Organoiron Complexes in Organic Synthesis. Part 21.[1] Methods for Controlling the Regioselectivity of Nucleophile Addition to Tricarbonyl-(cyclohexadienylium)iron Complexes

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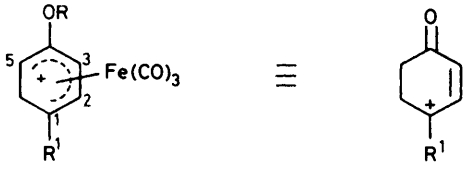
A study of the regioselectivity of enolate nucleophile addition to tricarbonyl(dienylium)iron complexes with structure (1) is reported. It has been found that better selectivity for the 1-substituted dienylium terminus is achieved using 4-isopropoxy-substituents than with 4-methoxy-substituents. The nature of the enolate counter-cation is also found to affect significantly the regioselectivity of its addition, and these results are discussed in terms of the factors which are likely to control the reaction.

OUR current work,[2] aimed at the application to natural product synthesis of organoiron complexes of general structure (1), which are synthetic equivalents of the cyclohexenone γ-cation (2), led us to investigate methods



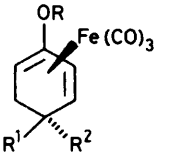
(1) (2)

a; R = Me, R^1 = H
b; R = Me, R^1 = Me
c; R = Me, R^1 = Et
d; R = Pr^i, R^1 = Et
e; R = Me, R^1 = $(CH_2)_2CO_2Me$
f; R = Me, R^1 = $(CH_2)_3$N–Phthaloyl

of controlling their reaction with nucleophiles. The need to undertake such investigations is amply illustrated by the observation that, whilst the reaction of complexes such as (1a) and (1b) with a range of useful carbon nucleophiles occurs regiospecifically at C-1 [2] giving complexes (3a) and (3b), complexes with sterically more demanding substituents (R^1) invariably produce mixtures of regioisomers with the general structures (3) and (4). Whilst structure (3) is usually the predominant product, we felt that greater potential utility for these organometallic systems could be realised were we to achieve *regiospecificity* during their reaction with a range of nucleophiles. The work described in this paper was undertaken toward this end; some of the results fortuitously reveal fundamental aspects of the chemistry of tricarbonyl(dienylium)iron complexes with respect to the factors which control the regiochemistry of nucleophile addition.

RESULTS AND DISCUSSION

Effect of Changing the Nature of the 4-Alkoxy-substituent.—It is no accident that hydride abstraction from complexes with structure (5; $R^1 \neq H$), during their reaction with the trityl cation, occurs with high regioselectivity from the methylene group adjacent to the methoxy-substituent to give complexes (1; $R^1 \neq H$). We have already pointed out [2b] that the major controlling factor is probably the formation of the dienyl cation which has the higher energy highest occupied molecular orbital (HOMO) and the lower energy lowest occupied molecular orbital (LUMO), thereby allowing greater synergic interaction with the metal d orbitals. One obvious way to force nucleophiles to react at the substituted C-1 terminus of complexes (1; $R^1 \neq H$) is to



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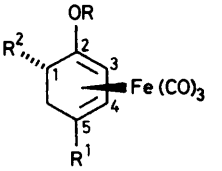
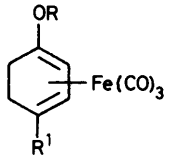


(4)

a; R = Me, R^1 = H, R^2 general
b; R = Me, R^1 = Me, R^2 general
c; R = Me, R^1 = Et, R^2 = $CH(CO_2Me)_2$
d; R = Pr^i, R^1 = Et, R^2 = $CH(CO_2Me)_2$
e; R = Me, R^1 = Et, R^2 = $CH(CN)_2$
f; R = Pr^i, R^1 = Et, R^2 = $CH(CN)_2$
g; R = Me, R^1 = Et, R^2 = $CH(CN)CO_2Me$
h; R = Pr^i, R^1 = Et, R^2 = $CH(CN)CO_2Me$
i; R = Me, R^1 = Et, R^2 = $CH(CO{\cdot}SEt)_2$
j; R = Pr^i, R^1 = Et, R^2 = $CH(CO{\cdot}SEt)_2$
k; R = Me, R^1 = Et, R^2 = $CH(CO_2Me)COMe$
l; R = Pr^i, R^1 = Et, R^2 = $CH(CO_2Me)COMe$
m; R = Me, R^1 = Et, R^2 = $-\overline{C(CO_2Me){\cdot}CO{\cdot}(CH_2)_2{\cdot}CH_2}$
n; R = Pr^i, R^1 = Et, R^2 = $-\overline{C(CO_2Me){\cdot}CO{\cdot}(CH_2)_2{\cdot}CH_2}$
o; R = Me, R^1 = Et, R^2 = CH_2CH_2OH
p; R = Pr^i, R^1 = Et, R^2 = CH_2CH_2OH
q; R = Me, R^1 = Me, R^2 = $-\overline{C(CO_2Me){\cdot}CO{\cdot}(CH_2)_2{\cdot}CH_2}$
r; R = Me, R^1 = $(CH_2)_2CO_2Me$, R^2 = $CH(CN)_2$
s; R = Me, R^1 = $(CH_2)_2CO_2Me$, R^2 = $CH(CN)CO_2Me$
t; R = Me, R^1 = $(CH_2)_2CO_2Me$, R^2 = $CH(CO_2Me)_2$
u; R = Me, R^1 = $(CH_2)_2CO_2Me$, R^2 = $CH(CO_2Me)COMe$
v; R = Me, R^1 = $(CH_2)_3$N–Phthaloyl, R^2 = $CH(CN)_2$
w; R = Me, R^1 = $(CH_2)_3$N–Phthaloyl, R^2 = $CH(CO_2Me)_2$

replace the 4-methoxy-substituent with a bulkier alkoxy-substituent, leading to greater steric hindrance of attack at C-5. However, at the outset of this work we were uncertain as to the outcome of hydride abstraction from the requisite precursor of structure (5), since a group large enough to affect nucleophile addition favourably might adversely affect hydride abstraction. In view of our suspicion that the latter process is under some kind of electronic control, we felt that, in fact, the nett effect would be highly favourable. We therefore carried

out the preparation of the simple methoxy- and isopropoxy-substituted diene complexes (5a) and (5b), respectively, and investigated their hydride abstraction reactions and the subsequent reactions of the resultant dienylium complexes with stable enolate nucleophiles. Each diene complex was readily prepared from the corresponding aromatic precursor (see Experimental



(5)
a; R = Me, R^1 = Et
b; R = Pr^i, R^1 = Et

section). We found that *both* complexes underwent *regiospecific* hydride abstraction on treatment with triphenylmethylium hexafluorophosphate to give the desired dienylium complexes (1c) and (1d) in essentially quantitative yields. The results of the reaction of each salt with a variety of stable carbanion nucleophiles are summarized in Table 1. The ratios of the regioisomeric

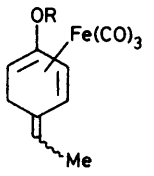
TABLE 1

Product ratios (3) : (4) for enolate anion additions to complexes (1c—d)

