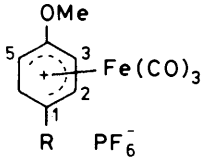
Organoiron Complexes in Organic Synthesis. Part 27.[1] Synthesis and Reactivity of Tricarbonyliron Derivatives of 1,2-Disubstituted 4-Alkoxycyclohexadienylium Cations

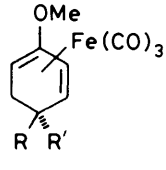
Anthony J. Pearson *,† **and Trevor R. Perrior**
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW
David A. Griffin
I.C.I.Plant Protection Division, Jealott's Hill Research Station, Bracknell, Berkshire RG12 6EY

The synthesis, and reactions with stable enolate nucleophiles, of 1,2-disubstituted 4-alkoxycyclohexadienylium(tricarbonyl)iron complexes (3a), (3b), (3c), and (3d) is described. Only the 1,2-dimethyl-4-isopropoxycyclohexadienylium complex (3b) was found to react with nucleophiles with sufficiently high regioselectivity to allow a useful method of preparation of 3,4,4-trisubstituted cyclohexenones.

As a logical extension of our current work [2] on the reactivity and synthetic applications of complexes of general structure (1), which for a range of substituents R undergo nucleophile addition predominantly to the substituted dienylium terminus C-1 to give complexes (2), we initiated the present study of complexes of structure (3), in order to determine the regioselectivity of nucleophile addition, and in the hope that synthetic programmes could be developed which exploit their behaviour. We have previously shown that the bicyclic derivatives (4) and (5) undergo high yielding addition of dimethyl sodiomalonate at the angular position, to give the complexes (6) and (7) respectively,[3] and so we anticipated similar behaviour for the monocyclic analogues (3). The present paper describes the results of these studies.

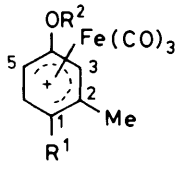


(1)

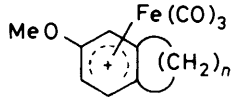


(2)

a ; R = Me
b ; R = $(CH_2)_2CO_2Me$

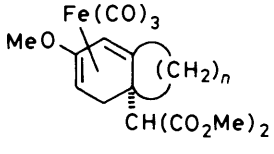


(3)

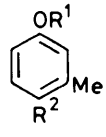


(4) $n = 3$
(5) $n = 4$

a ; $R^1 = R^2 = Me$
b ; $R^1 = Me, R^2 = Pr^i$
c ; $R^1 = (CH_2)_2CO_2Me, R^2 = Me$
d ; $R^1 = (CH_2)_2CO_2Me, R^2 = Pr^i$
e ; $R^1 = (CH_2)_3CH(CN)_2, R^2 = Me$



(6) $n = 3$
(7) $n = 4$



(8)

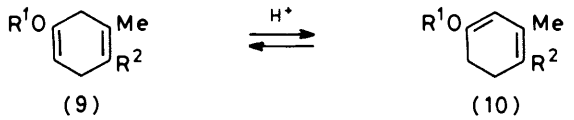
a ; $R^1 = R^2 = Me$
b ; $R^1 = Pr^i, R^2 = Me$
c ; $R^1 = Me, R^2 = CHO$
d ; $R^1 = Pr^i, R^2 = CHO$
e ; $R^1 = Me, R^2 = Br$
f ; $R^1 = Pr^i, R^2 = Br$
g ; $R^1 = Me, R^2 = CH{=}CHCO_2H$
h ; $R^1 = Pr^i, R^2 = CH{=}CHCO_2H$

Results and Discussion

(a) *Preparation of Complexes.*—We first focused our attention on the dimethyl substituted complexes (3a) and (3b), bearing methoxy- and isopropoxy-substituents at the 4-position, since we have previously shown [4] that, in general, use of a 4-isopropoxy-group leads to a greater preference for nucleophile addition to C-1. Thus, we could determine the relative directing power of methoxy- and isopropoxy-groups in this series of complexes. These compounds were readily available from the aromatic precursors (8a) and (8b) by standard methods. Thus, metal–ammonia reduction afforded the cyclohexa-1,4-diene derivatives (9a) and (9b) which were (partially) conjugated to the 1,3-dienes (10a) and (10b) and these were treated with pentacarbonyliron at elevated temperature to give the diene complexes (11a) and (11b) in good yield. Both of these complexes underwent regiospecific hydride abstraction on treatment with triphenylmethylium hexafluorophosphate to give the required dienylium complexes (3a) and (3b), respectively, despite the presence of the relatively bulky isopropoxy-group in complex (11b) (see later).

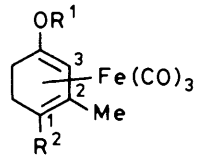
We next addressed ourselves to the problem of preparing complexes (3c) and (3d), which have a methyl substituent at C-2 and a terminally functionalised three-carbon chain at C-1, in anticipation that these complexes might provide useful intermediates for the synthesis of spirocyclic systems related to β-vetivone.[5] As precursors we required the aldehydes (8c) and (8d), and whilst (8c) has been reported [6] to be the only product from Vilsmeier formylation of 3-methylanisole, in our hands this method gave mixtures from formylation *ortho-* and *para-* to the methoxy-substituent, under a wide range of reaction conditions. Only a marginal improve-

† *Present address:* Department of Chemisty, Case Western Reserve University, Cleveland, Ohio 44106, U.S.A.



(9) (10)

a ; $R^1 = R^2 = Me$
b ; $R^1 = Pr^i$, $R^2 = Me$
c ; $R^1 = Me$, $R^2 = (CH_2)_2CO_2Me$
d ; $R^1 = Pr^i$, $R^2 = (CH_2)_2CO_2Me$

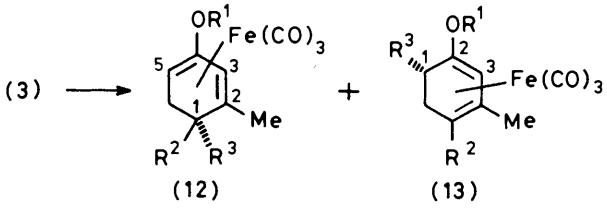


(11)

a ; $R^1 = R^2 = Me$
b ; $R^1 = Pr^i$, $R^2 = Me$
c ; $R^1 = Me$, $R^2 = (CH_2)_2CO_2Me$
d ; $R^1 = Pr^i$, $R^2 = (CH_2)_2CO_2Me$
e ; $R^1 = Me$, $R^2 = (CH_2)_2CH_2OH$
f ; $R^1 = Me$, $R^2 = (CH_2)_2CH_2OTs$
g ; $R^1 = Me$, $R^2 = (CH_2)_3CH(CN)_2$

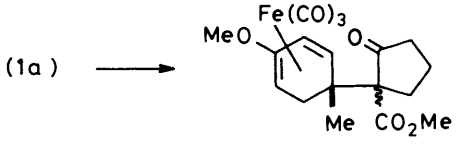
ment in *para*/*ortho* ratio was observed for 3-methylisopropoxybenzene, and we therefore adopted the indirect method recently described by Nelson and Uschak [7] for effecting this transformation. Thus 3-methylanisole was brominated to give the bromo-compound (8e), and the derived Grignard reagent was treated with *N*,*N*-dimethylformamide to give the desired aldehyde (8c) in good overall yield. Bromination of 3-methylisopropoxybenzene under the same conditions (−10 °C) resulted in the formation of considerable amounts of dibromination product, but this was improved by conducting the reaction at lower temperatures (−30 °C). The resulting bromide (8f) was converted into the aldehyde (8d) as above. Both aldehydes (8c) and (8d) were converted into the cinnamic acids (8g) and (8h) under conventional Knoevenagel reaction conditions. Birch reduction of the cinnamic acids, followed by immediate methylation gave the cyclohexa-1,4-diene derivatives (9c) and (9d) which were (partially) conjugated to (10c) and (10d), respectively, and the mixtures were converted into the required diene-$Fe(CO)_3$ complexes (11c) and (11d) by treatment with $Fe_2(CO)_9$ in warm acetone or toluene (pentacarbonyliron in hot di-n-butyl ether gave lower yields). These complexes were converted into the desired dienylium complexes (3c) and (3d), though the latter was obtained in disappointing yield (38%).

