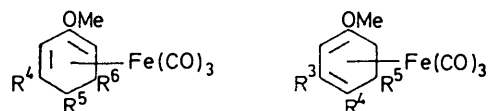# Organometallic Complexes in Synthesis. Part IV.[1] Abstraction of Hydride from some Tricarbonylcyclohexa-1,3-dieneiron Complexes and Reactions of the Complexed Cations with some Nucleophiles

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Isomeric 1- and 2-methoxy-derivatives of tricarbonylcyclohexa-1,3-dieneiron can frequently be separated by chromatography. The positions of removal of hydride from such complexes, relative to OMe and/or Me substituents, have been examined. Some of the resulting mesomeric cations have been treated with the nucleophiles borohydride, hydroxide, and morpholine to define positions of reaction relative to substitution. Among other nucleophiles which react are enamines and ketones. Conditions for removal of the tricarbonyliron group from the resulting complexes have been examined.

To be useful in organic synthesis,[1] the nucleophilic reactions which can be carried out with tricarbonyl-cyclohexadienyliron salts require to be supplemented with information of various sorts, as follows: (i) the experimental conditions required for good yields in re-action of iron carbonyls with the readily available cyclo-hexa-1,4-dienes to form tricarbonylcyclohexa-1,3-diene-iron complexes, and the effects of conditions on ratios of isomers produced; (ii) the methods, direct or indirect, which are effective in separation of isomeric complexes or which are capable of generating pure complexes; (iii) the effects of substituents in these complexes on positions of removal of hydride with triphenylmethyl fluoroborate to generate tricarbonylcyclohexadienyliron salts; (iv) The extent and positions, including stereo-chemistry, of reactions of nucleophiles of various types with such cations; (v) The most efficient methods of re-moval of the iron to give a desirable organic structure.

The present work was aimed to provide some of this in-formation, particularly with methoxy-dienes, since the presence of a methoxy-substituent introduces further possibilities of synthetic use.

A preliminary account [2] has been given of the formation of mixed complexes from some methoxycyclohexa-1,4-dienes, available from the Birch reduction of anisoles, but the product mixtures were not separated. We have now separated isomers from several such mixtures, notably the 1-methoxy- from the 2-methoxy-series, by chromatography on silica. We have been able therefore

to check hydride abstraction results [2] originally obtained by use of mixtures, and in several instances the conclu-sions must be modified.

(1) $R^4 = R^5 = R^6 = H$
(2) $R^4 = R^6 = H, R^5 = Me$
(3) $R^4 = Me, R^5 = R^6 = H$
(4) $R^4 = Me, R^5 = H, R^6 = endo$-Me
(5) $R^4 = Me, R^5 = H, R^6 = exo$-Me

(6) $R^3 = R^4 = R^5 = H$
(7) $R^3 = R^5 = H, R^4 = Me$
(8) $R^3 = Me, R^4 = R^5 = H$
(9) $R^3 = R^4 = H, R^5 = Me$
(10) $R^3 = R^5 = Me, R^4 = H$

The compounds listed in Tables 1 and 2 were obtained by the action of iron pentacarbonyl on the product of Birch reduction of the appropriate anisole, followed by separation except in the cases noted. The structures

TABLE 1

2-Methoxy-diene complexes. ^{1}H N.m.r. absorptions (solutions in carbon tetrachloride; δ values; J in Hz)

Compound	1-H	OMe	3-H	R^4	R^5	5-H	R^6	6-H
(1)	3·40dd, J 4, 1·5	3·58s	5·02dd, J 4, 1·5	2·70m	2·60m	2·60m	2·60m	2·60m
(2)	3·24bs	3·58s	5·0dd, J 4, 1·5	2·62dd, J 4, 2	0·92d, J 6	2·06m	2·06m	1·32dd, J 10, 2
(3)	3·32m	3·56s	4·94s	1·62s	2·8—2·2m		2·8—2·2m	2·8—2·2
(4)	3·14t, J 2	3·60s	4·96s	1·62s	2·0m	2·0m	1·0d, J 6	1·20m
(5)	3·26dd, J 2·5, 1·5	3·60s	5·10d, J 1·5	1·55s	1·96q, J 10, 8	1·0m	0·96d, J 6	2·28 octet

were deduced from the resonances shown. Tricarbonyl-1-methoxy-3-methylcyclohexa-1,3-dieneiron (8) and its 5-methyl isomer (9) could not be separated; results are deduced from reactions of the mixture. Tricarbonyl-2-methoxy-4,6-dimethylcyclohexa-1,3-dieneiron was ob-tained as a 1 : 1 mixture of the 6-*exo*- (5) and 6-*endo*-methyl (4) isomers. The *exo*-isomer was unaffected by brief treatment with triphenylmethyl fluoroborate, and its spectrum could thus be examined separately, per-mitting the spectral assignments shown.

Optimal conditions were sought for the preparation

[1] Part III, A. J. Birch and M. A. Haas, *J. Chem. Soc. (C),* 1971, 2465.

[2] A. J. Birch, P. E. Cross, J. Lewis, D. A. White, and S. B. Wild, *J. Chem. Soc. (A),* 1968, 332.

of the mixture of compounds (1) and (6) from 1-methoxycyclohexa-1,4-diene [2] and pentacarbonyliron (see Experimental section) and of tricarbonylcyclohexa-1,3-dieneiron from cyclohexa-1,4-diene. Improved yields were obtained and the procedure employed will probably improve the yields of complexes in other cases, although its application has not yet been extensively examined.

formulated from spectra; [2] hence the original 1-methoxydienyl structure can be deduced. The 2-methoxydienyl salts, which are stable to water, can be precipitated as the hexafluorophosphate salts, and their structures can be deduced from n.m.r. spectra.[2]

Compounds (1)—(4) (Table 3) gave only water-stable 2-methoxydienyliron salts (15) and (17); compound (5)

Table 2

1-Methoxy-diene complexes. ^{1}H N.m.r. absorptions (solutions in carbon tetrachloride; δ values; J in Hz) *

Compound	OMe	2-H	R³	R⁴	R⁵	5-H	6-H
(6)	3·43s	5·26d, J 4·5	5·00dd, J 4·5, 3·5	2·70m	2·2—1·7m		
(7)	3·40s	5·10d, J 4	4·84d, J 4	1·56s	2·3—1·4m		
(8) a	3·42s	n.o.	2·05s	n.o.	n.o.	n.o.	n.o.
(9) a,b	3·38	5·32d, J 5	4·96dd, J 5, 4	2·80m	0·96d, J 7	2·50m	1·30m
(10) b	3·40s	5·30s	2·08s	2·84m	0·98d, J 6	2·20m	2·40d, J 14; 1·20dd, J 14, 2

a Only obtained in mixtures. b Ca. 90% of exo-5-Me isomer.
* N.o. = Not observable

This improvement is important for synthetic purposes, since previous yields were usually good enough only to obtain materials as reagents from readily available starting materials. Yields of ca. 70—80% make possible considerations of use with precursors obtained after a series of synthetic stages.

Tables 3 and 4 report the positions of abstraction of hydride from the compounds in Tables 1 and 2. The

did not react, presumably because the exo-situation of the methyl prevented attack by the bulky triphenylmethyl group. Compound (2) gave only a low yield

Table 3

Hydride abstractions from 2-methoxy-diene complexes

| | | | | % Abstraction of hydride from | | Total yield of salt |
Compound	R⁴	R⁵	R⁶	C-5	C-6	(%)
(1)	H	H	H	100		95
(2)	H	Me	H	100		12
(3)	Me	H	H		100	98
(4)	Me	H	endo-Me		100	98
(5)	Me	H	exo-Me	0	0	0

Table 4

Hydride abstractions from 1-methoxy-diene complexes

| | | | | % Abstraction of hydride from | | Total yield of salt |
Compound	R³	R⁴	R⁵	C-5	C-6	(%)
(6)	H	H	H	80	20	98
(7)	H	Me	H	10	90	90
(8) a	Me	H	H	100		ca. 100 b
(9) a	H	H	Me	100		ca. 10 b
(10)	Me	H	Me	100		10

a Only obtained in admixture, including endo-, exo-Me (9).
b Mixed salts, the low yield from (9) presumed only from the endo-Me isomer.
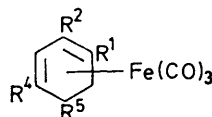
positions of abstraction are deducible from a combination of chemical and n.m.r. spectral [2] examination. The 1-methoxydienyl salts are unstable to water and are hydrolysed to neutral dienone complexes, which can be

(15) (16) (17) (18) (19) (20) (21) (22) (23) (24) (25)
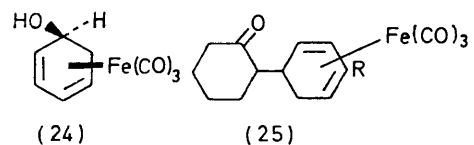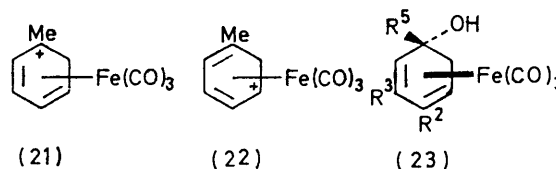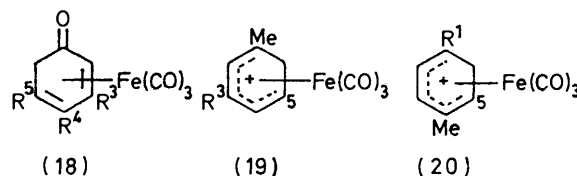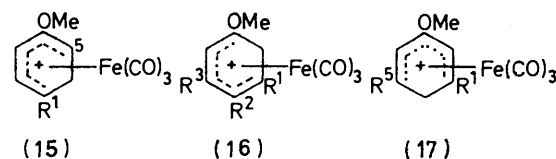
of salt, presumably because it is a mixture and the methyl group in position 5 is mostly in the exo-situation. Compounds (6) and (7) (Table 4) produced a mixture of salts, mainly hydrolysed to cyclohexadienone (from the 1-methoxy-salt). Compounds (8)—(10) gave solely 1-methoxy-salts (16), hydrolysed to cyclohexadienones

(18). Since compounds (8) and (9) could not be separated the dienones are also mixed, but the result is unequivocal in terms of the position of hydride abstraction from both. Table 5 illustrates some similar results

TABLE 5

Hydride abstractions from alkyl diene complexes

Compound	R¹	R²	R⁴	R⁵	% Abstraction of hydride from C-5	C-6	Total yield of salt (%)
(11)	H	Me	H	H	60	40	94
(12)	H	Me	Mc	H		100	96
(13)	H	Mc	H	Pr^i			0
(14)	Pr^i	H	Me	H	100		ca. 100

with hydrocarbon complexes. That from *p*-mentha-1,5-diene (13) was found not to undergo abstraction, in contrast to the complex of *p*-mentha-1,3-diene (14), which has a less hindered 5-position. The complex (12) reacted at the 6-position, generating a cation with terminal Me. The 2-Me of (11) exercises little influence.