Dienylium complex	Nucleophile	Products and Ratio (3) : (4) (% Yield)
(1c)	$KCH(CO_2Me)_2$	(c) 85 : 15 (96)
(1d)	$KCH(CO_2Me)_2$	(d) 100 : 0 (97)
(1c)	$NaCH(CN)_2$	(e) 88 : 12 (90)
(1d)	$NaCH(CN)_2$	(f) 94 : 6 (95)
(1c)	$NaCH(CN)CO_2Me$	(h) 90 : 10 (87)
(1d)	$NaCH(CN)CO_2Me$	(h) 96 : 4 (96)
(1c)	$KCH(COSEt)_2$	(i) 57 : 43 (83)
(1d)	$KCH(COSEt)_2$	(j) 89 : 11 (94)
(1c)	$KCH(CO_2Me)\cdot COMe$	(k) 67 : 33 (70)
(1d)	$KCH(CO_2Me)COMe$	(l) 95 : 5 (74)
(1c)	$MeO_2C\cdot\overline{C{:}CH(OK)\cdot(CH_2)_2\cdot CH_2}$	(m) *ca.* 50 : 50 (60) [a]
(1d)	$MeO_2C\cdot\overline{C{:}CH(OK)\cdot(CH_2)_2\cdot CH_2}$	(n) >95 : 5 (73) [b]
(1d)	$MeO_2C\cdot\overline{C{:}CH(ONa)\cdot(CH_2)_2\cdot CH_2}$	(n) *ca.* 95 : 5 (69) [b]

[a] Combined yield; excludes product (6a) which was also obtained (see Experimental section). [b] Yield of isolated product (3n); products include (6b) (see Experimental section).

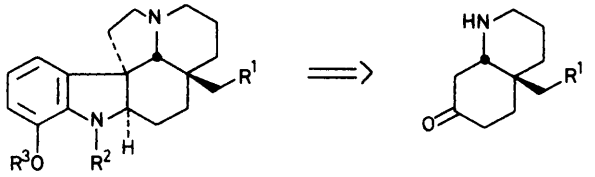
products were estimated from accurately integrated n.m.r. spectra, which show distinct signals for 3-H of complexes (3), and 2-H and 3-H of complexes (4) (Experimental section). Perhaps the most striking results are those for the diethyl dithiomalonate and methyl 2-oxocyclopentanecarboxylate anions, both of which give very poor regioselectivity with the methoxy-substituted complex (1c); this improves dramatically on going to complex (1d). In fact, the only side-reaction during the cyclic keto-ester addition to complex (1d) is deprotonation to give the ethylidene complex (6b). The simple dimethylmalonate anion as the potassium salt, adds to complex (1c) to give a 5.6 : 1 mixture of the



(6)
a; R = Me
b; R = Pr^i

isomers of (3c) and (4c), whilst complex (1d) gives only the isomer (3d) in essentially quantitative yield.

The products (3j), from diethyl dithiomalonate addition, and (3d), from dimethyl malonate addition, are extremely useful as precursors for the synthesis of aspidospermine (8). We have recently shown [3] that the methoxy-substituted derivative (3c) can be converted in two steps into the primary alcohol (3o) and thence to the *cis*-decahydroquinoline derivative (7), a compound used

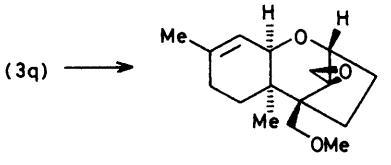


(8) R^1 = Me, R^2 = Ac, R^3 = Me
(12) R^1 = CH_2OH, R^2 = COEt, R^3 = H

(7) R^1 = Me

by Stork and Dolfini for the total synthesis of aspidospermine.[4] The higher regioselectivity observed with complex (1d) leads to a more efficient route for these intermediates. Even better, the dithiomalonate adduct (3j) can be converted directly, by treatment with Raney nickel,[5] into the primary alcohol (3p), thereby reducing the number of steps in the synthesis of this valuable intermediate.

We have recently achieved [6] the conversion of the cyclopentanone adduct (3q) into the trichothecene analogue (9). Clearly, the achievement of the controlled



(9)

addition of methyl 2-oxocyclopentanecarboxylate to complexes related to compound (1d) opens the way to a wide range of trichothecene derivatives, which are of potential value as antitumour agents.[7]

The control observed for nucleophile addition to the isopropoxy-complex (1d) compared to that for the methoxy-complex (1c) appears to be due solely to a steric effect of the isopropoxy-group. In view of the fact that the intervening oxygen atom places the bulky substituent somewhat further away from C-5 than might be expected to produce such pronounced effects, we also considered the possibility of a stronger electron donation

from this substituent leading to further electronic deactivation of C-5 (see later). This might be expected on the basis of increased electron release from the alkyl substituents present. However, comparison of the ^{13}C shieldings for the dienylium ligands of complexes (1c) and (1d) (Table 2) suggests that there is no decrease in

TABLE 2

^{13}C N.m.r. shieldings of dienylium carbon atoms for complexes (1c) and (1d)

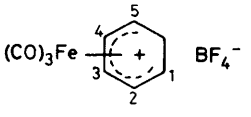
	Shieldings [a]					
Complex	C-1	C-2	C-3	C-4	C-5	C-6
(1c)	95.1	93.9	72.4	150.1	42.5	31.6
(1d)	93.4	93.2	71.7	148.9	42.3	30.6

[a] For solutions in CD_3CN, in p.p.m. downfield from Me_4Si internal standard.

positive charge at C-5 on replacing the methoxy- by an isopropoxy-group.

Effect of Enolate–cation Association.—Prior to preparing the above isopropoxy-substituted complexes, we were interested in methods of improving the selectivity of nucleophile addition to the methoxy-substituted complexes already at hand. To this end we looked at the effect of changing the nature of the cation associated with the enolates under investigation. Whilst there was at the time no rationale for embarking upon this work, we obtained some interesting results which we believe will point the way for more rigorous future investigations, designed to probe the factors which control the reactivity of a range of electrophilic organometallic complexes.

First, we digress to consider what is known about the nucleophile addition. ^{13}C n.m.r. studies [8] and molecular orbital calculations [9] indicate that for the parent tricarbonyl(cyclohexadienylium)iron salt (10) the positions of highest positive charge are C-2 and -4. If nucleophile addition to this complex was entirely subject to charge control we might have expected products of structure (11). These types of adduct are,



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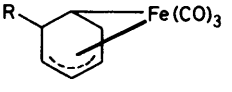

(11)

as far as we are aware, unknown in the cyclohexadiene-iron complex series, but have been observed during nucleophile addition to cycloheptadienylium and cyclooctadienylium complexes of iron, ruthenium, and osmium.[10] It appears likely that nucleophile addition to complex (10) is subject to frontier orbital control. In order to predict regioselectivity for this unsubstituted derivative, we need to known the exact nature of the LUMO, since it is this orbital which will interact with the HOMO of the nucleophile in forming the new bond.[11] The most favourable interaction would be at the carbon atom with the largest LUMO coefficient. Unfortunately, the exact nature of the LUMO is not known, and there are at least seven possible molecular orbitals which are very close in energy.[12] Indeed, it appears highly probable that subtle changes in the dienylium system, *e.g.* going from a six- to a seven-membered ring, could lead to significant alterations in these energy levels.

