Organoiron Complexes in Organic Synthesis. Part 6.[1] Dienolonium Equivalents: Tricarbonyl-[1-alkoxy-2-(1—5-η-4-methoxycyclohexa-2,4-dienylium)ethane]iron Hexafluorophosphates and Related Complexes leading to Masked 4,4-Disubstituted Cyclohexenones

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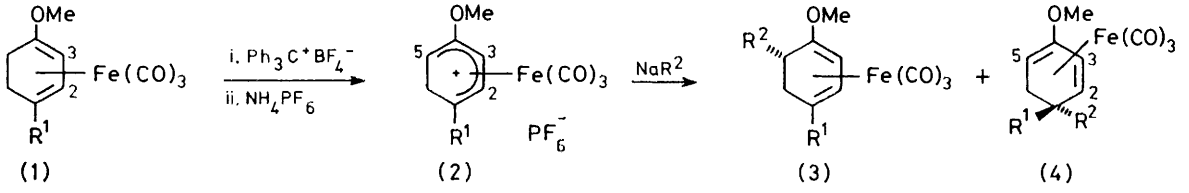
The dienolonium equivalents tricarbonyl-[2-methoxy-1-(1—5-η-4-methoxycyclohexa-2,4-dienylium)ethane]iron hexafluorophosphate (2e) and tricarbonyl-[2-methoxy-1-(1—5-η-4-methoxycyclohexa-2,4-dienylium)propane]-iron hexafluorophosphate (2i) react with sodiomalononitrile highly regioselectively to give functionalised *gem*-disubstituted cyclohexadiene complexes which are potential precursors of 4,4-disubstituted cyclohexenones. The reactions of these and related complexes with other carbanions are also reported.

PART of our current research programme is concerned with the scope of our recently discovered approach to functionalised 4,4-disubstituted cyclohexenones, potentially valuable synthetic precursors, which utilises the ability of the tricarbonyliron group to stabilise cyclohexadienylium cations equivalent to cyclohexenones showing polarity reversal at the 4-position.[2] We were interested in studying reactions of complexes (2) which



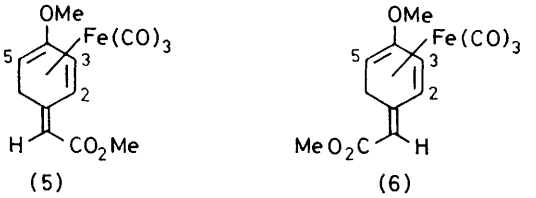
(1) (2) (3) (4)

a; $R^1 = CH_2CO_2Me$
b; $R^1 = CH_2CO_2H$
c; $R^1 = CH_2CH_2OH$
d; $R^1 = CH_2CH_2OAc$
e; $R^1 = CH_2CH_2OMe$
f; $R^1 = CH_2CMe{\cdot}OCH_2CH_2O$
g; $R^1 = CH_2CO{\cdot}Me$
h; $R^1 = CH_2CHOH{\cdot}Me$
i; $R^1 = CH_2CH(OMe){\cdot}Me$
j; $R^1 = CH_2CH_2CO_2Me$

a; $R^1 = CH_2CO_2Me$, $R^2 = CH(CO_2Me)_2$
b; $R^1 = CH_2CO_2Me$, $R^2 = CH(CN)_2$
c; $R^1 = CH_2CH_2OAc$, $R^2 = CH(CO_2Me)_2$
d; $R^1 = CH_2CH_2OAc$, $R^2 = CH(CN)_2$
e; $R^1 = CH_2CH_2OMe$, $R^2 = CH(CO_2Me)_2$
f; $R^1 = CH_2CH_2OMe$, $R^2 = CH(CN)_2$
g; $R^1 = CH_2CMe{\cdot}OCH_2CH_2O$, $R^2 = CH(CN)_2$
h; $R^1 = CH_2CMe{\cdot}OCH_2CH_2O$, $R_2 = CH(CO_2Et)CO{\cdot}Me$
i; $R^1 = CH_2CH(OMe)Me$, $R^2 = CH(CN)_2$
(4j) $R^1 = H$, $R^2 = CH_2CO{\cdot}Me$

have an oxygen functionality at the β-position of the 1-substituent [numbering as in (2)]. These were expected to furnish products having a masked cyclohexenone group [as the diene–$Fe(CO)_3$ complex] which could be usefully applied in a number of terpenoid syntheses.

First, the complex (2a) was prepared by the usual method:[3] Birch reduction of *p*-methoxyphenylacetic acid followed by esterification and reaction with pentacarbonyliron to give (1a) as the major product in good yield, which then underwent hydride abstraction on treatment with triphenylmethylium tetrafluoroborate giving (2a). This compound reacted with dimethyl sodiomalonate to give four products. Preparative t.l.c. allowed isolation of (3a) (7%), (4a) (12%), and the major products (5) and (6) which result from loss of the now very acidic proton α to the dienylium terminus. Surprisingly, although (5) and (6) were initially formed in approximately equimolar amounts (n.m.r.), multiple development preparative t.l.c. (partially separable without streaking) resulted in conversion of (5) into (6) and we obtained a new mixture from *both* bands containing 90% of (6) in 100% recovery and evidently representing the thermodynamic mixture, the initial mixture being formed under kinetic control. We have not undertaken further investigation of this interconversion but it is possible that the prolonged exposure to silica gel in multiple development is the cause. Structural assignment of the isomers was based on the low-field n.m.r.