Reactions of Dienylium Complexes with Nucleophiles.—The above dienylium complexes (3a—d) were treated with carbanions derived from dimethyl malonate and malononitrile, as their potassium and sodium salts, respectively (dimethyl potassiomalonate was previously found to give better regioselectivity for C-1 than sodio- or lithio-derivatives [8]), and the ratios of regioisomeric products (12) and (13), arising from nucleophile addition at C-1 and C-5, respectively, were estimated from accurately integrated expanded n.m.r. spectra. This was possible because the narrow doublet (long-range coupling) due to 3-H in complexes of structure (12) is clearly distinguishable from the singlet due to 3-H in complexes (13). The results of these studies are shown in the Table. The pure

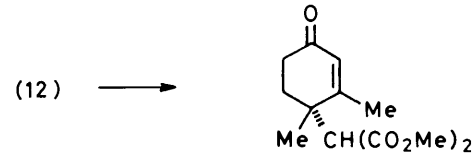


(12) (13)

a ; $R^1 = R^2 = Me$, $R^3 = CH(CO_2Me)_2$
b ; $R^1 = R^2 = Me$, $R^3 = CH(CN)_2$
c ; $R^1 = Pr^i$, $R^2 = Me$, $R^3 = CH(CO_2Me)_2$
d ; $R^1 = Pr^i$, $R^2 = Me$, $R^3 = CH(CN)_2$
e ; $R^1 = Pr^i$, $R^2 = Me$, $R^3 = MeO_2C \cdot \overline{CCO \cdot CH_2CH_2CH_2}$
f ; $R^1 = Me$, $R^2 = (CH_2)_2CO_2Me$, $R^3 = CH(CO_2Me)_2$
g ; $R^1 = Me$, $R^2 = (CH_2)_2CO_2Me$, $R^3 = CH(CN)_2$
h ; $R^1 = Pr^i$, $R^2 = (CH_2)_2CO_2Me$, $R^3 = CH(CO_2Me)_2$
i ; $R^1 = Pr^i$, $R^2 = (CH_2)_2CO_2Me$, $R^3 = CH(CN)_2$



(14)



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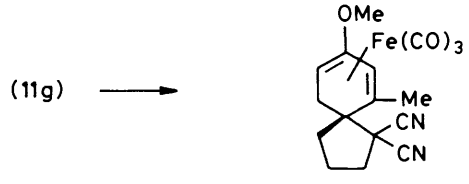

(16)

compounds were subsequently obtained by chromatography and/or crystallisation where this was possible. We also studied the reaction of the complex (3b) with methyl 2-oxo-1-sodiocyclopentanecarboxylate, which gave a mixture of (12e) and (13e) in a ratio of *ca.* 1 : 6. This result is in sharp contrast to the reaction of the disubstituted cyclohexadienylium complex (1a) with the same enolate nucleophile, which produces *exclusively* the complex (14) in essentially quantitative yield,[9] as a mixture of diastereoisomers. Reaction of (3a) with dimethyl malonate and malononitrile anions gave a more favourable ratio of products (12) and (13), but again this contrasts with the same reactions of (1a) which occur exclusively at C-1.[3] A considerable improvement in regioselectivity was obtained by employing the 4-isopropoxy-group, as noted in our earlier studies of disubstituted complexes,[4] now providing a more practical procedure for establishing a quaternary

Table. Reactions of dienylium complexes (3) with stable carbonium nucleophiles

Dienylium complex	Nucleophile	Products	Ratio	Yield (%)
(3a)	$KCH(CO_2Me)_2$	(12a) + (13a)	3.6 : 1	76
(3a)	$NaCH(CN)_2$	(12b) + (13b)	2.7 : 1	65
(3b)	$KCH(CO_2Me)_2$	(12c) + (13c)	9.0 : 1	86
(3b)	$NaCH(CN)_2$	(12d) + (13d)	10.4 : 1	61
(3b)	$NaC(CO_2Me)COCH_2CH_2$	(12e) + (13e)	*ca.* 1 : 6	43
(3c)	$KCH(CO_2Me)_2$	(13f)	*a*	89
(3c)	$NaCH(CN)_2$	(13g)	*a*	72
(3d)	$KCH(CO_2Me)_2$	(12h) + (13h)	1 : 3.6	97
(3d)	$NaCH(CN)_2$	(12i) + (13i)	1 : 2.0	85

[a] No isomer (12) detected.

centre at C-1. The potential utility of this reaction is demonstrated by the ready conversion of complex (12c) into the 3,4,4-trisubstituted cyclohexenone (15).

The functionalised complexes (3c) and (3d) were next studied. Reaction of the 4-methoxy-derivative (3c) with dimethyl potassiomalonate and sodiomalononitrile gave *exclusively* the products, (13f) and (13g), of addition at the unsubstituted dienyl terminus C-5. This again contrasts with the reactions of the disubstituted complex (1b) which gives *ca.* 85% of the complexes arising from addition to the substituted terminus C-1. Use of the 4-isopropoxy-group, in complex (3d), led only to marginal improvement, nucleophile attack still occurring predominantly at C-5.

In view of our inability to control the addition of nucleophile to complexes (3c) and (3d), we investigated the *intramolecular* nucleophile addition in this series, analogous to the spiroannelation reactions previously reported for simpler complexes.[10] Accordingly, the ester complex (11c) was reduced to the primary alcohol (11e) with di-isobutylaluminium hydride, and this was converted into tosylate (11) under standard conditions. Tosylate displacement was effected using an excess of sodiomalononitrile in refluxing THF to give the complex (11g) in 61% overall yield from the ester. Treatment of (11g) with trityl hexafluorophosphate resulted in the formation of a mixture of the dienylium complex (3e) and the spirocyclic compound (16). This mixture was not isolated but was treated directly with triethylamine to effect complete conversion of (3e) into (16) which could be isolated in 41% yield.

In summary, the extra substitution in complexes (3) compared to that in (1) poses serious problems of regioselectivity of nucleophile addition which can be overcome only in fairly simple cases by use of a 4-isopropoxy-substituent. However, intramolecular delivery of nucleophile does not appear to be affected by the presence of an extra substituent at C-2. The behaviour of complexes (3c) and (3d) is disappointing in view of the excellent regioselectivity observed for bicyclic systems (4) and (5), and presumably reflects the greater steric demand of freely rotating substituents at C-1 of the dienyl systems, compared to the conformationally fixed substituent found in the bicyclic compounds.

Experimental

I.r. spectra were recorded with a Perkin-Elmer 577, mass spectra with an A.E.I. MS12 (organometallics) or MS30 (organic compounds), and ^1H n.m.r. spectra with Varian EM390 (90 MHz) or Bruker WH250 (250 MHz) instruments. M.p.s were determined on a Kofler block and are uncorrected. All reactions and chromatographic operations involving iron complexes were conducted under an atmosphere of dry nitrogen.