When the cyclohexadienylium system is unsymmetrical, as with complex (1a), there is a choice between two termini. Whilst the overall frontier orbital effect dictates addition to a terminal carbon atom, a second factor now comes into play, namely the difference in charge between the termini. It is clear from ^{13}C n.m.r. studies [8] that for complex (1a) the carbon atom adjacent to the methoxy-group has less positive charge (is at higher field) than the remote terminus. Thus it can be argued that superimposed on the frontier orbital effect is coulombic control. With this simple picture in mind, it seemed unlikely that anything could be done to influence the regioselectivity of the reaction of a particular nucleophile with complexes such as (1b). We were therefore surprised to find that reactions of complexes (1), which are known to produce mixtures of the regioisomers (3) and (4), are affected quite significantly according to whether the lithium, sodium, or potassium salts of chelating enolates are used as nucleophiles. The results obtained so far are listed in Table 3; it is readily seen from this Table that the order of selectivity for the substituted (C-1) terminus, remote from the methoxy-substituent, is potassium > sodium > lithium enolates of dimethyl malonate and methyl acetoacetate. Furthermore, addition of crown ether to the sodium enolate prior to reaction with the complex leads to a mixture of isomers almost identical with that obtained from the potassium salt. This strongly suggests that association of the enolate with a cation leads to a greater proportion of attack at C-5. The less-strongly associated enolates, including the non-chelating systems derived from malononitrile and methyl cyanoacetate, appear to react

FIGURE Possible lowest unoccupied molecular orbital for tricarbonyl(cyclohexadienylium)iron and tricarbonyl(2-methoxycyclohexadienylium)iron complexes

predominantly at the more highly charged dienylium terminus, and we should indeed expect that these would be more subject to coulombic controlling effects. The observation that strongly associated enolates [*e.g.* $LiCH(CO_2Me)_2$] give a greater proportion of C-5 addition is indicative of a secondary frontier orbital effect coming into play. A plausible explanation may be arrived at if we assume that the LUMO of the tricarbonyl(cyclohexadienylium)iron complex is an antibonding combination of the dienyl ψ_2 and the iron hybrid orbitals (Figure); then we see that in the methoxy-substituted derivative the coefficients at the termini are altered as indicated, so that any frontier orbital effects will favour addition of the terminus *adjacent* to the methoxy-substituent. Association of enolates with cations has

the effect of lowering the HOMO energy level,[13] thereby bringing it closer to the LUMO of the complex and thus, resulting in a stronger orbital interaction.[14] Therefore, low-energy associated enolates show a greater tendency to add to C-5 of the complexes (1), although the coulombic effect still prevails. This may well also account for the different selectivities observed for keto-ester, malononitrile, and malonic ester derivatives.

TABLE 3

Effect of changing the enolate countercation on the product ratio (3) : (4)

Dienylium complex	Nucleophile	Products and ratio (3) : (4) (% Yield)
(1c)	$Li^+\bar{C}H(CO_2Me)_2$	(c) 75 : 25 (78)
(1c)	$Na^+\bar{C}H(CO_2Me)_2$	(c) 82 : 18 (77)
(1c)	$K^+\bar{C}H(CO_2Me)_2$	(c) 85 : 15 (96)
(1d)	$Li^+\bar{C}H(CO_2Me)_2$	(d) 89 : 11 (81)
(1d)	$Na^+\bar{C}H(CO_2Me)_2$	(d) 94 : 6 (77)
(1d)	$K^+\bar{C}H(CO_2Me)_2$	(d) 100 : 0 (97)
(1e)	$Li^+\bar{C}H(CN)_2$	(r) 81 : 19 (76)
(1e)	$Na^+\bar{C}H(CN)_2$	(r) 84 : 16 (85)
(1e)	$K^+\bar{C}H(CN)_2$	(r) 83 : 17 (85)
(1e)	$Li^+\bar{C}H(CN)CO_2Me$	(s) 74 : 26 (75)
(1e)	$Na^+\bar{C}H(CN)CO_2Me$	(s) 79 : 21 (82)
(1e)	$R^+\bar{C}H(CN)CO_2Me$	(s) 77 : 23 (79)
(1e)	$Li^+\bar{C}H(CO_2Me)_2$	(t) 68 : 32 (86)
(1e)	$Na^+\bar{C}H(CO_2Me)_2$	(t) 79 : 21 (75)
(1e)	$K^+\bar{C}H(CO_2Me)_2$	(t) 85 : 15 (81)
(1e)	$Na^+\bar{C}H(CO_2Me)_2$(18-crown-6)	(t) 85 : 15 (85)
(1e)	$Li^+\bar{C}H(CO_2Me)COMe$	(u) *a*
(1e)	$Na^+\bar{C}H(CO_2Me)COMe$	(u) 33 : 67 (73)
(1e)	$K^+\bar{C}H(CO_2Me)COMe$	(u) 55 : 45 (65)
(1f)	$Li^+\bar{C}H(CN)_2$	(v) 77 : 23 (90)
(1f)	$Na^+\bar{C}H(CN)_2$	(v) 77 : 23 (87)
(1f)	$K^+\bar{C}H(CN)_2$	(v) 77 : 23 (89)
(1f)	$Li^+\bar{C}H(CO_2Me)_2$	(w) 60 : 40 (92)
(1f)	$Na^+\bar{C}H(CO_2Me)_2$	(w) 74 : 26 (85)
(1f)	$K^+\bar{C}H(CO_2Me)_2$	(w) 82 : 18 (81)
(1f)	$Na^+\bar{C}H(CO_2Me)_2$(18-crown-6)	(w) 81 : 19 (82)

[a] No products corresponding to addition to the dienylium ligand could be isolated from this reaction.

Whilst the foregoing rationalisation is somewhat tentative at this stage, the results are strongly indicative of the fact that the following factors are involved in controlling nucleophile addition to tricarbonyl(dienylium)iron complexes: (*a*) overall frontier orbital control determines whether addition occurs to the dienylium termini or other carbon atoms; (*b*) steric effects play an important part in determining which terminus is attacked in an unsymmetrical complex; (*c*) polar substituents exert a pronounced coulombic effect which discriminates between the dienylium termini; and (*d*) superimposed on the coulombic effect is a secondary frontier orbital effect which becomes important for nucleophiles with low-energy HOMOs. Although the first three effects are fairly obvious, the last is rather more subtle. Despite a number of studies, which have already been reported, of kinetics [15] and regioselectivity [16] of reactions of these complexes with simple nucleophiles, so far the information revealed by the simple experiments described above has not been produced. Our conversion of complex (3t) into spiro[4.5]decane derivatives,[17] and our recently completed [18] conversion of complex (3w) into the C-18 oxygenated aspidosperma alkaloid, limaspermine (12), illustrate the need to achieve maximum selectivity in all of these nucleophile additions.

In conclusion, the work reported herein has led to a formula which can now be applied in order to obtain maximum control during the formation of remotely functionalised quaternary centres *via* organoiron complexes. We anticipate that our findings, in addition to providing useful fundamental information, will enhance the synthetic usefulness of these complexes.

EXPERIMENTAL

^1H N.m.r. spectra were recorded using a Varian EM 390, ^{13}C n.m.r. with a Varian XL 200, i.r. spectra with a Perkin-Elmer 577, and mass spectra with an A.E.I. MS12 spectrometer. M.p.s were measured on a Kofler block and are uncorrected. All reactions and chromatographic operations were conducted under an atmosphere of dry nitrogen.

