{gem} 15.5, $J_{5,6}$ 6 Hz, *endo*-6-H), 2.20 (3 H, s, COMe), and 2.7—2.04 (3 H, m, CH_2 and *exo*-6-H) (Found: C, 36.8; H, 3.35. Calc. for $C_{16}H_{17}F_6FeO_7P$: C, 36.81; H, 3.28%). All attempts to cyclise this material using the above procedures led only to considerable decomposition.

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