(5) (6)

signal for 2-H of (5) deshielded by CO_2Me compared to (6) and the higher-field signal of the vinyl-H α to CO_2Me in (5) [deshielded by the diene group in (6)]. Similar

olefinic products which we have previously isolated [4] were very unstable, whilst these new compounds could be stored at 0 °C for several weeks, the enhanced stability presumably being due to the presence of the ester carbonyl reducing the tendency for aromatisation and loss of $Fe(CO)_3$. In an attempt to overcome the formation of (5) and (6) we treated (2a) with sodiomalononitrile, which was expected to be less basic than the diester derivative, on the basis of the lower pK_a value of malononitrile.[5] In this case we obtained (3b) as the major product (38%), together with (4b) (21%) and a minor amount (6%) of the olefin mixture. Thus, although proton loss is now overcome, only a low yield of (4b) is produced. The results of regioselectivity are summarised in the Table. Presumably, the ester group is presenting steric hindrance to C-1, although we have experienced no similar difficulty with higher homologues of (2a).[3]

	Product ratio (4) : (3)	
Cation	$NaCH(CO_2Me)_2$	$NaCH(CN)_2$
(1a)	(a) 63 : 37	(b) 36 : 64
(1d)	(c) 50 : 50	(d) 75 : 25
(1e)	(e) 72 : 28	(f) 90 : 10
(1f)		(g) 0 : 100
(1i)		(i) 85 : 15

We next investigated complexes containing a protected primary alcohol in place of the ester group. Attempts to reduce (1a) with the nucleophilic reducing agent lithium aluminium hydride met with only limited success, since much decomposition of the complex occurred, presumably due to attack on the carbonyl ligands. Although di-isobutylaluminium hydride (DIBAL-H), an ' electrophilic ' reducing agent, has been extensively used to reduce esters to aldehydes,[6] its use for reduction directly to alcohols appears to have received only limited attention.[7] We have found it to be an excellent reagent, reduction of the ester (1a) to the primary alcohol (1c) proceeding in 90—95% yield. It also reduces the carboxylic acid (1b), which we have found easier to purify and therefore preferable to the ester, directly to (1c) in 97% yield. No decomposition of complex occurred in either case, therefore making this the reagent of choice. Complex (1c) was converted into its acetate (1d) and methyl ether (1e) by standard procedures in high yield, and both of these complexes underwent hydride abstraction to give exclusively (2d) and (2e), respectively. The results of addition of dimethyl sodiomalonate and sodiomalononitrile to these cations, both high-yield reactions, are given in the Table. It can be seen that greater regioselectivity for the substituted terminus C-1 is achieved for (2e) with sodiomalononitrile, indicating the importance of steric factors in this reaction, which we believe to be under charge control combined with orbital control. At present we have no explanation for the rather low regioselectivity observed during reaction with dimethyl sodiomalonate compared to that found previously for the complex (2j).[3]

The complex (2f) was our next consideration [we avoided ketone (2g) since it was expected to show deprotonation as for the ester (2a)]. We first attempted to prepare (1g) by reaction of the acid (1b) with methyllithium, which we have successfully applied to higher homologues,[1] but obtained disappointingly low yields and considerable over-reaction to give a tertiary alcohol. The preparation of (1f) was finally accomplished in moderate yield by acetalisation of *p*-methoxyphenylacetone and Birch reduction, followed by reaction of the diene with pentacarbonyliron to give the complex (1f) which was separable only with difficulty from aromatic material also produced in the reaction. Surprisingly, treatment of (1f) with triphenylmethylium tetrafluoroborate did not cleave the acetal [8] and gave the desired product (2f) isolated as the hexafluorophosphate. Steric hindrance from the acetal completely suppressed addition of sodiomalononitrile to the substituted terminus, and we obtained only the regioisomer (3g). This mode of addition corresponds to reversal of polarity at the (masked) ketone α-position. Hydrolysis of (1f) to the ketone (1g) proved troublesome, since extensive isomerisation to (4j) occurred, depending on the acid and conditions used. A moderate yield of (1g) was eventually obtained. Conversion into the methyl ether (1i) by sodium borohydride reduction and methylation followed by treatment of this complex with triphenylmethylium tetrafluoroborate gave the expected salt (2i) isolated as its hexafluorophosphate; this reacted with sodiomalonitrile predominantly at C-1 to give the desired isomer (4i). Thus, by suitable choice of 1-substituent in complexes (2) we can obtain products which correspond to *umpolung at either* C-4 *or* C-6 *of a cyclohexenone*, and we can in this way approach the synthesis of 4,4-disubstituted cyclohexenones with a wide range of functionality, since we have previously demonstrated the facile removal of $Fe(CO)_3$ in good yield from similar complexes.[1,2,3]

EXPERIMENTAL

I.r. spectra were determined with a Perkin-Elmer 577 spectrophotometer, mass spectra with an A.E.I. MS30 spectrometer, and 100-MHz ^1H n.m.r. spectra with a Varian HA100 spectrometer. All chromatographic operations involving organometallic compounds were conducted under nitrogen.

Tricarbonyl[*methyl* (1—4-η-4-*methoxycyclohexa*-1,3-*dienyl*)-*acetate*]*iron* (1a).—To a mechanically stirred solution of *p*-methoxyphenylacetic acid (10 g) in liquid ammonia (500 ml; 1-l flask fitted with solid CO_2–acetone condenser) containing t-butyl alcohol (15 ml) was added in small portions lithium metal (10 g). The resulting deep blue mixture was stirred for 10 h, after which time the colour was discharged by careful addition of methanol, and the ammonia was evaporated off under a stream of N_2. Salts were taken up in ice-cold water and the pH of the solution was adjusted to *ca.* 5—6 by addition of formic acid. Extraction with ether afforded crystalline crude 2,5-dihydrophenylacetic acid (8 g), δ ($CDCl_3$) 9.9 (1 H, br, CO_2H), 5.5 and 4.55 (each 1 H, s, br, vinyl), 3.5 (3 H, s, OMe), 3.0 (2 H, s, CH_2CO_2H), and 2.75 (4 H, 2 × CH_2). The crude acid was immediately esterified by treatment with dimethyl sulphate as previously described [3] to give methyl 2,5-dihydrophenylacetate (8.0 g,

92%); δ ($CDCl_3$) 5.45 (1 H, vinyl), 4.55 (1 H, vinyl), 3.60 (3 H, s, CO_2Me), 3.47 (3 H, s, OMe), and 2.95, 2.73, and 2.27 (6 H, 3 × CH_2). The crude ester (4.25 g) was stirred under reflux with pentacarbonyliron (10 ml) in di-n-butyl ether (40 ml) under nitrogen for 40 h, after which time the mixture was cooled and worked up in the usual way. Removal of unchanged starting material (0.5 g) by distillation followed by column chromatography on silica gel gave a yellow oil (5.68 g, 86% based on recovered diene) eluted with benzene. N.m.r. showed this to be greater than 90% pure *complex* (1a), there being a small singlet at δ 3.60 due to an impurity. This could not be removed by either use of distilled ester in its preparation, preparative t.l.c., or attempted low-temperature crystallisation, so the crude compound was used for the next stages, the products of which could be more rigorously characterised. The crude complex (1a) had $\nu_{max.}$ (film) 2 040, 1 970, and 1 740 cm^{-1}; δ ($CDCl_3$), 3.12 (2 H, AB q, 2- and 3-H), 3.65 (3 H, s, CO_2Me), 3.40 (3 H, s, OMe), 2.67 (2 H, s, CH_2CO_2Me), and 2.4—1.5 (4 H, m, 5- and 6-CH_2); M^+ 322.