Preparation of Dienylium Complexes.—Tricarbonyl[1—5-η-1-(2-methoxycarbonylethyl)-4-methoxycyclohexa-2,4-dienylium]iron hexafluorophosphate (1e) was available from our previous work.[17] We have recently employed the phthalimidoyl derivative (1f) in a total synthesis of limaspermine derivatives; full details of its preparation will be reported elsewhere.[18]

Tricarbonyl(1-ethyl-4-methoxycyclohexadienylium)iron hexafluorophosphate (1c). 4-Ethylanisole (50 g) was subjected to Birch reduction in liquid ammonia (1 l) containing tetrahydrofuran (THF) (50 ml) and ethanol (50 ml), using sodium metal (25 g). The usual work-up afforded crude 1-ethyl-4-methoxycyclohexa-2,5-diene (50 g), which was heated to 80 °C with toluene-4-sulphonic acid for 1.2 h to effect partial conjugation. The cooled product was washed with aqueous sodium carbonate and dried (Na_2CO_3) to afford a mixture (*ca.* 2 : 1, n.m.r.) of conjugated and unconjugated dienes (45 g). Part of the crude mixture (35 g) was treated with pentacarbonyliron (70 ml) in di-n-butyl ether at 140 °C under argon for 50 h. The cooled mixture was filtered through Celite and the solvent was removed at aspirator pressure and chromatographed to afford tricarbonyl(1-ethyl-4-methoxycyclohexadiene)iron (5a) as a yellow oil (26 g, 37%; not optimised), $\nu_{max.}(CHCl_3)$ 2 035 and 1 965 cm^{-1}; $\delta(CDCl_3)$ 5.13 (1 H, d, *J* 5 Hz), 4.86 (1 H, d, *J* 5 Hz), 3.41 (3 H, s), 2.4—1.4 (6 H, m), and 1.03 (3 H, t, *J* 7 Hz); *m/e* 278 (M^+). Treatment of complex (5a) (25 g) with triphenylmethylium hexafluorophosphate (36 g) in dry dichloromethane (500 ml; 23 °C; 1 h), followed by precipitation with moist diethyl ether, afforded the pure hexafluorophosphate (1c) (36 g, 95%), $\nu_{max.}$(Nujol) 2 105, 2 055, and 2 045 cm^{-1}; $\delta(CD_3CN)$ 6.79 (1 H, dd, *J* 6, 3 Hz, 3-H), 5.55 (1 H, d, *J* 6 Hz, 2-H), 3.90 (1 H, m, 5-H), 3.76 (3 H, s, OMe), 2.95 (1 H, dd, *J* 16, 6 Hz, *endo*-6-H), 2.30 (1 H, d, *J* 16 Hz, *exo*-6-H), 2.10 (2 H, q, *J* 7 Hz), and 1.93 (3 H, t, *J* 7 Hz) (Found: C, 33.75; H, 3.4. Calc. for $C_{12}H_{13}F_6FeO_4P$: C, 34.15; H, 3.11%).

Tricarbonyl(1-ethyl-4-isopropoxycyclohexadienylium)iron hexafluorophosphate (1d). Birch reduction of 4-ethylisopropoxybenzene,[19] followed by conjugation as above, gave a mixture (*ca.* 5 : 1) of 1,3- and 1,4-dienes after distillation (88% yield). Treatment of the mixture (44 g) with pentacarbonyliron (100 ml) in di-n-butyl ether (250 ml) as above gave the crude tricarbonyl(1-ethyl-4-isopropoxycyclohexadiene)iron (5b) (35 g, 43%). Flash chromatography on silica gel using 4% ethyl acetate in hexane afforded pure material as a golden oil, $\nu_{max.}$($CHCl_3$) 2 040 and 1 955 cm^{-1}; δ($CDCl_3$) 5.05 (1 H, d, *J* 5 Hz), 4.85 (1 H, d, *J* 5 Hz), 4.02 (1 H, hept, *J* 6 Hz), 2.3—1.3 (6 H, m, 3 × CH_2), 1.25 and 1.15 (each 3 H, d, *J* 6 Hz, diastereotopic Me_2), and 1.01 (3 H, t, *J* 7 Hz); *m/e* 304 (4%), 278 (26), 248 (27), and 220 (100). The pure complex (31.5 g) was heated under reflux in dry dichloromethane (700 ml) with triphenylmethylium hexafluorophosphate (46.5 g) for 2.5 h, cooled, and precipitated as above to afford analytically pure dienylium complex (1d) as a yellow powder (45.7 g, 100%), $\nu_{max.}$(Nujol) 2 120 and 2 060 cm^{-1}; δ(CD_3CN) 6.70 (1 H, dd, *J* 6, 3 Hz, 3-H), 5.55 (1 H, d, *J* 6 Hz, 2-H), 4.58 (1 H, hept, *J* 5 Hz), 3.88 (1 H, m, 5-H), 2.96 (1 H, dd, *J* 16, 7 Hz, *endo*-6-H), 2.35 (1 H, d, *J* 16 Hz, *exo*-6-H), 1.92 (2 H, q, *J* 7 Hz), 1.30 and 1.25 (each 3 H, d, *J* 5 Hz, diastereotopic Me_2), and 0.95 (3 H, t, *J* 7 Hz) (Found: C, 37.15; H, 3.8. Calc. for $C_{14}H_{17}F_6FeO_4P$: C, 37.35; H, 3.8%).

Reactions of Dienylium Complexes with Nucleophiles and the Determination of Regioisomer Ratios.—The procedure is given for the reaction of complex (1c) with dimethyl potassiomalonate. All the others were similar except that the sodium enolates were prepared from sodium hydride (50% dispersion in mineral oil, washed with pentane) and the lithium enolates were generated using n-butyl-lithium. To a stirred solution of potassium t-butoxide (3.4 g) in dry THF (100 ml) under nitrogen was added dropwise a solution of dimethyl malonate (4.4 g) in THF (20 ml). The mixture was stirred at room temperature for 15 min; the reaction flask was then briefly opened with back-flushing of nitrogen and the solid complex (1c) (12.0 g) was added in one portion. Stirring was continued until dissolution of the complex had occurred (*ca.* 15 min). The mixture was then poured into 10% brine (300 ml) and the product extracted with diethyl ether in the usual way. Evaporation of the ether afforded a crystalline mixture of the regioisomers (3c) and (4c). A small sample was subjected to preparative t.l.c., which does not separate the regioisomers, to remove the excess of dimethyl malonate, and the resulting mixture was examined by ^1H n.m.r. spectroscopy using expanded spectra and multiple integration. The ratio of isomers was estimated from the integrated intensities of the doublets at δ 5.21 and 4.85, due to 3-H and 2-H respectively of compound (4c), and the doublet doublet at δ 4.97, due to the 3-H of the isomer (3c). Comparison with the n.m.r. spectra obtained prior to chromatography revealed no difference in ratio (due, *e.g.*, to selective decomposition). In the case of methoxy-substituted complexes the ratio could be confirmed by comparing the heights of the methoxy-singlets at δ 3.57 [compound (3c)] and δ 3.34 [compound (4c)], and the methyl triplets at *ca.* δ 0.8 and 1.0 [(3c) and (4c) respectively], but this could not be used for isopropoxy-substituted derivatives. In some cases the higher field doublet due to 4-H of isomers (4) was coincident with the double doublets corresponding to 3-H of compound (3), but the ratio could still be estimated satisfactorily using the observable 2-H doublet, and making the appropriate adjustment. Recrystallisation of the mixture of isomers (3c) and (4c) from hexane afforded pure crystalline (3c) (9.0 g, 78%), and evaporation of the liquors gave an oil composed of both isomers (4c) (65%) and (3c) (35%). Full details of spectral and analytical data for these and all other compounds prepared in this study are listed below.