Attempts may be made to rationalise the effects of substitution on the position of abstraction on the basis of steric hindrance and of the stability of the cation. Steric hindrance is clearly important: for example compounds (5) and (13) are both unaffected, and, as already noted, the low yield of salt (10%) suggests that (2) contains a minor proportion of *endo*- and a major proportion of *exo*-isomer, and that only the former reacts. The presence of isomers probably also explains the low yield of salt from the complexes (9) and (10). The most outstanding effect of substitution is that the extra methyl group at position 4 in structures (3) and (4), as compared with (1) and (2), causes abstraction to occur from the 6- rather than the 5-position.

Within this series, the cation carrying a methyl group at one terminus seems to be favoured; this might be correlated with a stabilising effect of the group, resembling that in simple alkyl cations. However, as noted elsewhere,[3] a methoxycarbonyl group does not have the opposite effect, so this inference is doubtful.

In the 1-methoxy-series [(6)—(10)] the principal or the sole product corresponds to formation of the 1-methoxy-salt, which could be favoured by the donor properties of a terminal methoxy-group. However the presence of a 3-methoxy-group in the cation, where it is also attached to a carbon atom which is formally positively charged, does not seem to be similarly favourable since compounds (1) and (2) undergo alternative abstraction to give a 2-methoxy-group in the cation. The 3-methoxy-cations also do not undergo the aqueous hydrolysis to dienones characteristic of the 1-methoxy-series. This may be because formation of the resulting neutral complexes would involve the iron interacting with unconjugated double bonds, or because an intermediate

oxonium salt could not be formed for the same reason. The practical consequences of the process can be summarised by noting that 1-methoxycyclohexa-1,3-diene complexes tend to give finally cyclohexadienones and 2-methoxy-complexes give cations with a 2- or a 3-methoxy-group according to the position of the remaining substituent(s).

Reactions of Salts with Nucleophiles.—A cation such as (19) might suffer attack by a nucleophile at the 1-, 3-, or 5-position; however, reaction at the central position has not been observed (the resulting complex would be that of a 1,4-diene). We have investigated which nucleophiles react and how the position of reaction is related to the structures of the reacting species.

Borohydride reductions of similar cations[2] result sometimes in pure products, sometimes in mixtures of isomers; usually the less substituted position is predominantly or exclusively involved. However, with some halogeno- or methoxy-substituted arenecyclopentadienyliron cations reductions are apparently governed by electronic effects: Cl directs *ortho* and OMe directs *meta* addition.[4]

Table 6 shows the results of borohydride reductions of some substituted tricarbonylcyclohexadienyliron salts.

TABLE 6

Sodium borohydride reductions [numbering refers to formulae (15), (19), (20)]

Salt	R	% Addition to C-1	C-5	Total yield of product (%)
(19)	Me	15	85	85
	MeO	0	100	88
(20)	H	50	50	90
	Me	25	75	92
	Pr^i	0	100	85
(15)	H	100	0	88
	Me	60 *	40	90

* 1 : 1 Mixture of *exo*- and *endo*-methyl in product.

The figures given are based on proportions of products deduced from the ¹H n.m.r. spectra.[2,4] Although borohydride reduction in a simple case[2] was found to occur stereospecifically *exo* to the tricarbonyliron group, this is no longer true if a methyl group is situated at the centre reduced. Reduction of the cation (17; R¹ = R⁵ = Me) gave a mixture of the 5-*exo*- and 5-*endo*-methyl products in the ratio 1 : 2. The isomers could be distinguished by the fact that triphenylmethyl fluoroborate regenerated the cation from the latter but not from the former. The lack of stereospecificity may be due to the fact that *exo*-reduction forces the methyl group on to the same side of the ring as the tricarbonyliron, resulting in more unfavourable interactions than with the hydrogen analogue. *endo*-Attack is therefore competitive.

Table 7 records the results with morpholine and with

[3] A. J. Birch and D. H. Williamson, following paper.
[4] I. U. Khand, P. L. Pauson, and W. E. Watts, *J. Chem. Soc.* (C), 1969, 116.

hydroxide, those with borohydride being added for comparison. The nucleophiles differ in type: morpholine is a neutral molecule and hydroxide and borohydride are formally charged anions which differ in that the former adds directly, whereas reaction of the latter involves

TABLE 7

Reactions with morpholine, hydroxide, and borohydride
[numbering refers to formulae (15), (19), (20)]

Salt	% Addition to C-1		
	Hydroxide	Morpholine	Borohydride
(15; R = Me)	100	100	60
(19; R = Me)	90	10	15
(20; R = Me)	100	20	25

bond breaking to give hydride addition by any of a series of different reagents.

Hydroxide predominantly adds to a terminus carrying a methyl group in all three cases, *i.e.* to a localised form such as (21). This would be expected if a methyl group has the same effect on charge distribution as in a normal organic cation; in view of the Fe—C bonding this is an assumption which may be made only in the form

already been shown to react.[2] The range is mechanistically extendable to enamines, and possibly to ketones if these enolise readily enough. 1-Pyrrolidin-1-ylcyclohexene, in fact, readily gave the complex (25; R = OMe), reaction with the cation (15; R = H) occurring at the 5-position only. How general the process is remains to be seen since the pyrrolidine 3,5-dien-3-amines derived from testosterone and estr-4-ene-3,17-dione reacted only at the nitrogen atom to give quaternary salts of type (26).

The dienyl salts reacted directly with a number of ketones in refluxing ethanol to give the 5-substituted cyclohexa-1,3-diene complexes in good yield, *e.g.* (27; R = H, R^1 = CH_2·COMe) from acetone. The structures were assigned from spectra: the i.r. spectra show the usual metal carbonyl bands at 2060 and 1960 cm^{-1} and the ketone carbonyl band is found in the usual position. The ^1H n.m.r. spectra indicate the presence of two 'inner' and two 'outer' protons on the diene unit at δ *ca.* 5·4 and 3·1. The mass spectra show molecular ions and loss of 1—3 CO.

Reaction with cyclohexanone gave compound (25; R = H) in 70% yield. Aliphatic ketones appear to

TABLE 8

Solvent shifts [$\Delta = \delta(CCl_4) - \delta(C_6H_6)$] for substituted tricarbonyl-5-hydroxycyclohexa-1,3-dieneiron complexes

Compound	Δ(p.p.m.)						
	1-H	R^2	R^3	4-H	R^5	6-H	OH
(23; R^2 = R^3 = R^5 = H)	0·32	0·38	0·38	0·10	0·02	0·06,[a] 0·20 [b]	0·84
(23; R^2 = H, R^3 = R^5 = Me)	0·26	0·44	0·32	0·10	0·02	0·06	0·98
(23; R^3 = H, R^2 = R^5 = Me)	0·32	0·38	0·38	0·14	0·0	0·08	0·96
(24)	0·40	0·52	0·52	0·20	0·26	0·04,[b] 0·32 [a]	0·32

[a] *endo*-Proton.   [b] *exo*-Proton.

that the localisation required for reaction is easier in the form (21) than in the alternative (22).

In order to determine the stereochemistry at position 5 in the hydroxy-complexes the ^1H n.m.r. spectra of solutions in carbon tetrachloride and benzene were measured and the solvent shifts were compared with those of the known tricarbonyl-5-*exo*-hydroxycyclohexa-1,3-dieneiron (23; R^2 = R^3 = R^5 = H) and the 5-*endo*-isomer (24).[2] The results (Table 8) show that the solvent shift of the 5-methyl group is small and comparable with the shift of the 5-*endo*-proton in (23; R^1 = R^3 = R^5 = H), whereas the solvent shift of the 5-*exo*-proton in (24) is much larger. The solvent shift of the 5-*exo*-hydroxy-group is also much larger than that of the 5-*endo*-hydroxy-group. Thus the hydroxy-group is *exo* to the tricarbonyliron, as might be expected from reactivity considerations.

With morpholine and borohydride the results may be rationalised by taking into account the additional effect of steric hindrance, the extra substituent in (15) and (20) possibly tending to direct reaction back to the unsubstituted end.