Tricarbonyl-(1–4-η-4-*methoxycyclohexa*-1,3-*dienylacetic acid*)*iron* (1b).—The ester (1a) (4.5 g) was stirred in methanol (200 ml) under nitrogen whilst a solution of potassium hydroxide (10 g) in water (60 ml) was added dropwise. The resulting solution was stirred for 4 h and poured onto ice–hydrochloric acid. Removal of the acid by filtration, followed by thorough washing with water and drying *in vacuo*, afforded the crude acid (1b) (3.8 g, 90%). Recrystallisation from benzene–hexane gave pure (1b) as yellow *plates* (3.1 g, 74%), m.p. 120—122 °C; $\nu_{max.}$ ($CHCl_3$) 3 400—2 600, 2 043, 1 973, and 1 715 cm^{-1}; δ ($CDCl_3$) 10.2 (1 H, br, exch. D_2O, CO_2H), 5.26 (1 H, d, *J* 4 Hz, 2-H), 5.13 (1 H, d, *J* 4 Hz, 3-H), 3.47 (3 H, s, OMe), 2.77 (2 H, s, CH_2CO_2H), and 2.5—1.5 (4 H, m, 2 × CH_2); *m/e* 308 (1%), 280 (10), 252 (40), 224 (15), 222 (100), and 194 (50) (Found: C, 47.0; H, 4.0. $C_{12}H_{12}FeO_6$ requires C, 46.79; H, 3.93%).

Tricarbonyl[*methyl* (1–5-η-4-*methoxycyclohexa*-2,4-*dienylium*)*acetate*]*iron Tetrafluoroborate* (2a).—The ester (1a) (1.0 g) was heated under reflux in dry dichloromethane (30 ml) with triphenylmethylium tetrafluoroborate (1.2 g) under nitrogen for 30 min, then allowed to cool to room temperature. An excess of dry ether was added and the product was collected by filtration and washed with wet ether to afford pure (2a) as yellow *crystals* (0.70 g, 55%); $\nu_{max.}$ (Nujol) 2 110, 2 075, 2 055, and 1 725 cm^{-1}; δ (CD_3CN) 6.89 (1 H, dd, $J_{2,3}$ 6.0, $J_{3,5}$ 3.0 Hz, 3-H), 5.83 (1 H, d, *J* 6 Hz, 2-H), 3.95 (1 H, m, 5-H), 3.80 (3 H, s, CO_2Me), 3.69 (3 H, s, OMe), 3.03 (3 H, m, CH_2 AB q, and *endo*-6-H), 2.32 (1 H, d, J_{gem} 16 Hz, *exo*-6-H) (Found: C, 38.3; H, 3.4. $C_{13}H_{13}BF_4FeO_6$ requires C, 38.28; H, 3.21%).

Tricarbonyl-[2-(1–4-η-4-*methoxycyclohexa*-1,3-*dienyl*)-*ethanol*]*iron* (1c).—The procedure of DIBAL-H reduction is described for the carboxylic acid complex (1b) since this was most readily obtained pure. The ester (1a) could also be reduced by the same procedure but using 2 instead of 3 equivalents of DIBAL-H. The acid (1.7 g) was stirred at −78 °C under nitrogen in dry tetrahydrofuran (THF) (50 ml) whilst DIBAL-H [17 ml of 1M-solution in hexane (Aldrich)] was added dropwise. The solution was stirred overnight whilst the cooling bath reached room temperature. Methanol (5 ml), water (5 ml), and then ether (50 ml) were added and the mixture was stirred for 30 min and then filtered through Celite. The precipitate was washed with ether, and the extracts were washed with water, dried ($MgSO_4$), and evaporated to give the pure *alcohol* (1c) as a yellow oil, homogeneous on t.l.c. (1.5 g, 94%), $\nu_{max.}$ ($CHCl_3$) 3 620 (free OH), 3 440 (H-bonded), 2 040, and 1 967 cm^{-1}; δ ($CDCl_3$) 5.20 (1 H, d, *J* 4.5 Hz, 2-H), 4.99 (1 H, d, *J* 4.5 Hz, 3-H), 3.74 (2 H, t, *J* 6.0 Hz, CH_2OH), 3.44 (3 H, s, OMe), 2.5—1.5 (7 H, 1 exch. D_2O, 3 × CH_2 and OH); *m/e* 294 (20%), 266 (5), 238 (53), 208 (100), and 190 (70) (Found: M^+, 294.0190. $C_{12}H_{14}FeO_5$ requires *M*, 294.019 1).

Tricarbonyl-[2-*acetoxy*-1-(1–4-η-4-*methoxycyclohexa*-1,3-*dienyl*)*ethane*]*iron* (1d).—The alcohol (1c) (1.7 g) was treated with acetic anhydride (2 ml) in pyridine (20 ml) overnight at room temperature. Extraction with ether in the usual way afforded the acetate (1d) as a yellow *oil*, spectroscopically pure; $\nu_{max.}$ ($CHCl_3$) 2 040, 1 970, and 1 735 cm^{-1}; δ ($CDCl_3$) 5.20 (1 H, d, *J* 4.0 Hz, 2-H), 4.95 (1 H, d, *J* 4.0 Hz, 3-H), 4.15 (2 H, t, *J* 6.0 Hz, CH_2OAc), 3.48 (3 H, s, OMe), 2.10 (3 H, s, OAc), and 2.4—1.5 (6 H, m, 3 × CH_2); *m/e* 308 (30%) (M^+ − CO), 280 (25), 252 (25), and 250 (100) (Found: *m/e*, 308.035 7. $C_{13}H_{16}FeO_5$ requires *M* − CO, 308.034 7).