Spectral and Analytical Data for Complexes (3c)—(3w) *and* (4c)—(4w).—*Tricarbonyl[dimethyl (2—5-η-1-ethyl-4-methoxycyclohexa-2,4-dienyl)malonate]iron* (3c) *and tricarbonyl[dimethyl (2—5-η-5-ethyl-2-methoxycyclohexa-2,4-dienyl)malonate]iron* (4c). Complex (3c), m.p. 101.5—102 °C; $\nu_{max.}$($CHCl_3$) 2 055, 1 975, 1 757, 1 730, and 1 490 cm^{-1}; δ($CDCl_3$) 4.97 (1 H, dd, *J* 7,3 Hz, 3-H), 3.69 (3 H, s, CO_2Me), 3.67 (3 H, s, CO_2Me), 3.57 (3 H, s, 4-OMe), 3.50 (1 H, s, malonate CH), 3.25 (1 H, m, 5-H), 2.73 (1 H, d, *J* 7 Hz, 2-H), 2.48 (1 H, dd, *J* 15, 3 Hz, *endo*-6-H), 1.5 (3 H, m, *exo*-6-H and CH_2), and 0.77 (3 H, t, *J* 7 Hz, Me); *m/e* 408 (10%), 380 (25), 352 (2), and 324 (100) (Found: C, 50.05; H, 4.9. Calc. for $C_{17}H_{20}FeO_8$: C, 50.02; H, 4.94%). Complex (4c) (from enriched mixture), δ($CDCl_3$) 5.21 (1 H, d, *J* 5 Hz, 3-H), 4.85 (1 H, d, *J* 5 Hz, 4-H), 3.67 (3 H, s, CO_2Me), 3.64 (3 H, s, CO_2Me), 3.34 (3 H, s, 2-OMe), 2.0—1.3 (5 H, m), and 1.02 (3 H, t, *J* 7 Hz, Me).

Tricarbonyl[dimethyl (2—5-η-1-ethyl-4-isopropoxycyclohexa-2,4-dienyl)malonate]iron (3d) *and tricarbonyl[dimethyl (2—5-η-5-ethyl-2-isopropoxycyclohexa-2,4-dienyl)malonate]iron* (4d). Complex (3d), m.p. 115—116 °C; $\nu_{max.}$($CHCl_3$) 2 050, 1 970, 1 760, 1 730, and 1 465 cm^{-1}; δ($CDCl_3$) 4.95 (1 H, dd, *J* 7,2 Hz, 3-H), 4.20 (1 H, hept, *J* 6 Hz), 3.68 (3 H, s), 3.66 (3 H, s), 3.50 (1 H, s), 3.26 (1 H, dd, *J* 3, 2 Hz, 5-H), 2.72 (1 H, d, *J* 7 Hz, 2-H), 2.5 (1 H, dd, *J* 15, 3 Hz, *endo*-6-H), 1.65—1.0 (3 H, m, obscured, *exo*-6-H and CH_2), 1.40 (3 H, d, *J* 6 Hz), 1.28 (3 H, d, *J* 6 Hz), and 0.80 (3 H, t, *J* 7 Hz); *m/e* 436 (12), 408 (25), 380 (3), and 352 (100) (Found: C, 52.1; H, 5.5. Calc. for $C_{19}H_{24}FeO_8$: C, 52.31; H, 5.55%).

Tricarbonyl[(2—5-η-1-ethyl-4-methoxycyclohexa-2,4-dienyl)malononitrile]iron (3e) *and tricarbonyl[(2—5-η-5-ethyl-2-methoxycyclohexa-2,4-dienyl)malononitrile]iron* (4e) (3e), m.p. 115—117 °C; $\nu_{max.}$($CHCl_3$) 2 260, 2 060, 1 990, and 1 487 cm^{-1}; δ($CDCl_3$) 5.17 (1 H, dd, *J* 6, 2.5 Hz), 3.68 (3 H, s), 3.57 (1 H, s), 3.27 (1 H, m), 2.46 (1 H, d, *J* 6 Hz), 1.85—1.45 (4 H, m), and 0.89 (3 H, t, *J* 7.5 Hz); *m/e* 342 (10%), 314 (15), 286 (17), 258 (78), and 192 (100) (Found: C, 52.85; H, 3.95; N, 8.1. Calc. for $C_{15}H_{14}FeN_2O_4$: C, 52.66; H, 4.12; N, 8.19%). Complex (4e) (from mixture), δ($CDCl_3$) 5.40 (d, *J* 5 Hz, 3-H), 5.07 (d, *J* 5 Hz, 4-H), 3.93 [d, *J* 3 Hz, $CH(CN)_2$], 3.42 (s, OMe), and 1.08 (t, *J* 7 Hz, Me).

Tricarbonyl[(2—5-η-1-ethyl-4-isopropoxycyclohexa-2,4-dienyl)malononitrile]iron (3f) *and tricarbonyl[(2—5-η-5-ethyl-2-isopropoxycyclohexa-2,4-dienyl)malononitrile]iron* (4f). Complex (3f), m.p. 127—128 °C; $\nu_{max.}$($CHCl_3$) 2 260, 2 060, 1 986, and 1 465 cm^{-1}; δ($CDCl_3$) 5.11 (1 H, dd, *J* 6.5, 2.5 Hz), 4.30 (1 H, hept, *J* 6 Hz), 3.61 (1 H, s), 3.24 (1 H, dd, *J* 5.5, 2.5 Hz), 2.45 (1 H, d, *J* 6.5 Hz), 1.85—1.5 (4 H, m), 1.42 (3 H, d, *J* 6 Hz), 1.25 (3 H, d, *J* 6 Hz) and 0.86 (3 H t, *J* 7 Hz); *m/e* 370 (10%), 342 (10), 314 (18), and 286 (100) (Found: C, 54.9; H, 5.0; N, 7.4. Calc. for $C_{17}H_{18}FeN_2O_4$: C, 55.16; H, 4.90; N, 7.57%). Complex (4f) (from mixture), δ($CDCl_3$) 5.23 (d, *J* 5 Hz, 3-H), 5.02 (d, *J* 5 Hz, 4-H), and 4.05 (d, *J* 3 Hz, $CH(CN)_2$).

Tricarbonyl[methyl (2—5-η-1-ethyl-4-methoxycyclohexa-2,4-dienyl)cyanoacetate]iron (3g) *and tricarbonyl[methyl (2—5-η-5-ethyl-2-methoxycyclohexa-2,4-dienyl)cyanoacetate]iron* (4g). These complexes were obtained as oily 1 : 1 mixtures of diastereoisomers. Complex (3g), $\nu_{max.}$($CHCl_3$) 2 250,

2 055, 1 985, 1 740, and 1 485 cm^{-1}; δ($CDCl_3$) 5.06 (1 H, 2 overlapping dd, *J* 6, 2.5 Hz) 3.75 (3 H, s), 3.63 and 3.59 (3 H, 2 × s, 4-MeO, diastereoisomers), 3.36 and 3.31 [1 H, 2 × s, C*H*(CN)CO_2Me, diastereoisomers], 3.25 (1 H, m), 2.47 and 2.38 (1 H, 2 × d, *J* 6 Hz, 2-H, diastereoisomers), 2.35—1.1 (4 H, m), 0.84 and 0.81 (3 H, 2 × t, *J* 7 Hz, Me, diastereoisomers); *m/e* 375 (7%), 347 (17), 319 (8), and 291 (100). Complex (4g) (from mixture), δ($CDCl_3$) 5.34 (d, *J* 5 Hz, 3-H), 4.97 (d, *J* 5 Hz, 4-H), 3.36 (s, 2-OMe).