Enamines and Ketones.—Other nucleophiles, such as the readily enolised β-diketones or β-keto-esters, have

react at the more highly substituted position, probably through the more stable enol form; methyl ethyl ketone and methyl isopropyl ketone react respectively on the ethyl and on the isopropyl group to give compounds (27; R^1 = H, R^2 = CHMe·COMe or CMe_2·COMe). The structures were supported by spectra and, in the second case, by formation of the benzylidene derivative. There was no evidence of disubstitution. More complex ketones which reacted satisfactorily were 6-methoxy-1-tetralone and 4-methylpent-3-en-2-one (mesityl oxide) which gave mainly the isomer (28) through reaction with the fully conjugated enol at its terminus. The enolate anion from the latter is usually alkylated in the 3-position.

To see whether the reaction is base-catalysed, compound (15; R = H) was treated with cyclohexanone and triethylamine in ethanol. The product (85% yield) was the ethoxy-derivative (27; R^1 = OMe, R^2 = OEt).

The products undergo many of the normal reactions of ketones without interference by the complexed diene system. Borohydride reduction of compound (27; R^1 = H, R^2 = CH_2·COMe) gave the alcohol (27; R^1 = H, R^2 = CH_2·CHMe·OH), and the carbonyl group reacts normally with 2,4-dinitrophenylhydrazine. Condensation of benzaldehyde with compound (27; R^1 = H,

$R^2 = CH_2 \cdot COMe$) gave the enone (27; $R^1 = H$, $R^2 = CH_2 \cdot CO \cdot CH=CHPh$).

Prolonged refluxing of the initial reaction mixture led to some isomerisation of the diene complex. For example, after 7 h the complex (27; $R^1 = H$, $R^2 = CH_2 \cdot COMe$) was produced in 77% yield with only traces of other compounds. After 17 h two other isomers (29) and (30) could be detected from the n.m.r. spectrum,

(26)   (27)

(28)   (29)   (30)

(31)   (32)

(33)
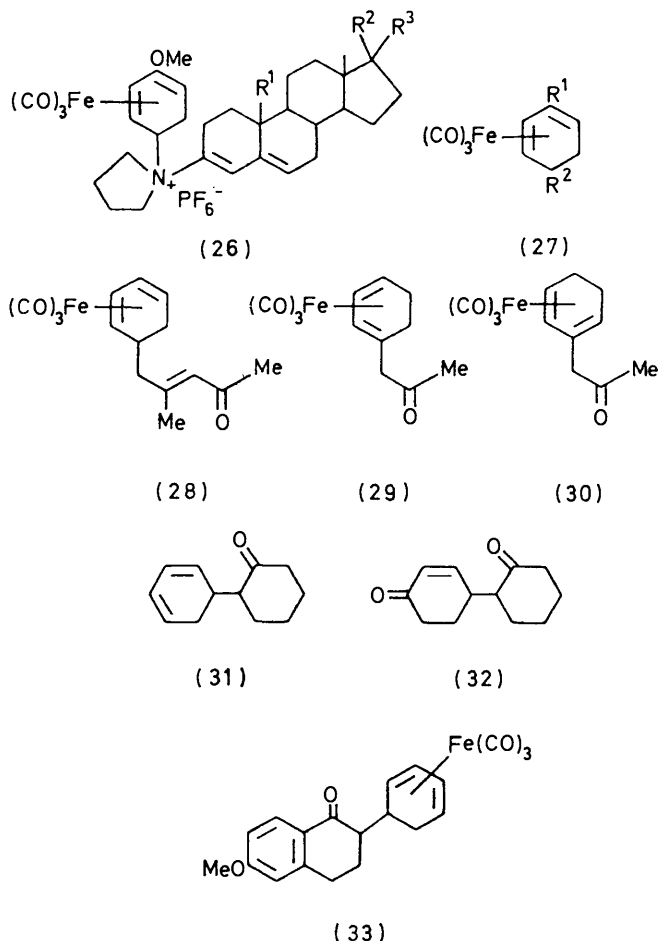
the ratios being about 10 : 4 : 1. In the belief that this reaction was acid-catalysed, we heated the complex (27; $R^1 = H$, $R^2 = CH_2 \cdot COMe$) under reflux with ethanolic fluoroboric acid; similar isomerisation results were obtained. Use of methanolic sulphuric acid (10%, v/v) caused a much more complete isomerisation to give a 1 : 2 : 7 mixture of compounds (27; $R^1 = H$, $R^2 = CH_2 \cdot COMe$), (29), and (30); these proportions did not change further, and probably represent the equilibrium situation. Complete chromatographic separation of the mixture was not achieved, but removal of (27; $R^1 = H$, $R^2 = CH_2 \cdot COMe$) from a mixture of (29) and (30) was accomplished.

The 5-substituted ketonic complexes did not react with triphenylmethyl fluoroborate, and the action of concentrated sulphuric acid on (27; $R^1 = H$, $R^2 = CH_2 \cdot COMe$) removed the side-chain to regenerate the original cation (27; $R^1 = H$, $R^2 = +$) in good yield. In contrast to the 5-substituted β-diketone or β-keto-ester [27; $R^1 = e.g.$ $CH(COMe)_2$], oxidation by manganese dioxide [5] did not produce cyclic ethers.

X-Ray crystallographic studies of one of the latter products [5] confirms the exo-attack of acetylacetone, and this is presumably true of the whole series [e.g. (25), (27), (33)].

Removal of Tricarbonyliron.—For use of the foregoing reactions in organic synthesis it is essential to be able to remove the tricarbonyliron group efficiently, to give the cyclohexadiene, or, in some instances, the dehydrogenated aromatic ring. The last mentioned procedure, for example, leads to a fairly direct introduction of a phenyl α to a carbonyl group.

The action of iron(III) chloride,[6] which is claimed to remove the group, has proved ineffective and capricious in our hands. Its efficacy is improved considerably by use in ethanolic hydrochloric acid;[7] for example compound (25; R = H) gave (31) in 75% yield. Similarly compound (25; R = OMe) gave (32) with accompanying hydrolysis of the enol ether. The reaction of thallium trifluoroacetate in refluxing carbon tetrachloride on (27; $R^1 = H$, $R^2 = CH_2 \cdot COMe$) gave methyl phenyl diketone in 55% yield, and use of lead tetra-acetate produced benzyl methyl ketone. The 6-methoxy-1-tetralone derivative (33) with lead tetra-acetate produced 2-phenyl-6-methoxy-1-tetralone in 45% yield. The reaction can also be carried out by successive removal of iron and dehydrogenation by palladium–charcoal; 2-phenyl-cyclohexanone was thus obtained in 50% overall yield from the diene complex (25; R = H). Experimental conditions still require further investigation, but the processes appear to have general application.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. I.r. spectra were examined with a JASCO IRA-1 instrument and u.v. spectra with a Unicam SP 800 spectrometer. ^{1}H N.m.r. spectra were measured with a Varian HA-100 or a JEOL JNH-MH-100 spectrometer (trimethylsilane as internal standard). Mass spectra and molecular weights were determined with an A.E.I. MS-902 instrument.

The complexes were prepared by heating under reflux with iron pentacarbonyl [1,2,8] in di-n-butyl ether, although not by the multi-stage process described here. We expect that yields would be raised by this process. The tricarbonyl-1- and -2-methoxycyclohexa-1,3-dieneiron isomers were separated on silica with pentane as the developing solvent, the 2-methoxy-isomer being the first eluted in all cases. The isolated pure 2-methoxy-derivatives were oils which could not be crystallised; the 1-methoxy-derivatives could be

[5] A. J. Birch, K. B. Chamberlain, and D. J. Thompson, J.C.S. Perkin I, 1973, 1900.
[6] R. Pettit, G. Emerson and J. Mahler, J. Chem. Educ., 1963, 40, 175.

[7] P. Schudel (Givaudan-Esrolko, Dübendorf, Zurich), personal communication.
[8] M. Cais and N. Maoz, J. Organometallic Chem., 1966, 5, 370.

obtained as pale yellow crystalline solids which melted below room temperature. The following compounds were obtained [structures attributed by ^1H n.m.r. spectra (Tables 1 and 2)]: tricarbonyl-1-methoxycyclohexa-1,3-dieneiron (6), tricarbonyl-2-methoxycyclohexa-1,3-dieneiron (1), tricarbonyl-1-methoxy-4-methylcyclohexa-1,3-dieneiron (7), tricarbonyl-2-methoxy-5-methylcyclohexa-1,3-dieneiron (2), tricarbonyl-2-methoxy-4-methylcyclohexa-1,3-dieneiron (3), and tricarbonyl-1-methoxy-3,5-dimethylcyclohexa-1,3-dieneiron (10). Tricarbonyl-1-methoxy-3-methylcyclohexa-1,3-dieneiron (8) and tricarbonyl-1-methoxy-5-methylcyclohexa-1,3-dieneiron (9) could not be separated by chromatography. Tricarbonyl-2-methoxy-4,6-dimethylcyclohexa-1,3-dieneiron was obtained as a 1 : 1 mixture of the 6-*exo*-methyl (5) and the 6-*endo*-methyl (4) isomers.

Reaction of p-*Mentha*-1,5-*diene with Pentacarbonyliron.*— The diene and iron pentacarbonyl were heated under reflux in di-n-butyl ether according to the general method to give a mixture of tricarbonyl-1-isopropyl-4-methylcyclohexa-1,3-dieneiron (14) and tricarbonyl-2-methyl-5-isopropylcyclohexa-1,3-dieneiron (13) (45%) in the ratio 1 : 9; δ (CDCl₃) 4·8 [d, 3-H of (13)] and 5·01 [s, 2-, 3-H of (14)].