Tricarbonyl-[2-*methoxy*-1-(1–4-η-4-*methoxycyclohexa*-1,3-*dienyl*)*ethane*]*iron* (1e).—To a stirred suspension of sodium hydride (0.5 g; 50% dispersion in oil, washed with pentane) in dry THF under nitrogen was added a solution of the alcohol (1c) (1.43 g) in THF (50 ml). Methyl iodide (5 ml) was added and the mixture was stirred for 16 h. The excess of sodium hydride was destroyed by dropwise addition of methanol. The mixture was poured into water and the product was extracted in the usual way to give spectroscopically and chromatographically pure (1e) as a yellow *oil* (1.41 g, 94%). A sample after preparative t.l.c. gave $\nu_{max.}$ ($CHCl_3$) 2 040 and 1 965 cm^{-1}; δ ($CDCl_3$) 5.19 (1 H, d, *J* 4.5 Hz, 2-H), 4.98 (1 H, d, *J* 4.5 Hz, 3-H), 3.48 (3 H, s, 4-OMe), 3.35 (3 H, s, OMe), *ca.* 3.4 obscured (2 H, CH_2OMe), and 2.5—1.5 (6 H, 3 × CH_2); *m/e* 308 (25%), 306 (60), 280 (15), 252 (85), 222 (100), 192 (65), and 190 (60) (Found: M^+, 308.036 4. $C_{13}H_{16}FeO_5$ requires *M*, 308.034 7).

Tricarbonyl-[2-*acetoxy*-1-(1–5-η-4-*methoxycyclohexa*-2,4-*dienylium*)*ethane*]*iron Hexafluorophosphate* (2d; PF_6^-).—The acetate (1d) (1.7 g) in dichloromethane (20 ml) was added to a solution of triphenylmethylium tetrafluoroborate (2.0 g) in the minimum volume of dichloromethane, and the mixture was left at room temperature for 1.5 h. The resulting solution was poured into an excess of ether and the tetrafluoroborate salts were extracted with water. To the aqueous extracts was added a solution of ammonium hexafluorophosphate (1.2 g) in water and the complex was extracted into dichloromethane. The combined organic layer was dried ($MgSO_4$) and the hexafluorophosphate salt was crystallised out by gradual addition of ether with scratching. Filtration afforded (2d; PF_6^-) as yellow *crystals* (1.3 g, 52%); $\nu_{max.}$ (Nujol) 2 102, 2 050, 1 735, and 1 505 cm^{-1}; δ (CD_3CN) 6.85 (1 H, dd, $J_{2,3}$ 6.0 $J_{3,5}$ 3.5 Hz, 3-H), 5.70 (1 H, d, $J_{2,3}$ 6.0 Hz, 2-H), 4.10 (2 H, t, *J* 6.0 Hz, CH_2OAc), 3.92 (1 H, m, 5-H), 3.78 (3 H, s, OMe), 3.03 (1 H, dd, J_{gem} 16, $J_{5,6}$ 6.0 Hz, *endo*-6-H), 2.6—1.9 (3 H, m, *exo*-6-H and CH_2), and 2.01 (3 H, s, OAc) (Found: C, 35.0; H, 3.3. $C_{14}H_{15}F_6FeO_6P$ requires C, 35.03; H, 3.15%).

Tricarbonyl-[2-*methoxy*-1-(1–5-η-4-*methoxycyclohexa*-2,4-*dienylium*)*ethane*]*iron Hexafluorophosphate* (2e, PF_6^-).—Treatment of the methyl ether (1e) (1.31 g) with triphenylmethylium tetrafluoroborate (1.6 g) in refluxing dichloromethane (30 ml) under nitrogen for 0.5 h, followed by work-up as for (2d) afforded the *hexafluorophosphate* (2e) as yellow crystals (1.35 g, 70%); $\nu_{max.}$ (Nujol) 2 113, 2 065, and 1 503 cm^{-1}; δ (CD_3CN) 6.85 (1 H, dd, $J_{2,3}$ 6.0, $J_{3,5}$ 3.0 Hz, 3-H),

5.66 (1 H, d, $J_{2,3}$ 6.0 Hz, 2-H), 3.92 (1 H, m, 5-H), 3.80 (3 H, s, 4-OMe), 3.48 (2 H, t, J 5.5 Hz, CH_2OMe), 3.28 (3 H, s, OMe), 3.03 (1 H, dd, J_{gem} 16 Hz, $J_{5,6}$ 6.0 Hz, *endo*-6-H), and 2.4—2.15 (3 H, m, *exo*-6-H and CH_2) (Found: C, 34.65; H, 3.45. $C_{13}H_{15}F_6FeO_5P$ requires C, 34.54; H, 3.34%).

Tricarbonyl-[2-*methyl*-2-(1–4-η-4-*methoxycyclohexa*-1,3-*dienylmethyl*)-1,3-*dioxolan*]*iron* (1f).—*p*-Methoxyphenylacetone (20 g) was acetalised (ethylene glycol, toluene-*p*-sulphonic acid, in benzene) in the usual way (25 g, 99%). The acetal (25 g) was reduced with lithium (4.0 g) in ammonia (500 ml) containing tetrahydrofuran (40 ml) and ethanol (40 ml). The usual work-up afforded a crude product (24 g, 94%) which was distilled to give the pure 1,4-diene (18.3 g, 72%), b.p. 90—95 °C at 1 mmHg. This compound (9.0 g) was treated with pentacarbonyliron (15 ml) in di-n-nbutyl ether (100 ml) at reflux temperature under nitrogen for 24 h. Work-up as for previous complexes, and removal of unchanged starting material and aromatic impurities under high vacuum gave the pure *complex* (1f) (11.0 g, 73%) as a yellow oil; $\nu_{max.}$ ($CHCl_3$) 2 050 and 1 960 cm^{-1}; δ ($CDCl_3$) 5.18 (2 H, s, 2- and 3-H), 3.95 (4 H, s, OCH_2CH_2O), 3.48 (3 H, s, OMe), 2.50—1.23 (6 H, 3 × CH_2), and 1.37 (3 H, s, Me); *m/e* 322 (M^+ — CO) and 264 (base peak).