Tricarbonyl[1—4-η-(4-*methoxy*-1,2-*dimethylcyclohexa*-1,3-*diene*)]*iron* (11a).—3,4-Dimethylanisole (8a) (52 g, 0.38 mol) was treated with sodium (30 g, 1.3 mol) in liquid ammonia (1.2 l) containing THF (200 ml) and ethanol (75 ml) for 3 h. Aqueous work-up and extraction with ether in the usual way gave the diene (9a) (44 g, 84%), b.p. 45 °C at 2 mmHg, $\nu_{max.}$ (CCl_4) 3 000—2 800, 1 705, and 1 675, cm^{-1}; δ(CCl_4) 4.44 (1 H, m, 5-H), 3.45 (3 H, s, OMe), 2.5br (4 H, methylenes), and 1.55 (6 H, s, 2 × Me); *m/z* (%) 138 (30) and 136 (100). Treatment of this compound (15.2 g) with a trace of toluene-*p*-sulphonic acid at 80 °C for 3 h, followed by work-up with aqueous sodium hydrogen carbonate and extraction with ether afforded a 1.4 : 1 mixture of the 1,3-diene (10a) and unchanged (9a) (14 g, 92%), as judged by the n.m.r. spectrum. Compound (10a) showed δ(CCl_4) 4.75 (1 H, s, 3-H), 3.57 (3 H, s, OMe), 2.18br (4 H, methylenes), and 1.67 (6 H, s, 2 × Me).

This mixture (14 g, 0.1 mol) was heated with pentacarbonyliron (35 ml) in refluxing dibutyl ether (90 ml) under nitrogen for 45 h. The reaction mixture was filtered through Celite, and solvent and pentacarbonyliron removed at aspirator pressure. The residue was chromatographed on alumina to give the *complex* (11a) as an orange oil (17.8 g, 64%), $\nu_{max.}$ (CCl_4) 2 040 and 1 965 cm^{-1}; δ($CDCl_3$) 5.13 (1 H, s, 3-H), 3.42 (3 H, s, OMe), 2.3—1.4 (4 H, m, methylenes), 2.06 (3 H, s, 2-Me), and 1.54 (3 H, s, 1-Me); *m/z* (%) 250 (22), 220 (18), and 192 (100).

Tricarbonyl[1—5-η-(4-*methoxy*-1,2-*dimethylcyclohexa*-2,4-*dienylium*)]*iron Hexafluorophosphate* (3a).—The diene complex (11a) (6.5 g, 23 mmol) was stirred with a solution of trityl hexafluorophosphate (15 g, 39 mmol) in refluxing dichloromethane (150 ml) for 5 h. Addition of a few drops of water to quench the excess of trityl cation followed by precipitation with ether and filtration gave the salt (3a) (10.4 g, 100%), $\nu_{max.}$ (CH_3CN) 2 105 and 2 060 cm^{-1}; δ(CD_3CN) 6.85 (1 H, d, *J* 3 Hz, 3-H), 3.90 (1 H, dd, *J* 6 and 3 Hz, 5-H), 3.78 (3 H, s, OMe), 3.02 (1 H, dd, *J* 15 and 6 Hz, *endo*-6-H), 2.30 (1 H, d, *J* 15 Hz, *exo*-6-H), 2.15 (3 H, s, 2-Me), and 1.72 (3 H, s, 1-Me) (Found: C, 34.0; H, 3.05. $C_{12}H_{13}F_6FeO_4P$ requires C, 34.15; H, 3.10%).

Tricarbonyl[1—4-η-(4-*isopropoxy*-1,2-*dimethylcyclohexa*-1,3-*diene*)]*iron* (11b).—4-Isopropoxy-1,2-dimethylbenzene (8b) (20 g, 0.12 mol) was subjected to Birch reduction with sodium (10 g, 0.43 mol) in liquid ammonia (500 ml), THF (80 ml), and ethanol (30 ml). Work-up as described for compound

(9a) gave the diene (9b) (17.8 g, 88%), b.p. 74 °C at 5 mmHg, $\nu_{max.}$ (CCl_4) 3 000—2 800 cm^{-1}; δ($CDCl_3$) 4.6br (1 H, 5-H), 4.30 (1 H, heptuplet, *J* 6 Hz, Me_2CH), 2.7br (4 H, methylenes), 1.70 (6 H, s, 2 × Me), and 1.24 (6 H, d, *J* 6 Hz, Me_2CH); *m/z* (%) 166 (14), 124 (30), 122 (36), and 109 (100). Conjugation of this compound (16 g) with toluene-*p*-sulphonic acid afforded a 1.5 : 1 mixture of (10b) and (9b) (14.4 g, 90%). Compound (10b) showed δ($CDCl_3$), 4.77 (1 H, s, 3-H), 4.32 (1 H, heptuplet, *J* 6 Hz, Me_2CH), 2.19 (4 H, br, methylenes), 1.70 (6 H, s, 2 × Me), and 1.21 (6 H, d, *J* 6 Hz, Me_2CH).

Treatment of this mixture with pentacarbonyliron as before gave the *complex* (11b) as an orange oil (71%), $\nu_{max.}$ ($CHCl_3$) 2 035, and 1 955 cm^{-1}; δ($CDCl_3$) 5.11 (1 H, s, 3-H), 4.06 (1 H, heptuplet *J* 6 Hz, Me_2CH), 2.3—1.3 (4 H, m, methylenes), 2.11 (3 H, s, 2-Me), 1.55 (3 H, s, 1-Me), and 1.3—1.1 (6 H, m, Me_2CH); *m/z* (%) 306 (5), 278 (34), 248 (36), and 220 (100).

Tricarbonyl[1—5-η-(4-*isopropoxy*-1,2-*dimethylcyclohexa*-2,4-*dienylium*]*iron Hexafluorophosphate* (3b).—The diene complex (11b) (3 g, 9.8 mmol) was subjected to hydride abstraction as described above for (3a) to afford the hexafluorophosphate (3b) (2.20 g, 45%), $\nu_{max.}$ (Me_3CN) 2 100 and 2 060 cm^{-1}; δ(CD_3CN) 6.74 (1 H, d, *J* 3 Hz, 3-H), 4.55 (1 H, heptuplet, *J* 6 Hz, Me_2CH), 3.90 (1 H, dd, *J* 6 and 3 Hz, 5-H), 3.02 (1 H, dd, *J* 15 and 3 Hz, *endo*-6-H), 2.35 (1 H, d, *J* 15 Hz, *exo*-6-H), 2.18 (3 H, s, 2-Me), 1.70 (3 H, s, 1-Me), 1.35 (d), and 1.30 (d) (6 H, *J* 6 Hz, diastereotopic Me_2CH) (Found: C, 37.25; H, 3.6. $C_{14}H_{17}F_6FeO_4P$ requires C, 37.36; H, 3.81%).

4-*Bromo*-3-*methylanisole* (8e).—Bromine (50 ml, 0.98 mol) was dissolved in carbon tetrachloride (300 ml) and added dropwise during 4 h to a well stirred suspension of iron filings (2 g) in *m*-methylanisole (103 ml, 0.82 mol) and carbon tetrachloride (800 ml) at −10 °C. After a further 7 h the excess of bromine was quenched by addition of water (3 l). Extraction with ether in the usual way and distillation of the organic residue afforded the *bromide* (145.4 g, 88%), b.p. 72 °C at 1.2 mmHg, $\nu_{max.}$ ($CHCl_3$) 1 610, 1 585, and 1 485 cm^{-1}; δ($CDCl_3$) 7.4 (1 H, d, *J* 9 Hz, 5-H), 6.8 (1 H, d, *J* 3 Hz, 2-H), 6.6 (1 H, dd, *J* 9 and 3 Hz, 6-H), 3.75 (3 H, s, OMe), and 2.35 (3 H, s, Me); *m/z* (%) 202 (100), 200 (92), and 121 (10) (Found: C, 47.5; H, 4.8. C_8H_9BrO requires C, 47.79; H, 4.51%).