Tricarbonyl[*methyl* (2—5-η-1-*ethyl*-4-*isopropoxycyclohexa*-2,4-*dienyl*)*cyanoacetate*]*iron* (3h) *and tricarbonyl*[*methyl* (2—5-η-5-*ethyl*-2-*isopropoxycyclohexa*-2,4-*dienyl*)*cyanoacetate*]*iron* (4h). These complexes were obtained as oily 1 : 1 mixtures of diastereoisomers. Complex (3h), $\nu_{max.}$($CHCl_3$) 2 255, 2 060, 1 980, 1 745, and 1 465 cm^{-1}; δ($CDCl_3$) 5.04 (1 H, 2 × dd, *J* 6, 2.5 Hz), 4.27 (1 H, 2 × hept, *J* 6 Hz), 3.77 (3 H, s), 3.50 and 3.47 (1 H, 2 × s), 3.26 (1 H, m), 2.48 and 2.38 (1 H, 2 × d, *J* 6 Hz), 2.23 and 2.07 (1 H, 2 × dd, *J* 15, 3 Hz, *endo*-6-H), 1.85—1.29 (9 H, complex due to diastereoisomers and diastereotopic groupings), 0.85 and 0.83 (3 H, 2 × t, *J* 7 Hz); *m/e* 403 (7%), 375 (12), 347 (11), and 319 (100). Complex (4h) (from mixture), δ($CDCl_3$) 5.23 (d, *J* 5 Hz, 3-H) and 4.97 (d, *J* 5 Hz, 4-H).

Tricarbonyl[S,S′-*diethyl* (2—5-η-1-*ethyl*-4-*methoxycyclohexa*-2,4-*dienyl*)*dithiomalonate*]*iron* (3i) *and tricarbonyl* [S,S′-*diethyl* (2—5-η-5-*ethyl*-2-*methoxycyclohexa*-2,4-*dienyl*)-*dithiomalonate*]*iron* (4i). These complexes were obtained as an oily inseparable mixture from preparative t.l.c. Complex (3i), $\nu_{max.}$($CHCl_3$) 2 040, 1 940, and 1 693 cm^{-1}; δ($CDCl_3$) 5.05 (1 H, dd, *J* 7.3, 2.7 Hz), 3.93 (1 H, s, C*H* thiomalonate), 3.59 (3 H, s), 3.27 (1 H, m), 3.35—0.7 (17 H, mixture does not permit individual assignments), and 2.60 (1 H, d, *J* 7.3 Hz, 2-H); *m/e* 468 (5%), 440 (9), 412 (9), 384 (20), 328 (8), 192 (80), 136 (60), and 121 (100) ($C_{19}H_{24}FeO_6S_2$ requires *M*$^+$, 468). Complex (4i), δ($CDCl_3$) 5.3 (1 H, dd, *J* 5, 1.3 Hz), 4.9 (1 H, d, *J* 5 Hz), 3.67 (1 H, dd, *J* 7, 1.3 Hz, C*H* thiomalonate), 3.35 (3 H, s), and 3.2—0.7 (18 H).

Tricarbonyl[S,S′-*diethyl* (2—5-η-1-*ethyl*-4-*isopropoxycyclohexa*-2,4-*dienyl*)*dithiomalonate*]*iron* (3j) *and tricarbonyl*-[S,S′-*diethyl* (2—5-η-5-*ethyl*-2-*isopropoxycyclohexa*-2,4-*dienyl*)*dithiomalonate*]*iron* (4j). These complexes were obtained as an oil from preparative t.l.c. Complex (3j), $\nu_{max.}$($CHCl_3$) 2 050, 1 940, and 1 680 cm^{-1}; δ($CDCl_3$) 4.97 (1 H, dd, *J* 6.6, 2.4 Hz), 4.20 (1 H, hept, *J* 6 Hz), 3.91 (1 H, s, CH thiomalonate), 3.29 (1 H, m), 3.07—2.65 (5 H, m, 2 × CH_2 and *endo*-6-H), 2.58 (1 H, d, *J* 6.6 Hz), and 2.15—0.6 (18 H, m), *m/e* 496 (3%), 468 (10), 440 (2), 412 (20), 220 (55), 160 (50), and 122 (100) ($C_{21}H_{28}FeO_6S_2$ requires *M*$^+$, 496). Complex (4j), δ($CDCl_3$) 5.10 (1 H, d, *J* 4.5 Hz), and 4.77 (1 H, d, *J* 4.5 Hz).

Tricarbonyl[*methyl* 2-(2—5-η-1-*ethyl*-4-*methoxycyclohexa*-2,4-*dienyl*)*acetoacetate*]*iron* (3k) *and tricarbonyl*[*methyl* 2-(2—5-η-5-*ethyl*-2-*methoxycyclohexa*-2,4-*dienyl*)*aceto-acetate*]*iron* (4k). These complexes were obtained as a diastereoisomeric mixture from which 95% pure single diastereoisomer (3k) was obtained by crystallisation from diethyl ether–pentane. N.m.r. data are quoted for this isomer, and for the mixture of diastereoisomers (4k). Complex (3k), $\nu_{max.}$($CHCl_3$) 2 045, 1 975, 1 737, 1 720, and 1 485 cm^{-1}; δ($CDCl_3$) 4.97 (1 H, dd, *J* 6.5, 2.5 Hz), 3.72 (1 H, s), 3.68 (3 H, s), 3.59 (3 H, s), 3.25 (1 H, m), 2.76 (1 H, d, *J* 6.5 Hz), 2.43 (1 H, dd, *J* 16, 3 Hz), 2.20 (3 H, s), 1.65—1.35 (3 H, m), 0.85 (3 H, t, *J* 7.5 Hz) (Found: *M*$^+$, 392; C, 52.1; H, 5.05. Calc. for $C_{17}H_{20}FeO_7$: *M*$^+$, 392; C, 52.06; H, 5.14%). Complex (4k) δ($CDCl_3$) 5.25 (1 H, 2 × overlapping d), 4.90 (1 H, 2 × d), 3.32 and 3.28 (3 H, 2 × s, 2-OMe), 2.13 and 2.15 (3 H, 2 × s, CO·Me), and 1.03 (3 H, t, *J* 7 Hz, Me).

Tricarbonyl[*methyl* 2-(2—5-η-1-*ethyl*-4-*isopropoxycyclohexa*-2,4-*dienyl*)*acetoacetate*]*iron* (3l) *and tricarbonyl*]*methyl* 2-(2—5-η-5-*ethyl*-2-*isopropoxycyclohexa*-2,4-*dienyl*)*aceto-acetate*]*iron* (4l). These complexes were obtained as an oily diastereoisomeric mixture of (3l) containing only trace amounts of (4l). Complex (3l), $\nu_{max.}$($CHCl_3$) 2 055, 1 975, 1 740, 1 715, and 1 465 cm^{-1}; δ($CDCl_3$) 4.89 and 4.87 (1 H, 2 × dd, *J* 6.5, 2.5 Hz), 4.18 (1 H, hept, *J* 6 Hz), 3.71 and 3.69 (3 H, 2 × s, CO_2Me), 3.69 (1 H, s, acetoacetate, obscured), 3.26 (1 H, m), 2.7 and 2.63 (1 H, 2 × d, *J* 6.5 Hz), 2.53 and 2.30 (1 H, 2 × dd, *J* 16, 3 Hz, *endo*-6-H), 2.21 and 2.15 (3 H, 2 × s, CO·Me), 1.8—1.1 (9 H, m, *exo*-6-H, CH_2, diastereoisomeric and diastereotopic i-Pr), and 0.86 and 0.85 (3 H, 2 × t, *J* 7 Hz); *m/e* 420 (12), 392 (36), and 336 (100).