Tricarbonyl-2-methylcyclohexa-1,3-dieneiron (11) and tricarbonyl-2,4-dimethylcyclohexa-1,3-dieneiron (12) were prepared as previously described.[1]

Tricarbonyl-1- *and* -2-*methoxycyclohexadieneiron.*—1-Methoxycyclohexa-1,4-diene (39 g) in pure di-n-butyl ether (320 ml) (purified by filtration through basic alumina, or by storage over sodium wire) and filtered iron pentacarbonyl (65 ml) were heated under reflux (dry pure nitrogen) for 18 h. The cooled solution was filtered through Celite, and the Celite was washed with di-n-butyl ether. The excess of diene, iron carbonyl, and solvent were distilled off in a rotary evaporator with efficient cooling (reduced pressure) and the distillate was again heated under reflux. After a repetition of the procedure the combined residues were distilled (nitrogen leak) giving the mixed complexes (50—54 g), b.p. 66—68° at 1 mmHg. The distillation residue could be purified on acidic alumina in light petroleum to give a further 5 g of material.

A similar procedure with cyclohexa-1,4-diene (58 g) gave tricarbonylcyclohexadieneiron (72 g, 46%). In this case cooling of the receiver with solid carbon dioxide–acetone is necessary in the evaporation stage, and it is probable that some diene is still lost. However the yield is about twice what we have been able to obtain by any single-stage procedure.

Tricarbonyl-1- *and* -2-*methoxycyclohexadienyliron Fluoroborates.*—The foregoing mixture of methoxy-derivatives (18 g) in a small volume of methylene chloride was added to freshly prepared triphenylmethyl fluoroborate (34 g) in the minimum volume of methylene chloride. After 20—30 min the solution was added to three times its volume of ether (A.R. grade, but not sodium-dried). A trace of moisture destroys any remaining triphenylmethyl fluoroborate and leads to a cleaner product. The mixed salts (21—22 g, 85—95%) were precipitated.

On heating with water (450 ml) on a steam-bath for 1 h, orange crystals separated. Extraction with ether (3 × 100 ml) gave tricarbonylcyclohexa-2,4-dienoneiron (18; R³ = R⁴ = R⁵ = H) (7—7·5 g). To the aqueous solution was added ammonium hexafluorophosphate (7·1 g) in water (30 ml), and the tricarbonyl-2-methoxycyclohexa-1,3-dienyliron fluorophosphate (15; R = H) (13 g) was filtered off.

Reaction of Other Complexes with Triphenylmethyl Fluoro-

borate.—The procedure was identical with that just described. The fluoroborate salts were dissolved in hot water; the solution was cooled and then extracted with ether. The ether layer was examined for the presence of tricarbonyl-cyclohexadienoneiron complexes. Addition of a 10% solution of ammonium hexafluorophosphate to the aqueous solution after ether extraction precipitated any water-stable salts.

Tricarbonyl-2-methoxycyclohexa-1,3-dieneiron (1) gave tricarbonyl-2-methoxycyclohexadienyliron fluoroborate (15; R = H).[2]

Tricarbonyl-1-methoxycyclohexa-1,3-dieneiron (6) gave a mixture of tricarbonyl-1-methoxycyclohexadienyliron fluoroborate (16; R¹ = R² = R³ = H) and tricarbonyl-2-methoxycyclohexadienyliron fluoroborate (15; R = H) in the ratio (4 : 1); δ (CF₃·CO₂H) 3·94 [OMe of (15; R = H)] and 3·84 [OMe of (16; R¹ = R² = R³ = H)]. From this mixture tricarbonylcyclohexadienoneiron (18; R³ = R⁴ = R⁵ = H), m.p. 102—104° (lit.,[2] 104—104·5°) and tricarbonyl-2-methoxycyclohexadienyliron hexafluorophosphate were obtained.

Tricarbonyl-2-methoxy-5-methylcyclohexa-1,3-dieneiron (2) gave tricarbonyl-4-methoxy-1-methylcyclohexadienyliron fluoroborate (15; R = Me); δ (CF₃·CO₂H) 6·92 (1H, d, J 4 Hz, 3-H), 5·56 (1H, d, J 4 Hz, 2-H), 3·86 (3H, s, OMe), 3·82 (1H, m, 5-H), 3·30 (1H, q, J 14 and 6 Hz, 6-H), 2·50 (1H, d, J 14 Hz, 6-H), and 1·84 (3H, s, Me).

Tricarbonyl-1-methoxy-4-methylcyclohexa-1,3-dieneiron (7) gave a mixture of tricarbonyl-1-methoxy-4-methylcyclohexadienyliron fluoroborate (16; R¹ = R³ = H, R² = Me); δ (CF₃·CO₂H) 2·28 (3H, s, 4-Me) and tricarbonyl-1-methyl-4-methoxycyclohexadienyliron fluoroborate (15; R = Me) in the ratio 9 : 1. From this mixture *tricarbonyl-4-methyl-cyclohexa*-2,4-*dienoneiron* (18; R³ = R⁵ = H, R⁴ = Me) was obtained as yellow plates, m.p. 88—89° (from pentane) (Found: C, 48·4; H, 3·3. C₁₀H₈FeO₄ requires C, 48·3; H, 3·2%); νmax. (Nujol) 2076, 2055, 1988, and 1664 cm⁻¹; λmax. (EtOH) 230 nm (ε 14,500); δ (CDCl₃) 5·98 (1H, d, J 6 Hz, 3-H), 3·16 (2H, m, 2-, 5-H), 2·20 (2H, m, 6-H₂), and 2·06 (3H, s, Me). Also obtained was tricarbonyl-1-methyl-4-methoxycyclohexadienyliron hexafluorophosphate (15; R = Me).[2]

Tricarbonyl-2-methoxy-4-methylcyclohexa-1,3-dieneiron (3) gave tricarbonyl-1-methyl-3-methoxycyclohexadienyliron fluoroborate (17; R¹ = Me, R⁵ = H); δ (CF₃·CO₂H) 6·03 (1H, d, J 8 Hz, 4-H), 5·71 (1H, s, 2-H), 4·24 (3H, s, OMe), 3·84 (1H, q, J 8 and 6 Hz, 5-H), 3·00 (1H, q, J 16 and 6 Hz, 6-H), 2·28 (1H, d, J 16 Hz, 6-H), and 1·96 (3H, s, Me).

The mixture of tricarbonyl-1-methoxy-3-methylcyclohexa-1,3-dieneiron (8) and tricarbonyl-1-methoxy-5-methylcyclohexa-1,3-dieneiron (9) gave a mixture of tricarbonyl-1-methoxy-3-methylcyclohexadienyliron fluoroborate (16; R³ = Me, R¹ = R² = H) and tricarbonyl-1-methoxy-5-methylcyclohexadienyliron fluoroborate (16; R² = R³ = H, R¹ = Me), which was converted into a mixture of tricarbonyl-3-methylcyclohexadienoneiron (18; R³ = Me, R⁴ = R⁵ = H) [δ (CDCl₃) 5·64 (1H, d, J 7 Hz, 4-H), 3·28 (1H, s, 2-H), 3·15 (1H, m, 5-H), 2·40 (2H, m, 6-H₂), and 2·30 (3H, s, Me)] and tricarbonyl-5-methylcyclohexa-2,4-dienoneiron (15; R³ = R⁴ = H, R⁵ = Me) [δ (CDCl₃) 6·60 (2H, m, 3-, 4-H), 3·12 (1H, d, J 6 Hz, 2-H), 2·20 (2H, m, 6-H₂), and 1·65 (3H, s, Me).

Tricarbonyl-1-methoxy-3,5-dimethylcyclohexa-1,3-diene-iron (10) gave tricarbonyl-1-methoxy-3,5-dimethylcyclohexadienyliron fluoroborate (16; R¹ = R³ = Me, R² = H),

which was converted into *tricarbonyl-3,5-dimethylcyclo-hexa-2,4-dienoneiron* (18; $R^3 = R^5 = $ Me, $R^4 = $ H), m.p. 54·5—55·5° (from pentane) (Found: C, 50·1; H, 4·0. $C_{11}H_{10}FeO_4$ requires C, 50·4; H, 3·8%); $\nu_{max.}$ (Nujol) 2077, 2057, 1990, and 1665 cm^{-1}; $\lambda_{max.}$ (EtOH) 231 nm (ε 14,450).

The mixture of tricarbonyl-3-methoxy-1,5-*exo*-dimethylcyclohexa-1,3-dieneiron (5) and tricarbonyl-3-methoxy-1,5-*endo*-dimethylcyclohexa-1,3-dieneiron (4) gave tricarbonyl-3-methoxy-1,5-dimethylcyclohexadienyliron fluoroborate (17; $R^1 = R^5 = $ Me), which was converted into the *hexafluorophosphate* (Found: C, 34·4; H, 2·8. $C_{12}H_{13}F_6FeO_4P$ requires C, 34·1; H, 3·1%); δ (CF$_3$·CO$_2$H) 5·80 (2H, s, 2-, 4-H), 4·19 (3H, s, OMe), 2·95 (1H, d, J 16 Hz, 6-H), 2·50 (1H, d, J 16 Hz, 6-H), and 1·90 (6H, s, 2 × Me).

After precipitation of tricarbonyl-3-methoxy-1,5-dimethylcyclohexadienyl fluoroborate (17; $R^1 = R^5 = $ Me), the combined methylene chloride and ether washings were collected, the solvent was removed *in vacuo*, and the residue was chromatographed on silica. Elution with pentane gave, after removal of the solvent, tricarbonyl-2-methoxy-4,6-*exo*-dimethylcyclohexa-1,3-dieneiron (5).

Tricarbonyl-2-methylcyclohexa-1,3-dieneiron (11) gave tricarbonyl-2-methylcyclohexadienyliron tetrafluoroborate (20; R = H) and tricarbonyl-3-methylcyclohexadienyliron tetrafluoroborate in the ratio (3 : 2) (94%); δ (CF$_3$·CO$_2$H) 7·22 (3-H of 2-Me isomer), 5·87 (4-H of 2-Me isomer and 2-H and 4-H of 3-Me isomer), 2·29 (Me of 3-Me isomer), 2·88 (Me of 2-Me isomer).