4-*Methoxy*-2-*methylbenzaldehyde* (8c).—A solution of the bromide (8e) (50 g, 0.25 mol) and ethyl bromide (37 ml, 0.5 mol) in ether (650 ml) was added dropwise to a mechanically stirred suspension of magnesium turnings (20.7 g, 0.85 mol) in refluxing ether (400 ml). After 1 h the flask was cooled to −20 °C, and a solution of dimethylformamide (60 ml, 0.77 mol) in ether (250 ml) added *slowly* with vigorous stirring; the latter was continued for a further 45 min. The slurry was poured into a well stirred 1 : 1 mixture of water and saturated aqueous ammonium chloride. Ether extraction and distillation gave unchanged bromide (3.6 g, 7%) and the *aldehyde* (31 g, 93% based on bromide consumed), b.p. 106 °C at 1.2 mmHg, $\nu_{max.}$ ($CHCl_3$) 1 690 and 1 595 cm^{-1}; δ($CDCl_3$) 10.1 (1 H, s, CHO), 7.7 (1 H, d, *J* 9 Hz, 6-H), 6.8 (1 H, dd, *J* 9 and 3 Hz, 5-H), 6.7 (1 H, d, *J* 3 Hz, 3-H), 3.82 (3 H, s, OMe), and 2.6 (3 H, s, Me); *m/z* (%) 150 (38) and 149 (100) (Found: C, 72.0; H, 6.75. $C_9H_{10}O_2$ requires C, 71.98; H, 6.71%).

4-*Methoxy*-2-*methylcinnamic Acid* (8g).—The aldehyde (8c) (31 g, 0.21 mol) was stirred with malonic acid (41.6 g, 0.4 mol) and piperidine (2 ml) in pyridine (100 ml) at 100 °C for 17 h. The mixture was allowed to cool to room temperature and then poured into briskly stirred 10% hydrochloric acid. The solid was collected by filtration, washed thoroughly with water, and dried *in vacuo* to give the *acid* (8g) (36 g, 91%). An analytical sample was prepared as needles, m.p. 187 °C (from chloroform), $\nu_{max.}$ ($CHCl_3$) 1 695, and 1.625 cm^{-1}; δ(CD_3COCD_3) 7.95 (1 H, d, *J* 15 Hz, C*H*=, *trans*-stereochemistry), 7.66 (1 H, d, *J* 9 Hz, 6-H), 6.8 (2 H, m, 3-H and 5-H), 6.3 (1 H, d, *J* 15 Hz, =C*H*CO_2H), 3.8 (3 H, s, OMe), 2.4 (3 H, s, Me); *m/z* (%) 192 (100), 177 (20), and 175 (33) (Found: C, 68.7; H, 6.3. $C_{11}H_{12}O_3$ requires C, 68.74; H, 6.29%).

Methyl 3-(4-*Methoxy*-7-*methylcyclohexa*-1,4-*dienyl*)*propionate* (9c).—The cinnamic acid (8g) (10 g, 50 mmol) was stirred in liquid ammonia (500 ml) containing t-butyl alcohol (40 ml) and lithium metal (10 g) for 10 h. The blue colouration was quenched by the addition of solid ammonium chloride, and the ammonia evaporated overnight under a stream of nitrogen. The solid residue was taken up in ice-cold water and the pH adjusted to 5.5 by addition of formic acid at 5 °C. Ether extraction followed by washing with water until the washings were neutral and evaporation under reduced pressure afforded crude, unstable 3-(4-methoxy-2-methylcyclohexa-1,4-dienyl)propionic acid. This was esterified by treatment with potassium carbonate (12 g, 90 mmol) in refluxing acetone (300 ml) for 30 min, followed by the addition of dimethyl sulphate (5.2 ml, 55 mmol) and heating for a further 4 h. Aqueous work-up and extraction with ether afforded the *ester* (10.4 g, 99%). An analytical sample was prepared by Kugelrohr distillation, b.p. 85 °C at 0.1 mmHg, $\nu_{max.}$ (CCl_4) 2 990, 1 735, 1 695, and 1 665 cm^{-1}; δ(CCl_4) 4.48 (1 H, t, *J* 3 Hz, 5-H), 3.62 (3 H, s, CO_2Me), 3.47 (3 H, s, OMe), 2.85—2.4 (4 H, m, ring methylenes), 2.3 (3 H, s, Me), and 1.68br (4 H, 2 × CH_2); *m/z* (%) 210 (35) and 121 (100) (Found: C, 68.5; H, 8.6. $C_{12}H_{18}O_3$ requires C, 68.55; H, 8.63%).

Tricarbonyl{1—4-η-[*methyl* 3-(4-*methoxy*-2-*methylcyclohexa*-1,3-*dienyl*)*propionate*]}*iron* (11c).—Distillation of the 1,4-diene (9c) (9 g, 43 mmol), b.p. 120 °C at 1.5 mmHg afforded a 1.9 : 1 mixture of the 1,3-diene (10c) [δ(CCl_4) 4.67 (1 H, s, 3-H), 3.60 (3 H, s, CO_2Me), 3.49 (3 H, s, OMe), 2.8—2.5 (4 H, m, ring methylenes), 2.10 (3 H, s, Me), and 1.65br (4 H, 2 × CH_2] and (9c) (6.8 g, 76%). A portion of this mixture (2.3 g, 11 mmol) was treated with enneacarbonyliron (5 g, 14 mmol) in acetone (30 ml) at 35 °C for 4 h. Chromatography of the crude reaction mixture an basic alumina with ether eluant afforded the *ester complex* (11c) (1.6 g, 42%) as yellow crystals, m.p. 72—75 °C, $\nu_{max.}$ ($CHCl_3$) 2 040, 1 970, and 1 735 cm^{-1}; δ($CDCl_3$) 5.16 (1 H, s, 3-H), 3.66 (3 H, s, CO_2Me), 3.41 (3 H, s, OMe), 2.65—0.7 (8 H, m, methylenes), and 2.10 (3 H, s, Me); *m/z* (%) 350 (1), 322 (7), 294 (37), and 264 (100) (Found: C, 51.35; H, 5.2. $C_{15}H_{18}FeO_6$ requires C, 51.45; H, 5.18%).

Tricarbonyl[1—5-η-[4-*methoxy*-1-*methoxycarbonylethyl*-2-*methylcyclohexa*-2,4-*dienylium*)]*iron Hexafluorophosphate* (3c).—The ester complex (11c) (600 mg, 1.7 mmol) was refluxed with trityl hexafluorophosphate (800 mg, 2.1 mmol) in dichloromethane (5 ml) for 1 h. Work-up as above gave the hexafluorophosphate salt (3c) (670 mg, 80%), $\nu_{max.}$ (MeCN) 2 100, 2 050, and 1 735 cm^{-1}; δ(CD_3CN) 6.82 (1 H, d, *J* 3 Hz, 3-H), 3.95 (1 H, dd, *J* 6 and 3 Hz, 5-H), 3.78 (3 H, s, OMe), 3.66 (3 H, s, CO_2Me), 3.0 (1 H, dd, *J* 14 and 6 Hz, *endo*-6-H), and 2.5—2.0 (8 H, m, methylenes, Me, *exo*-6-H) (Found: C, 36.5; H, 3.9. $C_{15}H_{17}F_6FeO_6P$ requires C, 36.46; H, 3.47%).