Tricarbonyl[*methyl* 1-(2—5-η-1-*ethyl*-4-*methoxycyclohexa*-2,4-*dienyl*)-2-*oxocyclopentanecarboxylate*]*iron* (3m), *tricarbonyl*[*methyl* 1-(2—5-η-5-*ethyl*-2-*methoxycyclohexa*-2,4-*dienyl*)-2-*oxocyclopentanecarboxylate*]*iron* (4m), *and tricarbonyl*(1—4-η-2-*methoxy*-5-*ethylidenecyclohexa*-1,3-*diene*)-*iron* (6a). These compounds were obtained from the reaction of the dienylium complex (1c) at 0 °C with methyl 2-oxo-1-potassiocyclopentanecarboxylate, in a *ca.* equimolar ratio (1 : 1 : 1) and in 89% combined yield. Preparative t.l.c. allowed only partial purification of each product. The exocyclic olefin (6a) was very unstable. Spectra data obtained from the partially purified products are as follows. Complex (3m), $\nu_{max.}$($CHCl_3$) 2 050, 1 970, 1 750, and 1 720 cm^{-1}; δ($CDCl_3$) 5.0 (1 H, dd, *J* 6.5, 2.5 Hz), 3.65 (3 H, s), 3.58 (3 H, s), 3.26 (1 H, m), 2.85 (1 H, d, *J* 6.5 Hz), 2.5—1.3 (10 H), and 0.70 (3 H, t, *J* 7.5 Hz); *M*$^+$, 418. Complex (4m) [obtained almost pure; contaminated with *ca.* 10% of complex (6a)], $\nu_{max.}$($CHCl_3$) 2 050, 1 970, 1 750, and 1 720 cm^{-1}; δ($CDCl_3$) 5.35 (1 H, d, *J* 5 Hz), 4.87 (1 H, d, *J* 5 Hz), 3.64 (3 H, s), 3.20 (3 H, s), 2.5—1.2 (11 H), and 1.00 (3 H, t, *J* 7 Hz); *M*$^+$, 418. Complex (6a) (obtained *ca.* 90% pure), $\nu_{max.}$($CHCl_3$) 2 070, 1 975, and 1 600 cm^{-1}; δ($CDCl_3$) 5.25 (1 H, m), 5.08 (1 H, dd, *J* 6.5, 2.5 Hz), 3.61 (3 H, s), 3.48 (1 H, m), 3.18 (1 H, d, *J* 6.5 Hz), 2.3 (2 H, m), and 1.37 (3 H, d, *J* 7.5 Hz). When the same reaction was commenced at −78 °C and allowed to warm to 0 °C a mixture (5 : 3 : 1) of the complexes (3m), (4m), and (6a) was produced (85% combined yield).

Tricarbonyl[*methyl* 1-(2—5-η-1-*ethyl*-4-*isopropoxy-cyclohexa*-2,4-*dienyl*)-2-*oxocyclopentanecarboxylate*]*iron* (3n) *and tricarbonyl*(1—4-η-2-*isopropoxy*-5-*ethylidenecyclohexa*-1,3-*diene*)*iron* (6b). These compounds were obtained in a combined yield of 86% from the reaction of complex (1d) at 0 °C with methyl 2-oxo-1-potassiocyclopentanecarboxylate in the ratio *ca.* 4 : 1 (estimated from the n.m.r. spectrum). Complex (6b) was not isolated in a pure state and was not further characterised. The regioisomer (4n) could not be detected in the n.m.r. spectrum. Preparative t.l.c. afforded a diastereoisomeric mixture of complex (3n) in 69% yield, from which a single diastereoisomer could be obtained by crystallisation from diethyl ether–pentane, m.p. 98.5—100.5 °C, $\nu_{max.}$($CHCl_3$) 2 050, 1 975, 1 745, and 1 730 cm^{-1}; δ($CDCl_3$) 4.92 (1 H, dd, *J* 6.5, 2.5 Hz), 4.21 (1 H, hept, *J* 6 Hz), 3.65 (3 H, s), 3.22 (1 H, m), 2.83 (1 H, d, *J* 6.5 Hz), 2.6—1.4 (10 H), 1.35 (3 H, d, *J* 6 Hz), 1.15 (3 H, d, *J* 6 Hz), and 0.74 (3 H, t, *J* 7.5 Hz) (Found: *M*$^+$, 446; C, 56.25; H, 5.8. Calc. for $C_{21}H_{26}FeO_7$: *M*$^+$, 446; C, 56.5; H, 5.85%). Use of the sodium enolate of methyl 2-oxocyclopentanecarboxyl-

ate gave a slightly improved yield (73%) of complex (3n).

Tricarbonyl{[2—5-η-4-*methoxy*-1-(2-*methoxycarbonylethyl*)*cyclohexa*-2,4-*dienyl*]*malononitrile*}*iron* (3r) *and tricarbonyl*{[2—5-η-2-*methoxy*-5-(2-*methoxycarbonylethyl*)-*cyclohexa*-2,4-*dienyl*]*malononitrile*}*iron* (4r). These compounds were obtained as a yellow oil. Complex (3r), $\nu_{max.}$($CHCl_3$) 2 250, 2 050, 1 975, 1 730, and 1 490 cm^{-1}; δ($CDCl_3$) 5.19 (1 H, dd, *J* 6 , 2.5 Hz), 3.70 [7 H, br s, CO_2Me, OMe, $CH(CN)_2$], 3.36 (1 H, dd, *J* 7, 2.5 Hz), 2.45 (1 H, d, *J* 6 Hz), and 2.4—1.8 (6 H, m); *m/e* 372 (16%, *M* − CO), 344 (42), 316 (79), 251 (95), and 250 (100). Complex (4r), δ($CDCl_3$) 5.43 (1 H, d, *J* 5 Hz), 5.13 (1 H, d, *J* 5 Hz), 4.10 [1 H, d, *J* 8 Hz, C*H*$(CN)_2$], and 3.43 (3 H, s, 2-OMe).

Tricarbonyl{*methyl* [2—5-η-4-*methoxy*-1-(2-*methoxycarbonylethyl*)*cyclohexa*-2,4-*dienyl*]*cyanoacetate*}*iron* (3s) *and tricarbonyl*{*methyl* [2—5-η-2-*methoxy*-5-(2-*methoxycarbonylethyl*)*cyclohexa*-2,4-*dienyl*]*cyanoacetate*}*iron* (4s). The mixture was obtained as a yellow oil. Complex (3s), $\nu_{max.}$($CHCl_3$) 2 250, 2 050, 1 975, 1 745, 1 735, and 1 490 cm^{-1}; δ($CDCl_3$) 5.11 and 5.09 (1 H, 2 × dd, *J* 6, 2 Hz, diastereoisomers), 3.78 (3 H, s), 3.68 (6 H, s), 3.45 (1 H, s), 3.29 (1 H, m), and 2.5—1.5 (7 H, m); *m/e* 433 (0.5%), 405 (6), 377 (20), 349 (33), and 250 (100). Complex (4s), δ($CDCl_3$) 5.40 (1 H, d, *J* 4.5 Hz), 5.10 (1 H, d, *J* 4.5 Hz), and 3.40 (3 H, s).

