Organometallic Complexes in Synthesis. Part V.[1] Some Tricarbonyliron Derivatives of Cyclohexadienecarboxylic Acids

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Reactions of iron pentacarbonyl with several methyl cyclohexadienecarboxylates lead to tricarbonyliron complexes. The most stable of these is the 'conjugated' isomer (2; R = Me), which can be obtained from the others by treatment with methanolic acid or in some cases with methanolic methoxide. The latter method is the first observed example of base-catalysed isomerisation in tricarbonylcyclohexadieneiron complexes. When deuteriated reagents are used the acidic procedure leads to incorporation of one deuterium atom only, in the 6-position, irrespective of the starting material. Reactions of the acids with diborane yield the carbinols, one of which [tricarbonyl-1-(hydroxymethyl)cyclohexa-1,3-dieneiron (8)], on treatment with acid, produces the rearranged carbonium salt (9). Hydride abstraction from the isomeric esters gives a series of carbonium salts, which react with water at various rates to produce hydroxy-complexes and dimeric ethers. Complexing of some methyl methylcyclohexa-1,4-dienecarboxylates is reported. Aspects of theory connected with hydrogen migration and hydride abstraction are discussed.

REACTIONS of iron carbonyls with some cyclohexa-1,4- and 1,3-dienes, substituted with Me or OMe, and further reactions of the complexes have been described.[1,2] In view of the different electronic character of substituents CO_2R, compared with those already examined, the formation and some reactions of tricarbonyliron complexes of cyclohexa-1,3-dienoic acids and esters have been investigated.

Attempts to form complexes directly from the acids resulted in decomposition, so the methyl esters were employed. Methyl cyclohexa-2,5-dienecarboxylate (methyl 1,4-dihydrobenzoate) reacted with iron pentacarbonyl to give in 34% yield an orange oil containing two isomeric complexes, the structures of which were elucidated from the ^1H n.m.r. spectrum of the mixture. The major component, tricarbonyl-5-methoxycarbonyl-cyclohexa-1,3-dieneiron (1; R = Me) has resonances at δ 3·68 (s, CO_2Me) and 5·4 p.p.m. (m, 'inner' 2- and 3-H).[2] The other component has resonances at δ 3·79 (s, CO_2Me) and 6·07 p.p.m. (dd, J 7 and 2 Hz) which could be assigned to an 'inner' hydrogen atom of either the 1- or the 2-substituted isomer [2-H of (2; R = Me) or 3-H of (3; R = Me)]. The peak due to 3-H of (3; R = Me) would, if this isomer were present, be expected to coincide with peaks due to the 'inner' hydrogen atoms of (1; R = Me). The structure of the minor isomer was assigned with certainty as (3; R = Me) only after synthesis of (2; R = Me) and (3; R = Me) (with CO_2Me peaks at δ 3·70 and 3·79, respectively). For no obvious reason the proportion of (3; R = Me) in the reaction product varied between ca. 20 and 50%. The stereochemistry of (1) is not known, although there is no spectral evidence of the presence of more than one isomer. The less hindered exo-CO_2Me system would be expected, and could be formed by enolisation no matter what the initial stereochemistry. One possible explana-

tion of the ratio of (1) to (3) is that it represents the ratio of attack of the iron carbonyl on the original diene from the two possible directions, relative to the CO_2Me group, conjugation by movement of H being sterically determined. Other possible considerations are outlined later. This question is under further investigation.

Conjugation of cyclohexa-2,5-dienecarboxylic acid with alkali gives cyclohexa-1,5-dienecarboxylic acid.[3] Reaction of the methyl ester of this acid with iron pentacarbonyl produced in 38% yield a complex shown by its ^1H n.m.r. spectrum to be pure (3; R = Me), produced without isomerisation: δ 1·5—1·9 (m, 5-H_2, 6-H_2), 3·36 (d, finely split, 4-H), 3·70 (d, finely split, 1-H), 3·79 (s, CO_2Me), and 6·07 (dd, J 7 and 2 Hz, 3-H).