Tricarbonyl-1,3-dimethylcyclohexa-1,3-dieneiron (12) gave *tricarbonyl-1,3-dimethylcyclohexadienyliron tetrafluoroborate* (19; R = Me) (96%) (Found: C, 33·5; H, 2·6. $C_{11}H_{11}BF_4FeO_3$ requires C, 33·7; H, 2·3%); δ (CF$_3$·CO$_2$H) 5·96 (1H, d, J 6 Hz, 4-H), 5·58 (1H, s, 2-H), 4·12 (1H, t, J 6 Hz, 5-H), 2·98 (1H, dd, J 6 and 16 Hz, 6-H), 2·86 (3H, s, 3-Me), 2·30 (1H, d, J 16 Hz, 6-H), and 1·96 (3H, s, 1-Me).

The mixture of tricarbonyl-1-isopropyl-4-methylcyclohexa-1,3-dieneiron (14) and tricarbonyl-2-methyl-5-isopropylcyclohexa-1,3-dieneiron (13) gave tricarbonyl-1-isopropyl-4-methylcyclohexadienyliron fluoroborate (20; R = CHMe$_2$) (10%), which was converted into the *hexafluorophosphate* (Found: C, 36·8; H, 3·0. $C_{13}H_{15}F_6FeO_3P$ requires C, 37·1; H, 3·5%); δ (CF$_3$·CO$_2$H) 7·04 (1H, d, J 6 Hz, 3-H), 5·42 (1H, d, J 6 Hz, 2-H), 4·04 (1H, d, J 6 Hz, 5-H), 3·0 (1H, q, J 6 and 16 Hz, 6-H), 2·4 (1H, m, CHMe$_2$), 2·26 (3H, s, 4-Me), 2·20 (1H, d, J 16 Hz, 6-H), 1·17 (3H, d, J 6 Hz, Me), and 1·06 (3H, d, J 6 Hz, Me). The recovered neutral complex was tricarbonyl-2-methyl-5-isopropylcyclohexa-1,3-dieneiron.

The mixture of tricarbonyl-1,4-dimethyl and -2,5-dimethylcyclohexa-1,3-dieneiron [2] gave *tricarbonyl-1,4-dimethylcyclohexadienyliron tetrafluoroborate* (20; R = Me) (Found: C, 33·6; H, 2·8. $C_{11}H_{11}BF_4FeO_3$ requires C, 33·7; H, 2·4%); δ (CF$_3$·CO$_2$H) 7·0 (1H, d, J 6 Hz, 3-H), 5·44 (1H, d, J 6 Hz, 2-H), 4·04 (1H, J 5 Hz, 5-H), 3·04 (1H, q, J 5 and 16 Hz, 6-H), 2·36 (1H, d, J 16 Hz, 6-H), 2·26 (3H, s, 4-Me), and 1·90 (3H, s, 1-Me).

Reduction of Cyclohexadienyl Salts with Sodium Borohydride.—To a cooled solution of the salt (0·3 g) in water were added portions of borohydride, the mixture being extracted with ether between additions. After an excess had been added, and extracts were no longer coloured, the combined ethereal extracts were washed with water and dried (MgSO$_4$). The residue was dissolved in pentane and filtered through a plug of silica. Removal of the solvent gave the neutral complexes, which were analysed by ¹H

n.m.r. spectroscopy and identified by comparison with known compounds when available.[1,2]

Tricarbonyl-1,3-dimethylcyclohexadienyliron tetrafluoroborate (19; R = Me) gave a mixture of tricarbonyl-1,3-dimethylcyclohexa-1,3-dieneiron (12) and tricarbonyl-3,5-dimethylcyclohexa-1,3-dieneiron (85%) in the ratio 85 : 15; δ (CDCl$_3$) 1·56 (1-Me of 1,3-Me$_2$ isomer), and 0·92 (5-Me of 3,5-Me$_2$ isomer).

Tricarbonyl-1-methyl-3-methoxycyclohexadienyliron tetrafluoroborate (19; R = OMe) gave tricarbonyl-1-methyl-3-methoxycyclohexa-1,3-dieneiron (3) (88%).

Tricarbonyl-2-methylcyclohexadienyliron hexafluorophosphate [1] (20; R = H) gave a mixture of tricarbonyl-1-methylcyclohexa-1,3-dieneiron and tricarbonyl-2-methylcyclohexa-1,3-dieneiron in the ratio 1 : 1 (90%); δ (CDCl$_3$) 2·08 (2-Me of latter) and 1·62 (1-Me of former).

Tricarbonyl-1,4-dimethylcyclohexadienyliron tetrafluoroborate (20; R = Me) gave a mixture of tricarbonyl-1,4-dimethylcyclohexa-1,3-dieneiron and tricarbonyl-2,5-dimethylcyclohexa-1,3-dieneiron (92%) in the ratio 75 : 25; δ (CDCl$_3$) 5·16 (d, 3-H of 2,5-Me$_2$ isomer), and 4·96 (s, 2-, 3-H of 1,4-Me$_2$ isomer).

Tricarbonyl-1-isopropyl-4-methylcyclohexadienyliron hexafluorophosphate (20; R = CHMe$_2$) gave tricarbonyl-1-isopropyl-4-methylcyclohexa-1,3-dieneiron (85%); δ (CDCl$_3$) 5·02 (2H, s, 2-, 3-H), 1·5—1·75 (5H, m, 5-, 6-H, CHMe), 1·47 (3H, s, 4-Me), 1·22 (3H, d, J 6 Hz, Me), and 1·08 (3H, d, J 6 Hz, Me).

Tricarbonyl-4-methoxy-1-methylcyclohexadienyliron hexafluorophosphate (15; R = Me) gave a mixture of tricarbonyl-1-methoxy-4-methylcyclohexa-1,3-dieneiron (7) and tricarbonyl-2-methoxy-5-methylcyclohexa-1,3-dieneiron (2) (90%) in the ratio 2 : 3. The mixture of isomers was separated by chromatography as already described (Tables 1 and 2). The ¹H n.m.r. spectrum of tricarbonyl-2-methoxy-5-methylcyclohexa-1,3-dieneiron (2) indicated that it was a 1 : 1 mixture of the 5-*exo*- and 5-*endo*-methyl isomers (it showed double peaks for the OMe and Me groups). Reaction of this mixture of isomers with triphenylmethyl fluoroborate gave a 50% yield of tricarbonyl-1-methyl-4-methoxycyclohexadienyliron tetrafluoroborate (15; R = Me). Chromatography of the neutral washings gave the pure 5-*endo*-methyl isomer.

Tricarbonyl-2-methoxycyclohexadienyliron hexafluorophosphate (15; R = H) gave tricarbonyl-2-methoxycyclohexa-1,3-dieneiron (1) (88%).

Tricarbonyl-3-methoxy-1,5-dimethylcyclohexadienyliron tetrafluoroborate (17; $R^1 = R^5 = $ Me) gave a mixture of tricarbonyl-3-methoxy-1,5-*exo*-dimethylcyclohexa-1,3-dieneiron and the 5-*endo*-1-methyl isomer in the ratio 1 : 2.

Reaction of the Cyclohexadienyl Salts with Morpholine.—Morpholine (1 ml) in water (5 ml) was added dropwise to an ice-cooled solution of the cation (0·4 g) in water and the mixture was shaken for 5 min. Extraction with ether, drying (MgSO$_4$), and evaporation gave the neutral complexes which were dissolved in pentane; the solution was filtered through a plug of alumina and evaporated, and the product was analysed by ¹H n.m.r. spectroscopy.

Tricarbonyl-1,3-dimethylcyclohexadienyliron tetrafluoroborate (19; R = Me) gave a mixture of tricarbonyl-1,3-dimethyl-5-morpholinocyclohexa-1,3-dieneiron and tricarbonyl-3,5-dimethyl-5-morpholinocyclohexa-1,3-dieneiron in the ratio 9 : 1; δ (CDCl$_3$) (3,5-Me$_2$ isomer) 5·40 (d, J 6 Hz. 2-H), and 1·25 (s, 5-Me). Crystallisation of the crude product gave pure *tricarbonyl-1,3-dimethyl-5-morpholino-*

cyclohexa-1,3-*dieneiron* (66%), m.p. 55—56° (from pentane) (Found: C, 54·0; H, 5·9; N, 4·03. $C_{15}H_{19}FeNO_4$ requires C, 54·1; H, 5·7; N, 4·2%); δ (CDCl₃) 5·16 (1H, s, 2-H), 3·50 (4H, t, *J* 5 Hz, C_4H_8NO), 3·10 (1H, dt, *J* 10 and 4 Hz, 5-H), 2·84br (1H, s, 4-H), 2·32 (4H, m, C_4H_8NO), 2·14 (3H, s, 3-Me), 2·0 (1H, m, 6-H), 1·48 (3H, s, 1-Me), and 1·34br (1H, d, *J* 16 Hz, 6-H).

Tricarbonyl-1,4-dimethylcyclohexadienyliron tetrafluoroborate (20; R = Me) gave a mixture of tricarbonyl-1,4-dimethyl-5-morpholinocyclohexa-1,3-dieneiron and tricarbonyl-2,5-dimethyl-5-morpholinocyclohexa-1,3-dieneiron in the ratio 4 : 1; δ (CDCl₃) 1·48 (1-Me of 1,4-Me₂ isomer) and 1·26 (5-Me of 2,5-Me₂ isomer).