2-*Bromo*-5-*isopropoxytoluene* (8f).—The *m*-isopropoxytoluene (100 g, 0.66 mol) was treated with bromide (43 ml, 0.84 mol) at −30 °C as above. Work-up and distillation (10-

cm fractionating column) afforded the *bromide* (8f) (125 g, 83%), b.p. (97—98 °C at 2.5 mmHg), $\nu_{max.}$ ($CHCl_3$) 2 980, 2 920, and 1 600 cm^{-1}; δ($CDCl_3$) 7.3 (1 H, d, *J* 9 Hz, 3-H), 6.7 (1 H, d, *J* 3 Hz, 6-H), 6.5 (1 H, dd, *J* 9 and 3 Hz, 4-H), 4.4 (1 H, heptuplet, *J* 6 Hz, Me_2CH), 2.25 (1 H, s, Me), and 1.2 (6 H, d, *J* 6 Hz, Me_2CH); *m/z* (%) 230 (16), 228 (19), 188 (97), and 186 (100) (Found: C, 52.35; H, 5.45. $C_{10}H_{13}BrO$ requires C, 52.42; H, 5.72%), together with 2,4-dibromo-5-isopropoxytoluene (34 g, 17%), b.p. 127 °C at 2.5 mmHg, δ($CDCl_3$) 7.68 (1 H, s, 3-H), 6.81 (1 H, s, 6-H), 4.49 (1 H, heptuplet, *J* 6 Hz, Me_2CH), 2.23 (3 H, s, Me), and 1.35 (6 H, d, *J* 6 Hz, Me_2CH).

4-*Isopropoxy*-2-*methylbenzaldehyde* (8d).—The bromide (8f) (20 g, 87 mmol) was treated with magnesium and then dimethylformamide as for (8e) above. Aqueous work-up and distillation gave the *aldehyde* (8d) (9.6 g, 70%), b.p. 116 °C at 1.3 mmHg, $\nu_{max.}$ ($CHCl_3$) 1 685 and 1 600 cm^{-1}; δ($CDCl_3$) 10.10 (1 H, s, CHO), 7.70 (1 H, d, *J* 9 Hz, 6-H), 6.72 (1 H, dd, *J* 9 and 2 Hz, 5-H), 6.70 (1 H, d, *J* 2 Hz, 3-H), 4.65 (1 H, heptuplet, *J* 5 Hz, Me_2CH), 2.60 (3 H, s, Me), 1.40 (6 H, d, *J* 5 Hz, Me_2CH); *m/z* (%) 178 (27), 136 (51), and 135 (100) (Found: C, 73.95; H, 7.8% $C_{11}H_{14}O_2$ requires C, 74.13, H, 7.92).

4-*Isopropoxy*-2-*methylcinnamic Acid* (8h).—Knoevenagel condensation of the aldehyde (8d) (9 g, 50 mmol) with malonic acid (13.3 g, 128 mmol) in pyridine (50 ml) and piperidine catalyst (0.5 ml) as for (8c) above, afforded the *cinnamic acid* (8h) (9 g, 73%). An analytical sample, prepared by recrystallisation from chloroform, had m.p. 124.5—125.5 °C, $\nu_{max.}$ ($CHCl_3$) 3 700br, 1 690, and 1 600 cm^{-1}; δ(CD_3COCD_3) 7.90 (1 H, d, *J* 16 Hz, =CHAr), 7.62 (1 H, d, *J* 9 Hz, 6-H), 6.78 (1 H, d, *J* 2 Hz, 3-H), 6.75 (1 H, dd, *J* 9 and 2 Hz, 5-H), 6.25 (1 H, d, *J* 16 Hz, $=CHCO_2H$), 4.65 (1 H, heptuplet, *J* 6 Hz, Me_2CH), 2.38 (3 H, s, Me), and 1.28 (6 H, d, *J* 6 Hz, Me_2CH); *m/z* (%) 220 (82) and 178 (100).

Methyl 3-(4-*Isopropoxy*-2-*methylcyclohexa*-1,4-*dienyl*)*propionate* (9d).—Birch reduction of (8h) (4 g, 18 mmol) as above, followed by acidification *to* p*H* 6 *at* −8 °C, and extraction with ether afforded the exceedingly unstable acid corresponding to (9d); it was esterified with dimethyl sulphate to afford the *ester* (9d) (3.1 g, 76%) b.p. 150 °C at 2 mmHg, contaminated with traces of aromatic material which could not be removed by chromatography or distillation. Compound (9d) showed $\nu_{max.}$ (CCl_4) 1 730 cm^{-1}; δ($CDCl_3$) 4.60 (1 H, br, 5-H), 4.38 (1 H, heptuplet, *J* 5 Hz, Me_2CH), 3.75 (3 H, s, CO_2Me), 3.0—2.1 (4 H, m, ring methylenes), 2.30 (3 H, s, Me), 1.8br (4 H, 2 × CH_2), 1.35 (6 H, d, *J* 5 Hz, Me_2CH); *m/z* (%) 238 (3), 236 (17), 194 (22), and 121 (100).

Tricarbonyl{1—4-η-[*methyl* 3-(4-*isopropoxy*-2-*methylcyclohexa*-1,3-*dienyl*)*propionate*]}*iron* (11d).—Distillation of the 1,4-diene (9d) (3 g, 12.6 mmol), b.p. 150 °C at 2 mmHg, afforded a 3 : 1 mixture of the 1,3-diene (10d) and unchanged (9d) (2.01 g, 67%) together with some aromatic material. Compound (10d) showed $\nu_{max.}$ (CCl_4) 1 730 and 1 600 cm^{-1}; δ($CDCl_3$) 4.85 (1 H, s, 3-H), 4.40 (1 H, heptuplet, *J* 5 Hz, Me_2CH), 3.75 (3 H, s, CO_2Me), 3.0—2.1 (4 H, m, obsc., ring methylenes), 2.30 (3 H, s, Me), 1.8 (4 H, m, obsc, 2 × CH_2), and 1.35 (6 H, d, *J* 5 Hz, Me_2CH).

This mixture was heated at 60 °C with enneacarbonyliron (5 g, 14 mmol) in toluene (20 ml) for 7 h. Chromatography of the crude reaction mixture on alumina with ether eluant afforded the *ester complex* (11d) (1.5 g, 47%) as an orange oil which could not be crystallised, $\nu_{max.}$ ($CHCl_3$) 2 035, 1 955, and 1 730 cm^{-1}; δ($CDCl_3$) 5.06 (1 H, s, 3-H), 4.30 (1 H, heptuplet, *J* 6 Hz, Me_2CH), 3.65 (3 H, s, CO_2Me), 2.6—1.4 (8 H, m, methylenes), 2.10 (3 H, s, Me), and 1.20 (d) and 1.12 (d) (6 H, *J* 6 Hz, diastereotopic Me_2CH); *m/z* (%) 378 (3), 350 (5), 322 (15), and 292 (100).