Tricarbonyl-[2-*methyl*-2-(1–5-η-4-*methoxycyclohexa*-2,4-*dienylium-methyl*)-1,3-*dioxolan*]*iron Hexafluorophosphate* (2f).—The complex (1f) (1.0 g) was treated at room temperature under nitrogen with triphenylmethylium tetrafluoroborate (1.7 g) in dry dichloromethane (20 ml), for 30 min. Work-up as for (2d) afforded the *salt* (2f) (0.71 g, 50%); $\nu_{max.}$ (Nujol) 2 110 and 2 055 cm^{-1}; δ (CD_3CN) 6.86 (1 H, dd, $J_{3,5}$ 3, $J_{2,3}$ 10.5 Hz, 3-H), 5.70 (1 H, d, $J_{2,3}$ 10.5 Hz, 2-H), 3.80 (3 H, s, OMe), 3.76—3.98 (5 H, m, OCH_2CH_2O and 5-H), 3.09 (1 H, dd, J_{gem} 15, $J_{5,6}$ 6.5 Hz, *endo*-6-H), 2.63 and 2.05 (2 H, AB q, J_{gem} 14 Hz, CH_2 side-chain, diastereotopic), and 2.35 (1 H, d, J_{gem} 15 Hz, *exo*-6-H) (Found: C, 36.1; H, 3.35. $C_{15}H_{17}F_6FeO_6P$ requires C, 36.46; H, 3.47%).

Tricarbonyl-[(1–4-η-4-*methoxycyclohexa*-1,3-*dienyl*)*propan*-2-*one*]*iron* (1g).—The acetal (1f) 1.4 g) was dissolved in a mixture of deoxygenated dioxan (25 ml), methanol (10 ml), water (5 ml), and concentrated hydrochloric acid (5 drops). After stirring at room temperature for 24 h, the solution was poured into ether (200 ml). The ether layer was washed with aqueous sodium hydrogencarbonate and water, dried ($MgSO_4$), and evaporated to give a mixture of the complexes (1g) and (4j). Column chromatography on silica gel (10% ethyl acetate in light petroleum) gave (1g) as the less-polar component (0.59 g; 48%); $\nu_{max.}$ ($CHCl_3$) 2 040, 1 970, and 1 720 cm^{-1}; δ ($CDCl_3$) 5.26 and 5.20 (each 1 H, AB q, J 4 Hz, 2- and 3-H), 3.46 (3 H, s, OMe), 3.04 (1 H, d, J_{gem} 16 Hz) and 2.68 (1 H, d, J_{gem} 16 Hz, CH_2COCH$_3$), 2.16 (3 H, s, CH_3CO), 2.35—2.10 and 1.98—1.60 (each 2 H, 2 × CH_2); *m/e* 278 (5%) (M^+ — CO), 250 (55), 222 (40), 166 (8), 164 (100) (Found: *m/e*, 278.022 7. $C_{13}H_{14}FeO_5$ requires M — CO, 278.024 2). Futher elution with 30% ethyl acetate in light petroleum afforded a small amount (*ca.* 0.1 g) of the complex (4j), identified by comparison (n.m.r.) with previously reported analogues.[9]

Tricarbonyl-[1-(1–4-η-4-*methoxycyclohexa*-1,3-*dienyl*)*propan*-2-*ol*]*iron* (1h).—The ketone (1g) (0.55 g) in ethanol (10 ml) was reduced with sodium borohydride (0.02 g) under nitrogen at room temperature for 1.5 h, after which time the mixture was poured into aqueous ammonium chloride. Extraction with ether in the usual way gave the diastereoisomeric complexes (1h) as an air-sensitive yellow oil (0.50 g, 91%); $\nu_{max.}$ ($CHCl_3$) 3 600, 3 440, 2 040, and 1 970 cm^{-1}; δ ($CDCl_3$) 5.12 (2 H, m, 2- and 3-H), 3.88 (1 H, m, CHOH), 3.46 (3 H, s, OMe), 1.36—2.82 (6 H, m, 3 × CH_2), 1.22 (3 H, d, J 6 Hz, Me); *m/e* 280 (M^+ — CO, 25%), 252 (100), 224 (90), and 168 (25).

Tricarbonyl-[2-*methoxy*-1-(1–4-η-4-*methoxycyclohexa*-1,3-*dienyl*)*propane*]*iron* (1i).—The alcohol (1h) (0.35 g) was treated with sodium hydride and methyl iodide, as for the preparation of (1e), to give a mixture of the diastereoisomeric methyl ethers (1i) as a yellow air-sensitive oil (0.19 g, 51%); $\nu_{max.}$ ($CHCl_3$) 2 040 and 1 965 cm^{-1}; δ ($CDCl_3$) 5.09 (2 H, m, 2- and 3-H), 3.44 (3 H, s, 4-OMe), 3.32 (3 H, s, OMe), 3.26—3.60 (1 H, m, CHOMe), 1.60—2.50 (6 H, m, 3 × CH_2), and 1.12 and 1.16 (each 1.5 H, d, J 6 Hz, Me diastereoisomers); *m/e* 266 (M^+ — 2CO, 40%), 238 (10), 182 (5), and 164 (100) (Found: *m/e*, 266.060 8. $C_{12}H_{18}FeO_3$ requires M — 2CO, 226.060 5).

Tricarbonyl-[2-*methoxy*-1-(1–5-η-4-*methoxycyclohexa*-2,4-*dienylium*)*propane*]*iron Hexafluorophosphate* (2i).—Treatment of (1i) (0.30 g) with triphenylmethylium tetrafluoroborate (0.35 g) at reflux temperature as above, followed by isolation as the hexafluorophosphate, gave the yellow crystalline *complex* (2i) (0.16 g, 32%); $\nu_{max.}$ (Nujol) 2 110, 2 070, and 2 050 cm^{-1}; δ (CD_3CN) 6.80 (1 H, dd, $J_{2,3}$ 6, $J_{3,5}$ 2Hz, 3-H), 5.53 (1 H, d, $J_{2,3}$ 6 Hz, 2-H), 3.80 (1 H, m, 5-H), 3.78 (3 H, s, 4-OMe), 3.42 (1 H, m, CHOMe), 3.20 (3 H, s, OMe), 2.97 (1 H, dd, J_{gem} 15, $J_{5,6}$ 7 Hz, *endo*-6-H), 2.28 (1 H, d, J_{gem} 15 Hz, *exo*-6-H), 1.80—2.02 (2 H, m, CH_2), and 1.12 (3 H, d, J 6 Hz, Me) (Found: C, 36.7; H, 3.75. $C_{14}H_{17}F_6FeO_5P$ requires C, 36.79; H, 3.63).