Tricarbonyl-1-methyl-4-methoxycyclohexadienyliron hexafluorophosphate (15; R = Me) gave *tricarbonyl-2-methoxy-5-methyl-5-morpholinocyclohexa*-1,3-*dieneiron* (65%), m.p. 83—84° (pentane) (Found: C, 51·4; H, 5·6; N, 3·8. $C_{15}H_{19}FeNO$ requires C, 51·6; H, 5·5; N, 4·0%); δ (CDCl₃) 5·18 (1H, q, *J* 5 and 2 Hz, 3-H), 3·66 (3H, s, OMe), 3·60 (4H, m, C_4H_8NO), 3·16 (1H, m, 1-H), 2·44 (4H, m, C_4H_8NO), 2·24 (1H, d, *J* 5 Hz, 4-H), 1·96 (1H, q, *J* 16, 2 Hz, 6-H), 1·66 (1H, q, *J* 16, 2 Hz, 6-H), and 1·16 (3H, s, 5-Me).

Reaction of the Cyclohexadienyl Salts with Aqueous Sodium Hydrogen Carbonate.—The cation (0·4 g) was dissolved in water and an excess of the reagent was added in portions, the temperature being kept below 10°. The mixture was extracted with ether after each portion and the combined extracts were worked up as described in the previous section.

Tricarbonyl-1,3-dimethylcyclohexadienyliron tetrafluoroborate (19; R = Me) gave a mixture of tricarbonyl-5-hydroxy-3,5-dimethylcyclohexa-1,3-dieneiron (23; R² = H, R³ = R⁵ = Me) and tricarbonyl-5-hydroxy-1,3-dimethylcyclohexa-1,3-dieneiron in the ratio 9 : 1; δ (CDCl₃) (1,3-Me₂ isomer), 4·84 (s, 2-H), and 4·12 (m, 5-H). Crystallisation of the crude product from pentane gave pure *tricarbonyl-5-hydroxy-3,5-dimethylcyclohexa*-1,3-*dieneiron* (23; R² = H, R³ = R⁵ = Me), m.p. 80—81° (Found: C, 49·8; H, 4·5. $C_{11}H_{12}FeO_4$ requires C, 50·0; H, 4·6%); δ (C_6H_6) 4·96 (1H, d, *J* 7 Hz, 2-H), 2·64 (1H, s, 4-H), 2·48 (1H, m, 1-H), 1·82 (3H, s, 3-Me), 1·8br (1H, s, OH), 1·76 (2H, m, 6-H₂), and 1·28 (3H, s, 5-Me).

Tricarbonyl-1,4-dimethylcyclohexadienyliron tetrafluoroborate (20; R = Me) gave *tricarbonyl-5-hydroxy-2,5-dimethylcyclohexa*-1,3-*dieneiron* (23; R² = R⁵ = Me, R³ = H) (70%), m.p. 83—84° (from pentane) (Found: C, 49·9; H, 4·5. $C_{11}H_{12}FeO_4$ requires C, 50·0; H, 4·6%); δ (C_6H_6) 4·84 (1H, d, *J* 6 Hz, 3-H), 2·64 (1H, s, 1-H), 2·54 (1H, d, *J* 6 Hz, 4-H), 1·86 (2H, m, 6-H₂), 1·74 (3H, s, 2-Me), 1·7br (1H, s, OH), and 1·30 (3H, s, 5-Me).

Tricarbonyl-1-methyl-4-methoxycyclohexadienyliron hexafluorophosphate (15; R = Me) gave *tricarbonyl-5-hydroxy-2-methoxy-5-methylcyclohexa*-1,3-*dieneiron* (23; R² = OMe, R³ = H, R⁵ = Me) (70%) m.p. 64—65° (pentane) (Found: C, 46·8; H, 4·7. $C_{11}H_{12}FeO_5$ requires C, 47·1; H, 4·3%); δ (C_6H_6) 4·68 (1H, dd, *J* 7 and 1·5 Hz, 3-H), 3·12 (3H, s, OMe), 3·06 (1H, m, 1-H), 2·32 (1H, d, *J* 7 Hz, 4-H), 2·3br (1H, s, OH), 1·84 (2H, m, 6-H₂), and 1·26 (3H, s, 5-Me).

Reactions of Enamines with Tricarbonyl-2-methoxycyclohexadienyliron Hexafluorophosphate.—(a) 1-(*Pyrrolidin-1-yl*)*cyclohexene*. A mixture of the complex salt (3 g) and the enamine [9] (2·5 ml) was heated under reflux in acetonitrile

⁹ G. Stork, A. Brizzolara, H. Landesman, J. S. Muszkovicz, and R. Terrel, *J. Amer. Chem. Soc.*, 1963, **95**, 207.

for 2 h. The solvent was removed *in vacuo* and the residue was dissolved in water (30 ml) and heated on a steam-bath for 15 min. The cooled solution was extracted with ether, and the ethereal layer was dried ($MgSO_4$). Removal of the solvent gave a yellow oil which was chromatographed on silica with chloroform as developing solvent to give *tricarbonyl-5-(2-oxocyclohexyl)cyclohexa*-1,3-*dieneiron* (25; R = OMe) (2·3 g) (88%), m.p. 106—110° (from MeOH) (Found: C, 55·2; H, 5·4%; M^+, 346. $C_{16}H_{18}FeO_5$ requires C, 55·4; H, 5·2%; *M*, 346); δ (CDCl₃) 5·10 (1H, dd, *J* 6 and 1·5 Hz, 3-H), 3·64 (3H, s, OMe), 3·26 (1H, m, 1-H), and 2·6—1·2 (13H, m).

When the salt and cyclohexanone were heated under reflux in ethanol in the presence of triethylamine for 1 h, *tricarbonyl-5-ethoxy-2-methoxycyclohexa*-1,3-*dieneiron* (27; R¹ = OMe, R² = OEt) was obtained as pale yellow plates (85%), m.p. 36—38° (from petroleum) (Found: C, 49·0; H, 4·55%; M^+, 294. $C_{12}H_{14}FeO_5$ requires C, 49·0; H, 4·75%; *M*, 294); δ (CDCl₃) 5·16 (1H, dd, *J* 6 and 1·5 Hz, 3-H), 3·64 (3H, s, OMe), 3·70 (1H, m, 5-H), 3·30 (2H, q, *J* 7 Hz, O·CH₂Me), 3·12br (1H, s, 1-H), 2·68 (1H, dd, *J* 6 and 4 Hz, 4-H), 2·20 (1H, m, 6-H), 1·60 (1H, d, *J* 14 Hz, 6-H), and 1·10 (3H, t, *J* 7 Hz, O·CH₂Me).

(b) 3-(*Pyrrolidin-1-yl*)*androsta-3,5-dien-17β-ol*, prepared (46%) in the standard way,[10] had m.p. 136—137° (from methanol) (Found: C, 80·7; H, 10·3. $C_{23}H_{35}NO$ requires C, 80·9; H, 10·3%); $ν_{max.}$ (Nujol) 3280, 1635, and 1602 cm⁻¹; $λ_{max.}$ (EtOH) 279 nm (both characteristic of steroidal 3-amino-3,5-dienes [10]). Reaction with the complex hexafluorophosphate as in (a) (reflux time 1 h) and recrystallisation from methanol gave a *quaternary ammonium hexafluorophosphate* (26; R¹ = H, R² = H, R³ = OH) (57%) (Found: C, 53·9; H, 6·0; N, 1·9. $C_{33}H_{44}F_6FeNO_5P$ requires C, 53·9; H, 6·0; N, 1·9%); $ν_{max.}$ (Nujol) 3360, 2040, 1955br, 1625, and 840 cm⁻¹; $λ_{max.}$ (EtOH) 277·5 nm (typical of enamines of 4-en-3-ones of the steroid series in acid [10]).

(c) 3-(*Pyrrolidin-1-yl*)*estra-3,5-dien-17-one*, similarly prepared (48%) from estr-4-ene-3,17-dione, had m.p. 189—190° (from methanol) (Found: C, 81·0; H, 9·3; N, 4·1. $C_{22}H_{31}NO$ requires C, 81·2; H, 9·5; N, 4·3%); $ν_{max.}$ (Nujol) 1742, 1630, and 1605 cm⁻¹; $λ_{max.}$ (EtOH) 278 nm. Reaction with the salt gave the *quaternary ammonium hexafluorophosphate* (26; R¹ = Me, R²R³ = O) (48%), which was recrystallised from methanol (Found: C, 53·1; H, 5·6; N, 1·8. $C_{32}H_{40}F_6NO_5P$ requires C, 53·4; H, 5·6; N, 2·0%); $ν_{max.}$ (Nujol) 2038, 1955br, 1742, 1625br, and 840 cm⁻¹; $λ_{max.}$ (EtOH) 275 nm.

Reaction of Salts with Ketones.—5-*Acetonylcyclohexa*-1,3-*dienetricarbonyliron* (27; R¹ = H, R² = CH₂·COMe). A mixture of tricarbonylcyclohexadienyliron fluoroborate (3·0 g), acetone (12 ml), and absolute ethanol (100 ml) was heated under reflux for 7 h. The cooled solution was poured into water and extracted with ether. The ethereal solution was washed with water and dried ($MgSO_4$). Evaporation gave a yellow oil which was chromatographed on silica. Elution with benzene produced a fast-running band consisting mainly of tricarbonylcyclohexa-1,3-dieneiron (0·2 g). Further elution with benzene produced a distinct yellow band which gave, after removal of the solvent, the *ketone* (2·1 g) (77%) as a yellow oil (M^+, 276. $C_{12}H_{12}FeO_4$ requires *M*, 276); $ν_{max.}$ (CHCl₃) 2050, 1960, and 1720 cm⁻¹; δ (CDCl₃) 5·40 (2H, m, 2-, 3-H), 3·12 (2H, m, 1-, 4-H), 2·40 (4H, m,

¹⁰ J. L. Johnson, M. E. Herr, J. C. Babcock, A. E. Fonken, J. E. Stafford, and F. W. Heyl, *J. Amer. Chem. Soc.*, 1956, **78**, 430.