Tricarbonyl[1—5-η-(4-*isopropoxy*-1-*methoxycarbonylethyl*-2-*methylcyclohexa*-2,4-*dienylium*]*iron Hexafluorophosphate* (3d).—Hydride abstraction from the complex (11d) (1.33 g, 3.5 mmol) according to the above procedure afforded the *hexafluorophosphate salt* (3d) (0.7 g, 38%), $\nu_{max.}$(CH_3CN) 2 100, 2 060, and 1 735 cm^{-1}; δ(CD_3CN) 6.65 (1 H, d, *J* 3 Hz, 3-H), 4.52 (1 H, heptuplet, *J* 6 Hz, Me_2CH), 3.88 (1 H, dd, *J* 6 and 3 Hz, 5-H), 3.60 (3 H, s, CO_2Me), 2.92 (1 H, dd, *J* 15 and 6 Hz, *endo*-6-H), 2.32 (3 H, s, CO_2Me), 2.20 (1 H, d, *J* 15 Hz, *exo*-6-H), 2.15 (4 H, s, methylenes), and 1.30 (d) and 1.25 (d) (6 H, *J* 6 Hz, diastereotopic Me_2CH) (Found: C, 38.75; H, 3.95. $C_{17}H_{21}F_6FeO_6P$ requires C, 39.10; H, 4.05).

Reactions of the Dienyl Complexes with Nucleophiles.—The reactions were conducted in dry THF suspensions as previously described.[4]

Complex (3a) *with dimethyl potassiomalonate.* The complex salt (3a) (200 mg, 0.47 mmol) gave, on reaction with dimethyl potassiomalonate (1.2 equiv.), a 3.6 : 1 mixture of *tricarbonyl*[2—5-η-(*dimethyl* 4-*methoxy*-1,2-*dimethylcyclohexa*-2,4-*dienylmalonate*)]*iron* (12a) and *tricarbonyl*[2—5-η-(*dimethyl* 2-*methoxy*-4,5-*dimethylcyclohexa*-2,4-*dienylmalonate*)]*iron* (13a) (147 mg, 76%). Compound (12a), isolated as yellow crystals from ether–pentane, had m.p. 113—115 °C, $\nu_{max.}$ ($CHCl_3$) 2 050, 1 970, 1 755, 1 730, and 1 490 cm^{-1}; δ($CDCl_3$) 4.93 (1 H, d, *J* 2 Hz, 3-H), 3.75 (s) and 3.67 (s) [6 H, diastereotopic $(MeO_2C)_2CH$], 3.70 [1 H, s, $(MeO_2C)_2CH$], 3.60 (3 H, s, OMe), 3.25 (1 H, ddd, *J* 3,3 and 2 Hz, 5-H), 3.00 (1 H, dd, *J* 16 and 3 Hz, *endo*-6-H), 1.63 (1 H, dd, *J* 16 and 3 Hz, *exo*-6-H) 1.57 (3 H, s, 2-Me), and 1.15 (3 H, s, 1-Me); *m/z* (%) 408 (12), 380 (59), and 324 (100) (Found: C, 49.95; H, 4.8. $C_{17}H_{20}FeO_8$ requires C, 50.02; H, 4.94). In the n.m.r. spectrum of the mixture, (13a) showed δ($CDCl_3$) 5.27 (1 H, s, 3 H) and 3.41 (3 H, s, OMe).

Complex (3a) *with sodiomalononitrile.* The hexafluorophosphate (3a) (200 mg, 0.47 mmol) was treated with sodiomalononitrile (1.2 equiv.), to give a 2.7 : 1 mixture of *tricarbonyl*[2—5-η-(4-*methoxy*-1,2-*dimethylcyclohexa*-2,4-*dienylmalononitrile*)]*iron*(12b) and *tricarbonyl*[2—5-η-(2-*methoxy*-4,5-*dimethylcyclohexa*-2,4-*dienylmalononitrile*)]*iron*(13b) (105 mg, 65%). Recrystallization from ether–pentane afforded (12b) as orange crystals, m.p. 107—109 °C, $\nu_{max.}$ ($CHCl_3$) 2 260, 2 060, 1.970, and 1 490 cm^{-1}; δ($CDCl_3$) 5.15 (1 H, d, *J* 3 Hz, 3-H), 3.78 (3 H, s, OMe), 3.60 [1 H, s, $(NC)_2CH$], 3.18 (1 H, ddd, $J_{3,5} = J_{exo\text{-}6,5} = J_{endo\text{-}6,5} = 3$ Hz, 5-H), 2.25 (1 H, dd, *J* 15 and 3 Hz, *endo*-6-H), 1.85 (1 H, dd, *J* 15 and 3 Hz, *exo*-6-H), 1.47 (3H, s, 2-Me), and 1.33 (3 H, s, 1-Me); *m/z* (%) 342 (12), 314 (24), 258 (59), and 192 (100) (Found: C, 52.4; H, 3.95; N, 7.95. $C_{15}H_{14}FeN_2O_4$ requires C, 52.66; H, 4.12; N, 8.19). In the n.m.r. spectrum of the mixture, compound (13b) showed δ($CDCl_3$) 5.38 (1 H, s, 3-H) and 3.44 (3 H, s, OMe), the remainder of the spectrum being obscured by its regioisomer.

Complex (3b) *with dimethyl potassiomalonate.* Compound (3b) (200 mg, 0.44 mmol) and dimethyl potassiomalonate (1.2 equiv.) gave a 9 : 1 mixture of *tricarbonyl*[2—5-η-(*dimethyl* 4-*isopropoxy*-1,2-*dimethylcyclohexa*-2,4-*dienylmalonate*)]*iron* (12c) and *tricarbonyl*[2—5-η-(*dimethyl* 2-*isopropoxy*-4,5-*dimethylcyclohexa*-2,4-*dienylmalonate*]*iron* (13c) (165 mg, 86%). Recrystallisation from ether–pentane afforded pure (12c) as yellow crystals, m.p. 114—115 °C; $\nu_{max.}$ ($CHCl_3$) 2 040,

1 940, 1 760, 1 730, and 1 460 cm^{-1}; δ($CDCl_3$) 4.89 (1 H, d, *J* 2 Hz, 3-H), 4.20 (1 H, heptuplet, *J* 6 Hz, Me_2CH), 3.75 (s) and 3.65 (s) (6 H, diastereotopic CH_3O_2C) 3.68 [1 H, s, $(MeO_2C)_2CH$], 3.22 (1 H, m, 5-H), 2.97 (1 H, dd, *J* 16 and 4 Hz, *endo*-6-H), 1.57 (1 H, dd, *J* 16 and 3 Hz, *exo*-6-H), 1.50 (3 H, s, 2-Me), 1.33 (d) and 1.27 (d) (6 H, *J* 6 Hz, diastereotopic Me_2CH), and 1.15 (3 H, s, 1-Me); *m/z* (%) 436 (10), 408 (38), 380 (10), and 352 (100) (Found: C, 52.35; H, 5.55. $C_{19}H_{24}FeO_8$ requires C, 52.31; H, 5.55).

Complex (3b) *with sodiomalononitrile*. The hexafluorophosphate (3b) (200 mg, 0.44 mmol) and sodiomalononitrile (1.2 equiv.) gave a 10.4 : 1 mixture of *tricarbonyl*[2—5-η-(4-*isopropoxy*-1,2-*dimethylcyclohexa*-2,4-*dienylmalononitrile*)*iron* (12d) and *tricarbonyl*[2—5-η-(2-*isopropoxy*-4,5-*dimethylcyclohexa*-2,4-*dienylmalononitrile*)*iron* (13d) (131 mg, 61%), from which compound (12d) could be obtained as yellow crystals, m.p. up 110—111 °C (from ether–pentane), $\nu_{max.}$ ($CHCl_3$) 2 260, 2 040, 1 940, and 1 460 cm^{-1}; δ($CDCl_3$) 5.07 (1 H, d, *J* 2 Hz, 3-H), 4.31 (1 H, heptuplet, *J* 6 Hz, Me_2CH), 3.62 [1 H, s, $(NC)_2CH$], 3.15 (1 H, ddd, *J* 3, 3 and 2 Hz, 5-H), 2.25 (1 H, dd, *J* 16 and 3 Hz, *endo*-6-H), 1.83 (1 H, dd, *J* 16 find 3 Hz, *exo*-6-H), 1.50 (3 H, s, 2-Me), 1.35 (d) and 1.30 (d) (6 H, *J* 6 Hz, Me_2CH), 1.18 (3 H, s, 1-Me), *m/z* (%) 370 (7), 342 (40), 314 (14), and 286 (100).