Reactions of Salts with Dimethyl Sodiomalonate.—The procedure was identical to that previously described.[2] The tetrafluoroborate (2a) (400 mg) gave, after separation by preparative t.l.c. (silica gel; 10% ethyl acetate–benzene), a mixture of the olefinic complexes (5) and (6) (100 mg, 32%), further chromatography of which resulted in almost complete conversion into (6) (recovery: faster band 60 mg, slower band 40 mg, 100%). Both stereoisomers showed $\nu_{max.}$ ($CHCl_3$) 2 050, 1 980, 1 695, 1 612, and 1 490. The (*E*)-isomer (5) had δ ($CDCl_3$) 5.56 (1 H, dd, J 6 and 2 Hz, 3-H), 5.52 (1 H, m, exocyclic vinyl), 4.76 (1 H, d, J 6 Hz, 2-H), 3.70 (3 H, s, CO_2Me), 3.66 (3 H, s, OMe), and 3.6 (1 H, m, obscured, 5-H). (Z)-*Tricarbonyl*[*methyl* (2–5-η-4-*methoxycyclohexa*-2,4-*dienylidene*)*acetate*]*iron* (6) showed δ 5.58 (1 H, m, exocyclic vinyl), 5.30 (1 H, dd, J 6 and 2 Hz, 3-H), 3.70 (3 H, s, CO_2Me), 3.62 (3 H, s, OMe), 3.6 (1 H, obscured, 5-H), 3.23 (1 H, dm, J_{gem} 20 Hz, *endo*-6-H), 3.09 (1 H, d, J 6 Hz, 2-H), and 2.08 (1 H, dm, J_{gem} 20 Hz, *exo*-6-H); *m/e* 292 (5%) (M^+ — CO), 264 (45), and 236 (100) (Found: *m/e*, 292.002 8. $C_{12}H_{12}FeO_5$ requires M — CO, 292.003 4). The second band gave *tricarbonyl*[*dimethyl* (2–5-η-4-*methoxy*-1-*methoxycarbonylmethylcyclohexa*-2,4-*dienyl*)*malonate*]*iron* (4a) as a yellow crystalline solid (55 mg, 12%), m.p. 111—112.5 °C; $\nu_{max.}$ ($CHCl_3$) 2 050, 1 975, 1 730, and 1 495 cm^{-1}; δ ($CDCl_3$) 4.95 (1 H, dd, J 6, 2 Hz, 3-H), 3.90 (1 H, s, malonyl CH), 3.65 (6 H, s) and 3.57 (3 H, s) (3 × CO_2Me), 3.55 (3 H, s, OMe), 3.25 (1 H, m, 5-H), 2.82 (1 H, d, J 6 Hz, 2-H), 2.67 (2 H, s, CH_2CO_2Me), and 2.55 (1 H, dd, J 16 and 3 Hz, *endo*-6-H), *m/e* 424 (20%) (M^+ — CO), 396 (80), and 368 (100) (Found: C, 47.7; H, 4.3. $C_{18}H_{20}FeO_{10}$ requires C, 47.81; H, 4.46%). The third band gave the complex (3a) as an oil (30 mg, 7%); $\nu_{max.}$ ($CHCl_3$) 2 045, 1 975, and 1 730 cm^{-1}; δ ($CDCl_3$) 5.25 (1 H, d, J 4 Hz, 2-H), 4.95 (1 H, d, J 4 Hz, 3-H), 3.62 and 3.60 (10 H, 3 × CO_2Me and malonyl CH, obscured), 3.30 (3 H, s, OMe), 3.27 (1 H, m, obscured, 5-H), 2.8 (1 H, m,

J_{gem} 16 Hz, *endo*-6-H), 2.58 (2 H, s, CH_2CO_2Me), 1.7 (1 H, dd, J 16 and 3 Hz, *exo*-6-H); *m/e* 424 (M^+ — CO).

The hexafluorophosphate (2d) (250 mg) gave a mixture of regioisomers (3c) and (4c) which could not be separated by multiple-development preparative t.l.c., and were characterised from the mixture by comparison with the separable isomers obtained later (yield 200 mg, 81%); $\nu_{max.}$ ($CHCl_3$) 2 050, 1 970, 1 750 (sh), and 1 733 cm^{-1}; δ ($CDCl_3$) [for (4c)] 5.0 (1 H, dd, J 6.5 and 2.5 Hz, 3-H), 4.08 (2 H, t, J 6 Hz, CH_2OAc), 3.72 and 3.70 (each 3 H, s, 2 × CO_2Me), 3.62 (3 H, s, OMe), 3.54 (1 H, s, malonate C*H*), 3.36 (1 H, m, 5-H), 2.77 (1 H, d, J 6.5 Hz, 5-H), 2.56 (1 H, dd, J 16 and 3.5 Hz, *endo*-6-H), 2.0 (3 H, s, OAc), and 2.3—1.5 (*exo*-5-H and CH_2); δ ($CDCl_3$) [for (3c)] 5.30 (1 H, d, J 4 Hz, 2-H), 4.96 (1 H, d, J 4 Hz, 3-H), 4.12 (2 H, t, J 6 Hz, CH_2OAc), 3.72 and 3.70 (each 3 H, s, 2 × CO_2Me), 3.39 (3 H, s, OMe), 2.06 (3 H, s, OAc), and 2.3—1.5 (methylenes); *m/e* 466 (10%), 410 (20), and 382 (100) (Found: M^+, 466.055 5. $C_{19}H_{22}FeO_{10}$ requires *M*, 466.056 2).