5-, 6-H, CH$_2$·CO), 2·08 (3H, s, Me), and 1·16 (1H, d, J 14 Hz, 6-H); 2,4-*dinitrophenylhydrazone*, m.p. 142—144° (from ethanol) (Found: C, 47·2; H, 3·5; N, 12·5%; M^+, 456. C$_{18}$H$_{16}$FeN$_4$O$_7$ requires C, 47·4; H, 3·6; N, 12·3%; M, 456).

When the reflux time was increased to 16 h the product consisted of a mixture of 5-acetonylcyclohexa-1,3-dienetricarbonyliron (27; R = H, R^1 = CH$_2$·COMe), 4-acetonyl-cyclohexa-1,3-dienetricarbonyliron (29), and 3-acetonyl-cyclohexa-1,3-dienetricarbonyliron (30) in the ratio 10 : 4 : 1. Preparative t.l.c. on silica gave a faster running band consisting of compounds (29) and (30) and a slower running band of pure compound (27; R^1 = H, R^2 = CH$_2$·COMe); δ (CDCl$_3$) [compound (29)] 5·40 (2H, m, 2-, 3-H), 3·20 (1H, m, 1-H), 2·92 (2H, q, J 16 Hz, CH_2·COMe), 2·20 (3H, s, COMe), and 1·68 (4H, m, 5-, 6-H$_2$); [compound (30)] 2·32 (3H, s, COMe).

When 5-acetonylcyclohexa-1,3-dienetricarbonyliron (27; R^1 = H, R^2 = CH$_2$·COMe) was heated under reflux in ethanol containing fluoroboric acid for 16 h a similar mixture of complexes was obtained.

When the same complex was heated under reflux in 10% v/v sulphuric acid–methanol for 16 h the complexes (27; R^1 = H, R^2 = CH$_2$·COMe), (29), and (30) were obtained in the ratio 1 : 2 : 7 (95% recovery).

Tricarbonyl-5-(2-oxocyclohexyl)cyclohexa-1,3-*dieneiron* (25; R = H). A mixture of tricarbonylcyclohexadienyliron fluoroborate (3·0 g), cyclohexanone, (3 ml) and absolute ethanol was heated under reflux for 7 h. The *ketone* (25; R = H) was isolated by a similar method to that just described as pale yellow plates (70%), m.p. 46—49° (from methanol) (Found: C, 57·0; H, 5·1%; M^+, 316. C$_{15}$H$_{16}$-Fe$_4$O requires C, 57·0; H, 5·2%; M, 316); ν$_{max.}$ (CHCl$_3$) 2060, 1960, and 1720 cm^{-1}; δ (CDCl$_3$) 5·28 (2H, q, 2-, 3-H), 3·0 (2H, m, 1-, 4-H), 2·50 (1H, m), 2·20—1·6 (10H, m), and 1·12 (1H, d, J 14 Hz, 6-H).

Tricarbonyl-5-(1,2,3,4-tetrahydro-6-methoxy-1-oxo-2-naphthyl)cyclohexa-1,3-*dieneiron* (33). This was prepared from 6-methoxy-1-tetralone (0·8 g) and tricarbonylcyclo-hexadienyliron fluoroborate (1·5 g) by a similar method. The *complex* crystallised from benzene–petroleum as plates (1·2 g, 60%), m.p. 148—154° (Found: C, 61·2; H, 4·8%; M^+, 394. C$_{20}$H$_{18}$FeO$_5$ requires C, 60·9; H, 4·6%; M, 394); ν$_{max.}$ 2060, 1960, 1680, and 1600 cm^{-1}; δ (CDCl$_3$) 8·10 (1H, d, J 7 Hz), 6·90 (1H, dd, J 7 and 1·5 Hz), 6·80 (1H, d, J 1·5 Hz), 5·46 (2H, m), 3·92 (3H, s), 3·06 (4H, m), 2·20 (3H, m), and 1·30 (3H, m).

Tricarbonyl-5-(1-methylacetonyl)cyclohexa-1,3-*dieneiron* (27; R^1 = H, R^2 = CHMe·COMe). A mixture of tricarb-onylcyclohexadienyliron fluoroborate (1·0 g), butan-2-one (4 ml), and ethanol (25 ml) was heated under reflux for 5 h, cooled, poured into water, and extracted with ether. The ethereal layer gave, after drying (MgSO$_4$), a yellow oil which was chromatographed on silica. Elution with benzene and removal of the solvent gave the *product* (27; R^1 = H, R^2 = CHMe·COMe) (75%) as a yellow oil (M^+, 290. C$_{13}$H$_{14}$FeO$_4$ requires M, 290); ν$_{max.}$ (CHCl$_3$) 2060, 1960, and 1715 cm^{-1}; δ (CCl$_4$) 5·34 (2H, m, 2-, 3-H), 3·0 (2H, m, 1-, 4-H), 2·20 (2H, m, 5-H, CHMe), 2·0 (1·5 H, s, ½MeCO), 1·98 (1·5 H, s, ½MeCO), 1·94 (1H, m, 6-H), 1·20 (1H, m, 6-H), 1·0 (1·5 H, d, J 6·5 Hz, ½MeCH), and 0·88 (1·5 H, d, J 6·5 Hz, ½MeCH). The complexity of the ^{1}H n.m.r. spectrum is presumably due to the presence of diastereoisomers. The 2,4-*dinitrophenylhydrazone* had m.p. 153—158° (from methanol) (Found: C, 48·6; H, 3·7; N,

11·7%; M^+, 470. C$_{19}$H$_{16}$FeN$_4$O$_7$ requires C, 48·5; H, 3·8; N, 11·9%; M, 470).

Tricarbonyl-5-(1,1-dimethylacetonyl)cyclohexa-1,3-*dieneiron* (27; R^1 = H, R^2 = CMe$_2$·COMe). This was prepared from tricarbonylcyclohexadienyliron fluoroborate (1·0 g) and methyl isopropyl ketone (4 ml) by a similar method. Chromatography on silica, with benzene as eluting solvent, gave the *product* (27; R^1 = H, R^2 = CMe$_2$·COMe) (82%) as plates, m.p. 55—58° (from methanol) (Found: C, 55·1; H, 5·4%; M^+, 304. C$_{14}$H$_{16}$FeO$_4$ requires C, 55·3; H, 5·3%; M, 304); ν$_{max.}$ (CHCl$_3$) 2060, 1960, and 1710 cm^{-1}; δ (CCl$_4$) 5·35 (2H, m, 2-, 3-H), 3·0 (1H, m, 1-H), 2·82 (1H, m, 4-H), 2·48 (1H, m, 5-H), 2·04 (3H, s, COMe), 1·80 (1H, m, 6-H), 1·16 (1H, d, J 16 Hz, 6-H), 1·0 (3H, s, Me), and 0·90 (3H, s, Me).

Tricarbonyl-5-(2-methyl-4-oxopent-2-enyl)cyclohexa-1,3-*dieneiron* (28). This was prepared from the salt (27; R^1 = H, R^2 = +) (1·0 g) and mesityl oxide (2 ml) by a similar method. Chromatography on silica, with benzene as eluting solvent, gave the *product* (28) (65%) as pale yellow plates, m.p. 48—51° (from methanol) (Found: C, 57·1; H, 5·2%; M^+, 316. C$_{15}$H$_{16}$FeO$_4$ requires C, 57·0; H, 5·1%; M, 316); ν$_{max.}$ (CHCl$_3$) 2060, 1960, 1680, and 1620 cm^{-1}, δ (CCl$_4$) 5·92 (1H, s, C=CH), 5·24 (2H, m, 2-, 3-H), 3·0 (2H, m, 1-, 4-H), 2·44 (1H, m, 5-H), 2·20 (2H, m, CH_2·C:C), 2·08 (3H, s, MeCO), 1·72 (1H, m, 6-H), 1·82 (3H, s, MeC:C), and 1·16 (1H, d, J 16 Hz, 6-H).

Tricarbonyl-5-(2-hydroxypropyl)cyclohexa-1,3-*dieneiron* (27; R^1 = H, R^2 = CH$_2$·CHMe·OH). A solution of the ketone (27; R^1 = H, R^2 = CH$_2$·COMe) (0·2 g) in ethanol was treated with an excess of sodium borohydride and stirred at room temp. for 15 min. The resulting solution was poured into water and extracted with ether. The dried ethereal layer, after filtering through silica, gave a yellow oil which was crystallised from pentane to give plates of the *alcohol* (27; R^1 = H, R^2 = CH$_2$·CHMe·OH) (0·19 g), m.p. 96—101° (Found: C, 51·8; H, 5·0%; M^+, 278. C$_{12}$H$_{14}$FeO$_4$ requires C, 51·8; H, 5·2%; M, 278); δ (CCl$_4$) 5·28 (2H, m, 2-, 3-H), 3·62 (1H, m, CH·OH), 3·02 (2H, m, 1-, 4-H), 2·76 (1H, s, OH), 2·10 (2H, m, 5-, 6-H), 1·24 (3H, m, CH_2·CH·OH and 6-H), and 1·06 (3H, d, J 6 Hz, Me).