Complex (3b) *with methyl* 2-*oxo*-1-*sodiocyclopentanecarboxylate*. To a stirred suspension of sodium hydride (21 mg, 0.88 mmol) in THF (3 ml) was added dropwise methyl 2-oxocyclopentanecarboxylate (0.14 ml, 1.1 mmol). The suspension was stirred for 15 min and then cooled to 0 °C. The hexafluorophosphate (3b) (200 mg, 0.44 mmol) was added in portions. Ether extraction in the usual way, followed by preparative t.l.c. afforded a 6 : 1 mixture of (13e) and (12e) (84 mg, 43%). A pure sample of *tricarbonyl*{2—5-η-[*methyl* 1-(2-*isopropoxy*-4,5-*dimethylcyclohexa*-2,4-*dienyl*)-2-*oxocyclopentanecarboxylate*]} *iron* (13e) as a 0.8 : 1 mixture of diastereoisomers, was obtained by recrystallisation from ether–pentane, $\nu_{max.}$ 2 040, 1 960, 1 760, and 1 720 cm^{-1}; *m/z* (%) 446 (3), 418 (14), 390 (17), and 362 (100) (Found: C, 56.7; H, 5.8. $C_{21}H_{26}FeO_7$ requires C, 56.52; H, 5.87). The ^1H n.m.r. spectrum was complicated owing to the mixture of diastereoisomers, allowing only the following assignments to be made: δ($CDCl_3$) diastereoisomer A: 5.60 (1 H, s, 3-H), 3.92 (1 H, heptuplet, *J* 6 Hz, Me_2CH), 3.64 (3 H, s, CO_2Me), 2.04 (3 H, s, 2-Me), and 1.44 (3 H, s, 1-Me); diastereoisomer B: 5.56 (1 H, s, 3-H), 3.92 (1 H, heptuplet, *J* 6 Hz, Me_2CH), 3.56 (3 H, s, CO_2Me), 2.04 (3 H, s, 2-Me), and 1.44 (3 H, s, 1-Me).

Complex (3c) *with dimethyl potassiomalononate*. The ester salt (3c) (100 mg, 0.2 mmol) and a suspension of dimethyl potassiomalonate (1.2 equiv.) in THF (4 ml) gave, after chromatography, *tricarbonyl*[2—5-η-(*dimethyl* 2-*methoxy*-5-*methoxycarbonylethyl*-4-*methylcyclohexa*-2,4-*dienylmalonate*)]*iron* (13f) (85 mg, 89%), $\nu_{max.}$ ($CHCl_3$) 2 040, 1 970, and 1 735 cm^{-1}; δ($CDCl_3$) 5.20 (1 H, s, 3-H), 3.7—3.65 (9 H, 3 × s, 3 × CO_2-Me), 3.36 [1 H, d, *J* 7 Hz, $(MeO_2C)_2CH$] 3.33 (3 H, s, OMe), 2.50 (1 H, dd, *J* 7 and 3 Hz, 5-H), 2.4—2.0 (4 H, m, 2 × CH_2), 2.25 (1 H, d, *J* 15 Hz, *endo*-6-H), 2.06 (3 H, s, Me) 1.58 (1 H, dd, *J* 15 and 3 Hz, *exo*-6-H); *m/z* (%) 480 (<1), 452 (1), 424 (7), 396 (33), and 264 (100).

Complex (3c) *with sodiomalononitrile*. The ester salt (3c) (167 mg, 0.34 mmol) with sodiomalononitrile (2 equiv.) gave *tricarbonyl*[2—5-η-(2-*methoxy*-5-*methoxycarbonylethyl*-4-*methylcyclohexa*-2,4-*dienylmalonate*)]*iron* (13 g) (100 mg, 72%) as a yellow oil which could not be crystallised, $\nu_{max.}$ ($CHCl_3$) 2 040, 1 970, 1 725, and 1 490 cm^{-1}; δ($CDCl_3$) 5.35 (1 H, s, 3-H), 3.92 [1 H, d, *J* 4 Hz, $(NC)_2CH$], 3.68 (3 H, s, CO_2Me), 3.42 (3 H, s, OMe), 2.65—1.9 (6 H, m, methylenes, 5-H and *endo*-6-H), 2.15, (3 H, s, Me), and 1.65 (1 H, dd, *J* 9 and 4 Hz, *exo*-6-H); *m/z* (%) 414 (<1), 386 (4), 358 (25), 330 (29), and 265 (100).

Complex (3d) *with dimethyl potassiomalonate*. Reaction of the salt (3d) (200 mg, 0.38 mmol) with dimethyl potassiomalonate (1.2 equiv.) afforded a 3.6 : 1 mixture of *tricarbonyl*[2—5-η-(*dimethyl* 2-*isopropoxy*-5-*methoxycarbonylethyl*-4-*methylcyclohexa*-2,4-*dienylmalonate*)]*iron* (13h) and *tricarbonyl*[2—5-η-(*dimethyl* 4-*isopropoxy*-1-*methoxycarbonylethyl*-1,2-*dimethylcyclohexa*-2,4-*dienylmalonate*)]*iron* (12h) as a homogeneous yellow oil (200 mg, 97%), $\nu_{max.}$ ($CHCl_3$) 2 040, 1 960, and 1 730 cm^{-1}; *m/z* (%) 508 (1), 480 (4), 452 (7), 424 (29), and 292 (100). The n.m.r. spectra of these compounds overlapped, but the following assignments could be made: compound (13b): δ(CD_2Cl_2): 5.07 (1 H, s, 3-H), 4.00 (1 H, s, 3-H), 4.00 (1 H, heptuplet, obscured, Me_2CH), 3.7—3.6 [10 H, obscured, 3 × CO_2Me and $(MeO_2C)_2CH$], 3.3—4.4 (7 H, m, methylenes and 1-H), 2.06 (3 H, s, Me), 1.3—1.0 (6 H, m, obscured, (Me_2CH); compound (12h): δ(CD_2Cl_2) 4.85 (1 H, d, *J* 2 Hz, 3-H), 4.12 (1 H, heptuplet, obscured, Me_2CH), 3.6—3.7 [10 H, obscured, 3 × CO_2Me and $(MeO_2C)CH$], 3.3—1.5 (7 H, m, methylenes and 5-H), 2.06 (3 H, s, Me), 1.18 (d) and 1.15 (d) (6 H, *J* 6 Hz, diastereotopic Me_2CH).

Complex (3d) *with sodiomalononitrile*. Treatment of the hexafluorophosphate (3d) (200 mg, 0.38 mmol) with sodiomalononitrile (1.3 equiv.) as above gave a 2 : 1 mixture of *tricarbonyl*[2—5-η-(2-*isopropoxy*-5-*methoxycarbonylethyl*-4-*methylcyclohexa*-2,4-*dienylmalononitrile*)] (13i) and *tricarbonyl*-[2—5-η-(4-*isopropoxy*-1-*methoxycarbonylethyl*-2-*methoxycyclohexa*-2,4-*dienylmalononitrile*)]*iron* (12i) as a homogeneous yellow oil (142 mg, 85%), $\nu_{max.}$ ($CHCl_3$) 2 260, 2 050, 1 970, 1 735, and 1 470 cm^{-1}; *m/z* (%) 442 (<1), 414 (6), 358 (35), 298 (65), and 293 (100).