Tricarbonyl{*dimethyl* [2—5-η-4-*methoxy*-1-(2-*methoxycarbonylethyl*)*cyclohexa*-2,4-*dienyl*]*malonate*}*iron* (3t) *and tricarbonyl*{*dimethyl* [2—5-η-2-*methoxy*-5-(2-*methoxycarbonylethyl*)*cyclohexa*-2,4-*dienyl*]*malonate*}*iron* (4t). These complexes have been described elsewhere.[17]

Tricarbonyl{*methyl* [2—5-η-4-*methoxy*-1-(2-*methoxycarbonylethyl*)*cyclohexa*-2,4-*dienyl*]*acetoacetate*}*iron* (3u) *and tricarbonyl*{*methyl* [2—5-η-2-*methoxy*-5-(2-*methoxycarbonylethyl*)*cyclohexa*-2,4-*dienyl*]*acetoacetate*}*iron* (4u). The mixture of regioisomers and diastereoisomers was obtained as a yellow oil, inseparable by t.l.c. Complex (3u), $\nu_{max.}$($CHCl_3$) 2 040, 1 970, 1 730, 1 710, and 1 490 cm^{-1}; δ($CDCl_3$) 4.95 (1 H, dd, *J* 7,3 Hz), 3.8—3.6 [9 H, 3 × s, obscured by signals from (4u)], 3.4 (1 H, m), 3.34 (1 H, s, acetoacetate C*H*), 2.7—1.2 (7 H, m), and 2.2 and 2.15 (3 H, 2 × s, MeCO diastereoisomers); *m/e* 450 (1%), 422 (11), 396 (20), and 386 (100). Complex (4u), δ($CDCl_3$) 5.28 and 5.22 (1 H, 2 × d, *J* 5 Hz), 5.05—4.85 (1 H, 2 × d, obscured), 3.29 (3 H, s, 2-OMe), and 2.19 and 2.15 (3 H, 2 × s, diastereoisomers).

Tricarbonyl{[2—5-η-4-*methoxy*-1-(2-*phthalimidoylethyl*)-*cyclohexa*-2,4-*dienyl*]*malononitrile*}*iron* (3v) *and tricarbonyl*-{[2—5-η-2-*methoxy*-5-(2-*phthalimidoylethyl*)*cyclohexa*-2,4-*dienyl*]*malononitrile*}*iron* (4v). The mixture was obtained as a yellow oil which could not be crystallised, and the compounds were inseparable on t.l.c. Complex (3v), $\nu_{max.}$($CHCl_3$) 2 260, 2 060, 1 970, 1 775, 1 715, and 1 491 cm^{-1}; δ($CDCl_3$) 7.77 (4 H, m), 5.16 (1 H, dd, *J* 6.3, 2.4 Hz), 3.68 (5 H, s, 4-OMe and C*H*$_2$N), 3.40 (1 H, s), 3.23 (1 H, m), 2.46 (1 H, d, *J* 6.3 Hz), and 1.9—1.2 (6 H); *m/e* 501 (0.5%), 473 (0.1), 445 (3), 417 (20), 351 (70), 295 (90), and 121 (100). Complex (4v), δ($CDCl_3$) 7.77 (4 H, m), 5.40 (1 H, dd, *J* 3.6, 1.2 Hz), 5.10 (1 H, d, *J* 3.6 Hz, part obscured), and 3.98 [1 H, d, *J* 4 Hz, $CH(CN)_2$].

Tricarbonyl{*dimethyl* [2—5-η-4-*methoxy*-1-(2-*phthalimidoylethyl*)*cyclohexa*-2,4-*dienyl*]*malonate*}*iron* (3w) *and tricarbonyl*{*dimethyl* [2—5-η-2-*methoxy*-5-(2-*phthalimidoylethyl*)*cyclohexa*-2,4-*dienyl*]*malonate*}*iron* (4w). The mixture of regioisomers obtained from the dimethyl potassiomalonate reaction was subjected to fractional crystallisation from diethyl ether, to give pure complex (3w), m.p. 155.5—156.5 °C, $\nu_{max.}$($CHCl_3$) 2 055, 1 950, 1 771, 1 755, 1 732, 1 713, and 1 490 cm^{-1}; δ($CDCl_3$) 7.80 (4 H, m), 4.98 (1 H, dd, *J* 6,2 Hz), 3.71 (3 H, s), 3.69 (3 H, s), 3.61 (3 H, s), 3.7 (2 H, m, obscured, C*H*$_2$N), 3.47 (1 H, s), 3.27 (1 H, m), 2.72 (1 H, d, *J* 6 Hz), 2.50 (1 H, dd, *J* 15, 2 Hz), and 1.8—1.3 (5 H); *m/e* 567 (1%), 539 (0.5), 511 (2), 483 (4), 425 (10), 351 (30), 295 (40), and 107 (100) (Found: C, 54.8; H, 4.65; N, 2.5. Calc. for $C_{26}H_{25}FeNO_{10}$: C, 55.0; H, 4.44; N, 2.47%). The mother-liquor contained predominantly the isomeric complex (4w) which could not be crystallised, $\nu_{max.}$(CCl_4) 2 040, 1 970, 1 770, 1 756, 1 735, and 1 715 cm^{-1}; δ($CDCl_3$) 7.75 (4 H, m), 5.20 (1 H, d, *J* 4.6 Hz), 4.93 (1 H, d, *J* 4.6 Hz), 4.0 (1 H, d, *J* 6 Hz), 3.70 (3 H, s), 3.67 (3 H, s), 3.70 (2 H, m), 3.35 (3 H, s), and 2.8—1.0 (7 H); *m/e* 567 (0.5%), 511, 483 (4), 452 (10), 425 (20), 365 (8), 351 (50), and 295 (100).

Tricarbonyl[2-(2—5-η-4-*isopropoxy*-1-*ethylcyclohexa*-2,4-*dienyl*)*ethanol*]*iron* (3p). To the mixture of isomeric complexes (3j) and (4j) obtained from the reaction of complex (1b) with *S,S'*-diethyl potassiodithiomalonate (50 mg, 0.10 mmol), was added W2 Raney nickel (1.5 ml settled volume) suspended in benzene (4 ml). After being stirred at room temperature for 45 min, the mixture was decanted and the residue washed thoroughly with benzene and then methanol. Removal of solvent, followed by preparative t.l.c., afforded pure complex (3p) as an oil which could not be crystallised (15.3 mg, 44%; not optimised), $\nu_{max.}$(CCl_4) 3 640, 2 045, 1 950, and 1 472 cm^{-1}; δ($CDCl_3$) 5.03 (1 H, dd, *J* 7 , 2.5 Hz), 4.27 (1 H, hept, *J* 6 Hz), 3.63 (2 H, t, *J* 7 Hz, sharpens on shaking with D_2O), 3.28 (1 H, m), 2.49 (1H, d, *J* 7 Hz), 1.7—8 (15 H, m and 1 H, exchanges with D_2O, 3 × CH_2, 3 × Me, OH); *m/e* 350 (2%), 322 (10), 294 (2), 266 (21), and 220 (100) ($C_{16}H_{22}FeO_5$ requires M^+, 350).

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