Tricarbonyl-5-(2-oxo-4-phenylbut-3-enyl)cyclohexa-1,3-*di-eneiron* (27; R^1 = H, R^2 = CH$_2$·CO·CH=CHPh). To a solution of the ketone (27; R^1 = H, R^2 = CH$_2$·COMe) (1·0 g) and benzaldehyde (0·4 g) in methanol (8 ml) was added aqueous 3N-sodium hydroxide (2 ml). The resulting solution was stirred at room temp. for 2 h, acidified (3N-HCl), and extracted with ether. The ethereal layer, after washing with water and drying (MgSO$_4$), gave a yellow oil which was chromatographed on silica. Elution with benz-ene gave the *product* (27; R^1 = H, R^2 = CH$_2$·CO·CH=CHPh) (80%) as pale yellow plates, m.p. 104—105° (from methanol) (Found: C, 49·0; H, 4·6%; M^+, 364. C$_{19}$H$_{16}$-FeO$_4$ requires C, 49·0; H, 4·7%; M, 364); λ$_{max.}$ (EtOH) 224 (ε 21,500) and 291 nm (ε 24,900); ν$_{max.}$ (CHCl$_3$) 2040, 1960, 1680, 1650, and 1610 cm^{-1}; δ (CDCl$_3$) 7·30 (6H, m), 6·60 (1H, d, J 16 Hz, =CH·CO), 5·26 (2H, m, 2-, 3-H), 3·0 (2H, m, 1-, 4-H), 2·52 (2H, s, CH$_2$·CO), 2·56 (1H, m, 5-H), 2·1 (1H, dt, J 14 and 4 Hz, 6-H), and 1·22 (1H, d, J 14 Hz, 6-H).

Tricarbonyl-5-(1,1-dimethyl-2-oxo-4-phenylbut-3-enyl)-cyclohexa-1,3-*dieneiron* (27; R^1 = H, R^2 = CMe$_2$·CO·CH=CHPh). To a solution of tricarbonyl-5-(1,1-dimethyl-acetonyl)cyclohexa-1,3-dieneiron (0·6 g) and benzaldehyde

(0·21 g) in methanol (4 ml) was added aqueous 3N-sodium hydroxide (1 ml). The resulting solution was stirred for 3 h. The pale yellow precipitate was filtered off, washed well with water, and crystallised from methanol to give the *product* (85%) as pale yellow plates, m.p. 108—110° (Found: C, 64·5; H, 5·0%; M^+, 392. $C_{21}H_{20}FeO_4$ requires C, 64·3; H, 5·1%; M, 392); $\lambda_{max.}$ (EtOH) 223 (ε 26,800) and 294 nm (ε 22,100); $\nu_{max.}$ (CHCl₃) 2060, 1960, 1675, and 1605 cm⁻¹; δ (CDCl₃) 7·72 (1H, d, J 16 Hz), 7·48 (5H, m), 7·06 (1H, d, J 16 Hz), 5·36 (2H, m, 2-, 3-H), 2·94 (2H, m, 1-, 4-H), 2·60 (1H, dt, J 10 and 4 Hz, 5-H), 1·80 (1H, ddd, J 16, 10, and 4 Hz, 6-H), 1·26br (1H, d, J 16 Hz, 6-H), 1·10 (3H, s, Me), and 1·02 (3H, s, Me).

Removal of the Tricarbonyliron Group from the Complexes. —*Oxidation of 5-acetonylcyclohexa-1,3-dienetricarbonyliron* (27; R^1 = H, R^2 = CH₂·COMe). (a) *Iron*(III) *chloride.* A mixture of the complex (1·0 g), iron(III) chloride (5·0 g), conc. hydrochloric acid (5 ml), and ethanol (50 ml) was stirred at room temperature for 3 h. The solution was poured into water and extracted with ether. The ethereal layer, after washing with water and drying (MgSO₄), gave a yellow oil which was chromatographed on silica. Elution with benzene gave 5-*acetonylcyclohexa*-1,3-*diene* as an oil (70%) (Found: M^+, 136·0890. $C_9H_{12}O$ requires M, 136·0889); $\lambda_{max.}$ (cyclohexane) 260 nm (ε 4300); δ (CCl₄) 4·0 (4H, m), 2·88 (1H, m), 2·58 (2H, d, J 6 Hz), 2·16 (3H, s), and 2·14 (2H, m); m/e 136, 134, 93, 91, 79, 77, 58, and 43.

(b) *Lead tetra-acetate.* A solution of the complex (0·6 g) and lead tetra-acetate (2·0 g) in glacial acetic acid was stirred at room temperature for 2 h, poured into water, and extracted with hexane. The organic layer was washed with water and dried (MgSO₄). Removal of the solvent gave an oil which was chromatographed on silica with benzene as developing solvent to give 1-phenylpropan-2-one (55%); δ (CCl₄) 7·30 (5H, m), 3·60 (2H, s), and 2·04 (3H, s).

(c) *Thallium trifluoroacetate.* A solution of the complex (0·3 g) and thallium trifluoroacetate (2·0 g)[11] was heated under reflux in carbon tetrachloride for 2 h, cooled, filtered, and evaporated *in vacuo*. The residue was chromatographed on silica with benzene to give 1-phenylpropane-1,2-dione as a yellow oil (50%); $\nu_{max.}$ 1720, 1680, 1610, and 1590 cm⁻¹; δ (CCl₄) 8·5 (2H, dd, J 4 and 1·5 Hz), 7·50 (3H, m), and 2·44 (3H, s).

(d) *Manganese dioxide.* A mixture of the complex (0·3 g) and manganese dioxide (2 g) in benzene was heated under reflux for 16 h, cooled, filtered through silica, and evaporated to give only starting material (85% recovery).

Oxidation of tricarbonyl-5-(2-oxocyclohexyl)cyclohexa-1,3-dieneiron (25; R = H). Reaction of the complex (1·0 g) with iron(III) chloride (5·0 g) [as in (1)] gave, after chromatography on silica, 5-(2-oxocyclohexyl)cyclohexa-1,3-diene (31) as an oil (75%) (Found: M^+, 176·1202. $C_{12}H_{16}O$ re-

[11] A. McKillop, J. S. Fowler, M. J. Zelesko, J. D. Hunt, E. C. Taylor, and G. McGillivray, *Tetrahedron Letters*, 1969, 2423.

quires M, 176·1201); $\lambda_{max.}$ (cyclohexane) 261 nm (ε 4300); δ (CCl₄) 5·8 (4H, m), 2·7 (1H, m), and 2·2—1·6 (11H, m).

A mixture of the diene (31) (1·0 g) and 10% palladium-charcoal (1·0 g) in benzene (10 ml) was heated under reflux for 16 h, cooled, filtered, and evaporated to leave an oil which was crystallised from petroleum to give 2-phenylcyclohexanone (90%), m.p. 57—59° (lit.,[12] 59°); 2,4-dinitrophenylhydrazone, yellow needles (from methanol), m.p. 136—138° (lit.,[12] 139°).

Oxidation of tricarbonyl-5-(1,2,3,4-tetrahydro-6-methoxy-1-oxo-2-naphthyl)cyclohexa-1,3-dieneiron (33). A solution of the complex (0·8 g) and lead tetra-acetate (2·0 g) in glacial acetic acid was stirred at room temperature for 2 h, poured into water, and extracted with ether. Work-up in the usual way gave an orange oil which was chromatographed on silica with benzene to give rosettes of 3,4-dihydro-6-methoxy-2-phenylnaphthalen-1(2H)-one (45%), m.p. 112—114° (lit.,[13] 113—116°); $\lambda_{max.}$ (EtOH) 277 and 225 nm; $\nu_{max.}$ (CHCl₃) 1680, 1610, and 1580 cm⁻¹; δ (CDCl₃) 8·28 (1H, d, J 8 Hz), 7·44 (5H, m), 7·02 (1H, dd, J 8 and 1·5 Hz), 6·90 (1H, d, J 1·5 Hz), 3·96 (3H, s), 3·90 (1H, m), 3·10 (2H, m), and 2·48 (2H, m).

Oxidation of tricarbonyl-2-methoxy-5-(2-oxocyclohexyl)-cyclohexa-1,3-dieneiron (25; R = OMe). Reaction of the complex (1·0 g) with iron(III) chloride (5·0 g) [as in (a)] gave, after chromatography on silica, 4-(2-oxocyclohexyl)cyclohex-2-en-1-one (32) (50%) as an oil (Found: M^+, 192·1151. $C_{12}H_{16}O_2$ requires M, 192·1152); $\nu_{max.}$ (CHCl₃) 1720 and 1680 cm⁻¹; δ (CCl₄) 6·82 (1H, d, J 10 Hz), 5·96 (1H, d, J 10 Hz), 3·0 (1H, m), and 2·6—1·4 (13H, m).

Reaction of 5-acetonylcyclohexa-1,3-dienetricarbonyliron (27; R^1 = H, R^2 = CH₂·COMe) *with triphenylmethyl fluoroborate.* Triphenylmethyl fluoroborate (0·4 g) in methylene dichloride was added to a solution of the complex in the same solvent. After 30 min the mixture was poured into ether and filtered. Removal of the solvent from the filtrate gave a yellow oil which gave, after chromatography on silica, the starting material (80% recovery).

Reaction of 5-acetonylcyclohexa-1,3-dienetricarbonyliron (27; R^1 = H, R^2 = CH₂·COMe) *with concentrated sulphuric acid.* A solution of the complex (0·2 g) in concentrated sulphuric acid (1 ml) was kept at room temperature for 10 min, then saturated with dry ether (50 ml), causing the salt to be precipitated as a gum. Repeated trituration with dry ether removed any neutral complexes and the salt was dissolved in a small volume of water. Addition of ammonium hexafluorophosphate solution (10%) precipitated tricarbonylcyclohexadienyliron fluorophosphate (27; R^1 = H, R^2 = +) (85%), which was filtered off.

[3/492 *Received, 6th March,* 1973]

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