Attempted synthesis of pure (1; R = Me) by solvolysis of the corresponding known nitrile (4; R = CN)[2,4] (presumably the exo-isomer) with methanolic sulphuric acid gave a product isomeric with the expected one. The carbonyl stretching frequency ($\nu_{max.}$ 1698 cm^{-1}) was at a lower wavenumber than in (1; R = Me) (1718 cm^{-1}) and (3; R = Me) (1717 cm^{-1}), suggesting the formation of (2; R = Me). This structure was supported by the ^1H n.m.r. spectrum: δ 1·3—2·4 (m, 5-H_2, 6-H_2), 3·36 (d, finely split, 4-H), 3·70 (s, CO_2Me), 5·36 (dd, J 6 and 4 Hz, 3-H), and 6·05 (d, J 4 Hz, 2-H).

The complexes (1; R = Me) and (3; R = Me) were both converted into (2; R = Me) by refluxing methanolic acid. Isomerisations of tricarbonyliron complexes of methoxy- and alkyl-cyclohexa-1,3-dienes under much more drastic acidic conditions have been reported,[2,5] although later work than this[1,6] has shown that isomerisation under these conditions is not unusual and is not confined to ester derivatives.

Reactions of cyclohexadiene complexes with deuterio-acids result in exchange of $endo$-allylic ^1H by ^2H.[7] It is questionable whether the isomerisation process is identi-

[1] Part IV, A. J. Birch, K. B. Chamberlain, M. A. Haas, and D. J. Thompson, preceding paper.

[2] J. A. Arnet and R. Pettit, *J. Amer. Chem. Soc.*, 1961, **88**, 9354; A. J. Birch, P. E. Cross, J. Lewis, D. A. White, and S. B. Wild, *J. Chem. Soc.* (*A*), 1968, **332**; E. O. Fischer and R. D. Fischer, *Angew. Chem.*, 1960, **72**, 919.

[3] H. Plieninger, G. Ege, F. Jung, and W. Maier-Borst, *Chem. Ber.*, 1961, **94**, 2088; M. E. Kuehne and B. F. Lambert, *J. Amer. Chem. Soc.*, 1959, **81**, 4278.

[4] M. A. Hashmi, J. D. Munro, P. L. Pauson, and J. M. Williamson, *J. Chem. Soc.* (*A*), 1967, 240.

[5] A. J. Birch and M. A. Haas, *Tetrahedron Letters*, 1968, 3705.

[6] A. J. Birch, B. Chauncy, and D. J. Thompson, to be published.

[7] T. H. Whitesides and R. W. Arhart, *J. Amer. Chem. Soc.*, 1971, **93**, 5298; D. A. T. Young, J. R. Holmes, and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1969, **91**, 6968; B. F. G. Johnson, J. Lewis, and D. Yarrow, *J.C.S. Chem. Comm.*, 1972, 235.

cal with the exchange process, although it may be related. A possible exchange mechanism,[7,8] accompanying isomerisation, could take place through addition to the carbon system to form a π-allyl complex. This could explain the result with the unsubstituted cyclohexadiene complex, where an isomerisation product is structurally identical with the starting material. It does not explain the result of exchange in deuteriomethanol of the 5-methoxycarbonyl derivative (1). All three isomers (1)—(3) in fact gave compound (6); this would arise naturally according to the foregoing mechanism from (3), and could be produced by specific exchange with (2), but compound (5) would have been expected from (1), if we assume the usual *endo*-configuration.