The hexafluorophosphate (2e) (230 mg) gave the two regioisomers (3e) and (4e) which were separated by preparative t.l.c. (10% ethyl acetate in benzene; silica gel). The faster-running band gave *tricarbonyl{dimethyl [2–5-η-4-methoxy-1-(2-methoxyethyl)cyclohexa-2,4-dienyl]malonate}iron* (4e) (125 mg, 56%) as a pale yellow solid, m.p. 64—65 °C; $\nu_{max.}$ ($CHCl_3$) 2 055, 1 970, 1 753, 1 729, and 1 488 cm^{-1}; δ ($CDCl_3$) 4.94 (1 H, dd, J 7 and 2.5 Hz, 3-H), 3.66 and 3.64 (each 3 H, s, 2 × CO_2Me), 3.58 (1 H, s, malonyl CH), 3.56 (3 H, s, 4-OMe), 3.32 (2 H, t, J 6 Hz, CH_2OMe), *ca.* 3.25 (1 H, obscured, 5-H), 3.19 (3 H, s, OMe), 2.79 (1 H, d, J 7 Hz, 2-H), 2.52 (1 H, dd, J 15 and 3 Hz, *endo*-6-H), 1.80 (2 H, t, J 6 Hz, CH_2), 1.59 (1 H, dd, J 15 and 3 Hz, *exo*-6-H); *m/e* 438 (35%), 410 (10), 382 (32), and 354 (100) (Found: C, 48.95; H, 4.85. $C_{18}H_{22}FeO_9$ requires C, 49.33; H, 5.06%). Elution of the slower band gave *tricarbonyl{dimethyl [2–5-η-2-methoxy-5-(2-methoxyethyl)cyclohexa-2,4-dienyl]malonate}iron* (3e) (50 mg, 22%) as a yellow oil; $\nu_{max.}$ ($CHCl_3$) 2 055, 1 960, 1 750, and 1 730 cm^{-1}; δ ($CDCl_3$) 5.26 (1 H, d, J 4 Hz, 4-H), 4.95 (1 H, d, J 4 Hz, 3-H), 3.72 and 3.70 (2 × CO_2Me), *ca.* 3.71 (1 H, malonate CH, obscured), 3.38 (3 H, s, 2-OMe), 3.31 (3 H, s, OMe), 3.4 (2 H, t, part obscured CH_2OMe), and 2.5—1.5 (5 H), *m/e* 410 (10%, M^+ — CO), 382 (1), and 354, (100) (Found: *m/e*, 410.067 5. $C_{17}H_{22}FeO_8$ requires *M* — CO, 410.066 4).

Reactions of Salts with Sodiomalononitrile.—The sodium salt of malononitrile was prepared in THF and treated with the dienylium salts by the method described for the reactions with dimethyl malonate. The tetrafluoroborate (2a) (275 mg) gave, after preparative t.l.c., a minor amount of (5) and (6) (15 mg). A middle band was eluted to give *tricarbonyl[methyl (2–5-η-1-dicyanomethyl-4-methoxycyclohexa-2,4-dienyl)acetate]iron* (4b) (55 mg, 21%) as a pale yellow solid, m.p. 116—117 °C; $\nu_{max.}$ ($CHCl_3$) 2 260, 2 065, 1 985, 1 730, and 1 495 cm^{-1}; δ ($CDCl_3$) 5.17 (1 H, dd, J 6.5 and 2.5 Hz, 3-H), 4.86 [1 H, s, $CH(CN)_2$], 3.71 (3 H, s, CO_2Me), 3.68 (3 H, s, OMe), 3.25 (1 H, m, 5-H), 2.64 (2 H, s, CH_2CO_2Me), 2.46 (1 H, d, J 6.5 Hz, 2-H), 2.04 (1 H, dd, ABX, J 16 and 3 Hz, *endo*-6-H), and 1.76 (1 H, dd, ABX, J 16 and 3 Hz, *exo*-6-H); *m/e* 358 (M^+ — CO; 5%), 330 (43), and 302 (100) (Found: C, 49.55; H, 3.7; N, 7.35%; *m/e*, 358.025 3. $C_{16}H_{14}FeN_2O_6$ requires C, 49.77; H, 3.65; N, 7.25%. $C_{15}H_{14}FeN_2O_5$ requires *M* — CO, 358.025 2). Elution of the third band gave (3b) as a yellow oil; $\nu_{max.}$ ($CHCl_3$) 2 260, 2 060, 1 985, and 1 740 cm^{-1}; δ ($CDCl_3$) 5.50 (1 H, dd, J 4.5 and 1.2 Hz, 2-H), 5.22 (1 H, d, J 4.5 Hz, 3-H), 3.96 [1 H, d, J 3.5 Hz, $CH(CN)_2$], 3.78 (3 H, s, CO_2Me), 3.49 (3 H, s, OMe), 3.19 (1 H, ddd, J 10, 4.0, and 3.5 Hz, 5-H), 2.74 (2 H, AB q, J 16 Hz, CH_2CO_2Me, diastereotopic), 2.54 (1 H, dd, J 14 and 10 Hz, *endo*-6-H), and 1.79 (1 H, dd, J 14 and 4.0 Hz, *exo*-6-H).

The hexafluorophosphate (2d) (240 mg) gave a single band on preparative t.l.c., elution of which gave a mixture of (3d) and (4d) (1 : 3 mixture, 170 mg, 85%) as an oil; $\nu_{max.}$ ($CHCl_3$) 2 260, 2 060, 1 980, 1 740, and 1 492 cm^{-1}; δ ($CDCl_3$) [for (3d)] 5.48 (1 H, d, J 4 Hz, 2-H), 5.14 (1 H, d, J 4 Hz, 3-H), 4.0 [1 H, d, J 3 Hz, $CH(CN)_2$], 3.47 (3 H, s, OMe), 2.11 (3 H, s, OAc); δ ($CDCl_3$) [for (4d)] 5.23 (1 H, dd, J 6.5 and 2.5 Hz, 2-H), 4.2 [2 H, m, CH_2OAc + same of (3d)], 3.95 [1 H, s, $CH(CN)_2$], 3.76 (3 H, s, OMe), 3.33 (1 H, m, 5-H), 2.53 (1 H, d, J 6.5 Hz, 2-H), 2.10 (3 H, s, OAc), and 2.1—1.8 (methylene, *exo*- and *endo*-6-H, both isomers); *m/e* 372 (20%, M^+ — CO), 344 (25), 316 (65), 284 (10), 261 (20), 251 (77), and 250 (100) (Found: *m/e* 372.040 3. $C_{16}H_{16}FeN_2O_5$ requires *M* — CO 372.040 8).