Compound (13i) showed: δ($CDCl_3$) 5.20br (1 H, 3-H), 4.05 (1 H, heptuplet, *J* 6 Hz, Me_2CH), 4.03 [1 H, d, *J* 4 Hz, $(NC)_2CH$], 3.67 (3 H, s, CO_2Me), 2.5—1.5 (7 H, m, methylenes and 1-H), 2.15 (3 H, s, Me), 1.23 (d) and 1.17 (d) (6 H, *J* 6 Hz, diastereotopic Me_2CH).

Compound (12i) showed: δ($CDCl_3$) 5.15 (1 H, d, *J* 2 Hz, 3-H), 4.35 (1 H, heptuplet, *J* 6 Hz, Me_2CH), 3.80 [1 H, s, $(NC)_2CH$], 3.67 (3 H, s, CO_2Me), 2.5—1.5 [7 H, m, methylenes and 5-H), 1.43 (d) and 1.39 (d) (6 H, *J* 6 Hz, diastereotopic Me_2CH).

Dimethyl 1,2-*Dimethyl*-4-*oxocyclohex*-2-*enylmalonate*.—Treatment of the complex (12c) (134 mg, 0.3 mmol) with trimethylamine *N*-oxide (340 mg, 4.5 mmol) in dimethylacetamide (8 ml) at room temperature for 15 h, followed by aqueous work-up, afforded the crude dienol ether (62 mg, 70%). This was immediately dissolved in methanol (1 ml) and a solution of oxalic acid (45 mg) in water (0.3 ml) added. After 20 h, addition of aqueous sodium hydrogen carbonate and extraction with ether afforded the *enone* (15) (42 mg, 78%), $\nu_{max.}$ (CCl_4) 1 765, 1 775, 1 680, and 1 625; δ(CCl_4) 5.77 (1 H, s, 3-H), 3.80 (s) and 3.74 (s) (6 H, diastereotopic CO_2Me), 3.71 [1 H, s, $(MeO_2C)_2CH$], 2.5—2.1 (4 H, m, 2 × CH_2), 1.94 (3 H, s, 2-Me), and 1.38 (3 H, s, 1-Me); *m/z* (%) 254 (6) and 122 (100).

Tricarbonyl{1—4-η-[3-(4-*methoxy*-2-*methylcyclohexa*-1,3-*dienyl*)*propanol*]}*iron* (11e).—DIBAL (di-isobutylaluminium hydride) (2.3 ml of a 1M solution in hexane, 2.3 mmol) was added dropwise to a solution of the ester complex (11c) (320 mg, 0.91 mmol) in THF (8 ml) at −78 °C. The stirred mixture was allowed to reach room temperature overnight after which time methanol (2 ml) and water (4 ml) were added with stirring. The solution was filtered through Celite, extracted with ether in the usual way and chromatographed (silica gel, 10% ethyl acetate–benzene) to give the *alcohol* (11e) (271 mg, 92%) as an oil, chromatographically and spectroscopically pure, $\nu_{max.}$ ($CHCl_3$) 3 620, 3 460br, 2 035, and 1 965; δ($CDCl_3$), 5.22

(1 H, s, 3-H), 3.7 (2 H, t, *J* 5 Hz, CH_2OH), 3.48 (3 H, s, OMe), 2.35—1.50 (9 H, m, methylenes and OH), and 2.13 (3 H, s, Me); *m/z* (%) 322 (3), 294 (8), 266 (30), and 236 (100).

Tricarbonyl{1—4-η-[3-(4-*methoxy*-2-*methylcyclohexa*-1,3-*dienyl*)*propyl toluene*-p-*sulphonate*]}*iron* (11f).—Toluene-*p*-sulphonyl chloride (260 mg, 1.4 mmol) was added to a solution of the alcohol (11e) (270 mg, 0.84 mmol) in pyridine (5 ml) at 0 °C. After 24 h at 0 °C the reaction mixture was poured into ice-cold 10% hydrochloric acid (50 ml), extracted with ether, and the extract washed with saturated aqueous sodium hydrogencarbonate and then water, and finally dried ($MgSO_4$). Preparative t.l.c. gave the *tosylate* (309 mg, 77%) as a yellow oil, $\nu_{max.}$ ($CHCl_3$) 2 040, 1 970, 1 365, and 1 175; δ($CDCl_3$) 7.85 (2 H, d, *J* 9 Hz, 2 × ArH), 7.38 (2 H, d, *J* 9 Hz, 2 × ArH) 5.17 (1 H, s, 3-H), 4.08 (2 H, t, *J* 3 Hz, CH_2OTs), 3.43 (3 H, s, OMe), 2.42 (3 H, s, ArMe), 2.3—1.4 (8 H, m, methylenes), and 2.03 (3 H, s, Me); *m/z* (%) 476 (<1), 448 (2), 420 (23), 392 (32), and 292 (100).

Tricarbonyl{1—4-η-[3-(4-*methoxy*-2-*methylcyclohexa*-1,3-*dienyl*)*propyl*]*malononitrile*}*iron* (11g).—The tosylate (11f) (309 mg, 0.65 mmol) and sodiomalonitrile (10 equiv.) gave, after 5 h in refluxing THF (20 ml), aqueous work-up, extraction, and chromatography (silica gel, 10% ethyl acetate–benzene) the complex (11g) (206 mg, 86%) as a yellow oil, $\nu_{max.}$ ($CHCl_3$) 2 270, 2 030, and 1 960; δ($CDCl_3$) 5.29 (1 H, s, 3-H), 3.81 [1 H, t, *J* 6 Hz, $CH(CN)_2$], 3.55 (3 H, s, OMe), and 2.5—1.2 (10 H, m, methylenes); *m/z* (%) 370 (3), 342 (17), 314 (7), 286 (78), and 284 (100).

Tricarbonyl{6—9-η-(1,1-*dicyano*-8-*methoxy*-6-*methylspiro*-[4.5]*deca*-6,8-*diene*)}*iron* (16).—The complex (11g) (75 mg, 0.2 mmol) was stirred with trityl hexafluorophosphate (175 mg, 0.45 mmol) at reflux in dichloromethane (8 ml) for 5.5 h, cooled to 0 °C and triethylamine (0.08 ml, 0.57 mmol) added.

The reaction mixture was well washed with water, dried ($MgSO_4$), and chromatographed (silica gel, chloroform) to afford the *spirocyclic complex* (16) as yellow crystals (30 mg, 41%), m.p. 133—135 °C $\nu_{max.}$ ($CHCl_3$) 2 260, 2 040, 1 970, and 1 490 cm^{-1}; δ($CDCl_3$) 5.38 (1 H, d, *J* 2 Hz, 3-H), 3.72 (3 H, s, OMe), 3.16 (1 H, ddd, *J* 5, 3.5 and 2.5 Hz, 5-H), 2.65—1.65 6 H, m, methylenes), 2.17 (1 H, dd, *J* 16 and 3.5 Hz, *endo*-6-H), 1.88 (1 H, dd, *J* 16 and 2.5 Hz, *exo*-6-H), and 1.83 (3 H, s, Me); *m/z* (%) 368 (11), 340 (23), 312 (16), and 264 (100) (Found: C, 55.5; H, 4.25; N, 7.7. $C_{17}H_{16}FeN_2O_4$ requires C, 55.46, H, 4.38, N, 7.61).

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