X = Fe(CO)₃
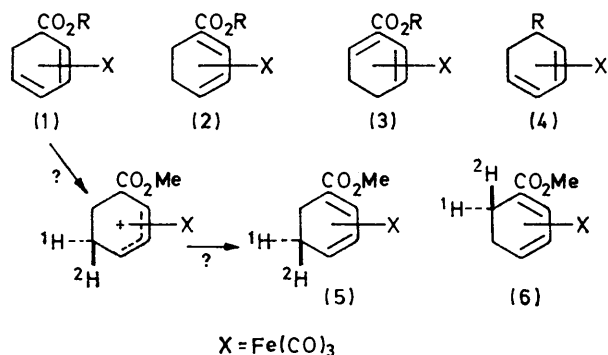
That each of the complexes (1)—(3) gave largely the same monodeuteriated product is shown by mass and ¹H n.m.r. spectra. The relative intensities of peaks at *m/e* 278, 279, 280, and 281 indicated in this instance the presence of 17% $^2H_0$, 3% $^2H_2$, 1% $^2H_3$, and the remaining 79% $^2H_1$ species. The ¹H n.m.r. spectra of products from different isomeric esters are identical, indicating that the same single H [δ 2·0—2·4(m) in the spectrum of (2; R = Me)] has been replaced by deuterium in each case. The methylene signals now extend only from δ 1·3 to 2·0, and integration confirmed the presence of only three protons. The chemical shift of the proton which is exchanged is downfield with respect to those of other methylene protons, suggesting that this proton is the 6-H, adjacent to CO_2Me. That only one hydrogen atom here is exchanged is evidence for stereospecificity, the ²H probably being *endo*. In contrast to the cyclohexadiene complex,[7] one of the two allylic positions, that next to CO_2Me, exhibits much more rapid exchange than the other, for reasons at present not apparent.

These results indicate that initial protonation of the 'cyclohexadiene' nucleus is not the isomerisation mechanism. Probably no deuterium exchange occurs during the conversions, since the product (2) itself exchanges so readily.

A possible isomerisation mechanism without deuterium incorporation would involve protonation of the

⁸ R. Pettit, G. Emerson, and J. Mahler, *J. Chem. Educ.*, 1963, **40**, 175; H. Alper, P. C. LePorte, and S. Wolfe, *J. Amer. Chem. Soc.*, 1969, **91**, 7553.

iron, and then a 1,2-migration of hydride around the ring to generate the stable isomer. The subsequent exchange would be a slower reaction, but might also be related to protonation of the iron.
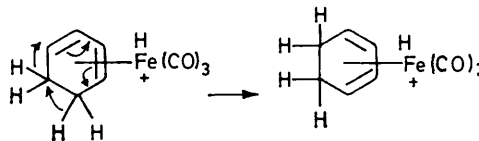
Alkaline hydrolysis of the nitrile (4; R = CN) resulted in some decomposition, but yielded crystalline neutral 1-carbamoylcyclohexa-1,3-dienetricarbonyliron [δ 1·4—2·1 (m, 5-H_2, 6-H_2), 3·29 (d, finely split, 4-H), 5·38 (dd, *J* 6 and 4 Hz, 3-H), 5·90br (s, exchanged D_2O, CO·NH_2), and 6·10 (dd, *J* 4 and 1 Hz, 2-H)]. The i.r. and ¹H n.m.r. spectra of the residue from crystallisation of the neutral fraction showed it to consist of tricarbonyl-1-cyanocyclohexa-1,3-dieneiron {$v_{max.}$ 2210 cm⁻¹ [strong, *cf.* weak band at 2240 cm⁻¹ in (4; R = CN)]; δ 3·46 (d, with fine splitting, 4-H), 4·21 (d, *J* 6 Hz, 2-H shielded by adjacent CN), and 5·34 (dd, *J* 6, 4 Hz, 3-H)}. A small acidic fraction contained mainly decomposition products, but the ¹H n.m.r. spectrum indicated the presence of some tricarbonyl-5-carboxycyclohexa-1,3-dieneiron (4; R = CO_2H) as the only iron complex [δ 2·91 (m, 5-H), 3·28 (m, 1-, 4-H), and 5·58 (m, 2-, 3-H)]. Therefore the hydrolytic procedure probably follows two pathways. In one of these, hydrolysis of the CN system in (4; R = CN) gives (4; R = CO_2H), which is stable to isomerisation by alkali under these conditions, and in the other isomerisation of the 5-cyano-1,3-diene complex into the 1-cyano-1,3-diene complex is followed by hydrolysis to the amide (the last two steps may also take place in reverse order). That the presumed intermediate amide (4; R = CO·NH_2) is converted into the acid, whereas the 'conjugated' 1-carboxamide is stable, is paralleled by the difference in rates of hydrolysis of the similar esters described later.