The hexafluorophosphate (2e) (220 mg) gave, after preparative t.l.c., *tricarbonyl-{[2–5-η-4-methoxy-1-(2-methoxyethyl)-cyclohexa-2,4-dienyl]malononitrile}iron* (4f) (130 mg, 72%) as a pale yellow solid, m.p. 96—97.5 °C; $\nu_{max.}$ ($CHCl_3$) 2 240, 2 060, 1 980, and 1 490 cm^{-1}; δ ($CDCl_3$) 5.22 (1 H, dd, J 6 and 2 Hz, 3-H), 4.51 [1 H, s, $CH(CN)_2$], 3.75 (3 H, s, 4-OMe), 3.52 (2 H, t, J 6 Hz, CH_2OMe), 3.32 (3 H, s, OMe), 3.32 (1 H, m, 5-H), 2.57 (1 H, d, J 6 Hz, 2-H), and 1.90 (4 H, 2 × CH_2), *m/e* 344 (25%; *M* — CO), 316 (60), and 288 (100) (Found: C, 52.45; H, 4.25; N, 7.4. $C_{16}H_{16}FeN_2O_5$ requires C, 51.64; H, 4.33; N, 7.23%). Elution of a second band gave (3f) (15 mg, 8%) as a yellow oil; $\nu_{max.}$ ($CHCl_3$) 2 240, 2 055, and 1 970 cm^{-1}; δ ($CDCl_3$) 5.44 (1 H, dd, J 5 and 1 Hz, 2-H), 5.15 (1 H, d, J 5 Hz, 3-H), 3.94 [1 H, d, J 4 Hz, $CH(CN)_2$], 3.50 (2 H, t, J 6 Hz, CH_2OMe), 3.47 (3 H, s, 4-OMe), 3.38 (3 H, s, OMe), and 2.7—1.5 (5 H); *m/e* 344 (*M* — CO).

The hexafluorophosphate (2i) (0.16 g) gave, after preparative t.l.c., *tricarbonyl-{[2–5-η-4-methoxy-1-(2-methoxypropyl)cyclohexa-2,4-dienyl]malononitrile}iron* (4i) as pale yellow crystals (0.11 g, 80%), m.p. 115—116 °C (from hexane); $\nu_{max.}$ ($CHCl_3$) 2 250, 2 060, 1 985, and 1 490 cm^{-1}; δ ($CDCl_3$) 5.21 (1 H, dd, $J_{2,3}$ 7, $J_{3,5}$ 2 Hz, 3-H), 4.82 [1 H, s, $CH(CN)_2$], 3.66 (3 H, s, 4-OMe), 3.24 (3 H, s, OMe), 3.18—3.60 (2 H, m, C*H*OMe and 5-H), 2.59 (1 H, d, $J_{2,3}$ 7 Hz, 2-H), 1.48—2.04 (4 H, m, 2 × CH_2), and 1.19 (3 H, d, J 6 Hz, Me), *m/e* 358 (M^+ — CO, 30%), 330 (90), and 302 (100) (Found: C, 52.65; H, 4.7. $C_{17}H_{18}FeN_2O_5$ requires, C, 52.87; H, 4.70%). A small amount (*ca.* 20 mg) of a more-polar component was also isolated, presumably (3i) on account of its t.l.c. behaviour and i.r. spectrum [compared with (3f)], but was not further characterised.

The hexafluorophosphate (2f) (0.56 g) gave, after preparative t.l.c. exclusively *tricarbonyl-{[2–5-η-2-methoxy-5-(2-methyl-1,3-dioxolan-2-ylmethyl)cyclohexa-2,4-dienyl]-malononitrile}iron* (3g) (0.39 g, 83%) as a yellow oil; $\nu_{max.}$ ($CHCl_3$) 2 260, 2 050, and 1 975 cm^{-1}; δ ($CDCl_3$) 5.42 (2 H, m, 2- and 3-H), 3.96 (4 H, m, OCH_2CH_2O), 3.70 [1 H, d, J 4 Hz, $CH(CN)_2$], 3.43 (3 H, s, OMe), 3.12 (1 H, ddd, $J_{5.6endo}$ 11, $J_{5.6exo}$ 4, $J_{5.5'}$ 4 Hz, 5-H), 1.90—2.58 (4 H, m, 2 × CH_2), and 1.34 (3 H, s, Me); *m/e* 386 (M^+ — CO, 10%), 358 (25), 330 (90), and 265 (100) (Found: *m/e*, 358.063 4. $C_{16}H_{18}FeN_2O_4$ requires *M* — 2CO, 358.061 6).

Reaction of the hexafluorophosphate (2f) (0.29 g) with ethyl sodio-acetoacetate, as previously described,[2] gave, after preparative t.l.c., exclusively *tricarbonyl{ethyl [2–5-η-2-methoxy-5-(2-methyl-1,3-dioxolan-2-ylmethyl)cyclohexa-*

2,4-*dienyl*]*acetoacetate*}*iron* (3h) (0.25 g, 88%) as a mixture of diastereoisomers. Fractional crystallisation from n-pentane afforded a pure sample of one of the diastereoisomers, m.p. 108—109 °C, which gave $\nu_{max.}$ ($CHCl_3$) 2 050, 1 970, 1 730, and 1 710 cm^{-1}; δ ($CDCl_3$) 5.26 and 5.16 (2 H, AB q, *J* 6 Hz, 2- and 3-H), 4.17 (2 H, q, *J* 6 Hz, CH_2CH_3), 3.98—3.86 (4 H, m, OCH_2CH_2O), 3.31 (3 H, s, OMe), 3.44—3.21 (2 H, m, H-5 and H-5'), 2.38—1.76 (4 H, m, 2 × CH_2), 2.20 (3 H, s, dioxolan Me), 1.29 (3 H, t, *J* 6 Hz, CH_3CH_2); *m/e* 394 (M^+ — 3CO) (Found: C, 52.85; H, 5.65. $C_{21}H_{26}FeO_9$ requires C, 52.74; H, 5.48%).

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