Isomerisation of tricarbonylcyclohexadieneiron complexes under the influence of base has not previously been reported and presumably results from abstraction of the acidic proton adjacent to the nitrile or amide group to give a mesomeric anion involving the complexed system. When a mixture of the esters (1; R = Me) and (3; R = Me) was refluxed in methanolic sodium methoxide, the recovered neutral complex proved to be entirely (2; R = Me). Some acidic material consisted of a mixture of (1; R = H) and (3; R = H) in a ratio identical with that of the starting materials. Abstraction of the appropriate protons for isomerisation therefore occurs in the esters but is inhibited in the carboxylate anions.

The mixture of esters (1; R = Me) and (3; R = Me) was hydrolysed to the acids without isomerisation or decomposition by aqueous methanolic potassium hydroxide at room temperature. The mixture of acids (1; R = H) and (3; R = H) could not readily be separated

by crystallisation, but pure (3; R = Me) gave the pure crystalline acid (3; R = H).

The complex (2; R = Me) did not undergo hydrolysis under the same mild conditions. The existence of some ' conjugation ' of the complexed diene system with the ester probably reduces the electrophilic character of the ester carbonyl group. Hydrolysis of (2; R = Me) to form (2; R = H) was accomplished by refluxing with aqueous sulphuric acid, which is effective also with (1; R = Me) and (3; R = Me) giving in both cases pure (2; R = H) by ready isomerisation.

The position of the CO_2R group on the complexed diene system affects the carbonyl absorptions (Table 1)

I.r. bands (solutions in $CHCl_3$; error ± 1 cm^{-1})

Substituent	$v_{max.}$ C≡O/cm^{-1}	$v_{max.}$ C=O/cm^{-1}
H	2045, 1975	—
5-CO_2Me [a]	2050, 1977	1718
2-CO_2Me	2053, 1983	1717
1-CO_2Me	2056, 1987	1698
2-CO_2H [a]	2051, 1976	1709
2-CO_2H	2053, 1983	1706
1-CO_2H	2057, 1988	1666

[a] In the presence of 20% of the 2-substituted isomer.

in expected ways. The complexed C≡O groups show the effects of electron withdrawal by the substituent at the 1- and 2-positions. The carbonyl band of the 1-CO_2R group is at a considerably lower wavenumber, indicating more effective conjugation, while compounds with a 5-CO_2R group show little sign of interaction of this with the complexed system.

The complexed acids (1—3; R = H) were reduced by diborane to the corresponding primary alcohols. Surprisingly, the esters (1—3; R = Me) were unaffected by lithium aluminium hydride. The pure alcohols (7) and (8) were obtained from the corresponding pure acids, and a mixture containing 80% of (4; R = $CH_2\cdot OH$) was with 20% of (7) was obtained from the corresponding mixture of (1; R = H) and (3; R = H).

The tetrahydropyranyl ether or the acetate of 3-hydroxymethylcyclohexa-1,4-diene (from reduction of methyl 1,4-dihydrobenzoate) on reaction with iron pentacarbonyl gave the corresponding derivative of (4; R = $CH_2\cdot OH$). Appropriate hydrolyses gave (4; R = CH_2OH). The derivatives could be re-formed from (4; R = $CH_2\cdot OH$) in the usual ways. The functionalised series (4; R = $CH_2\cdot OH$), (7), and (8) is likely to be a useful one in synthesis, since all the compounds are obtainable pure without any tedious separation procedures.

The alcohol (8) reacted with fluoroboric acid in propionic anhydride to give immediately a fluoroborate salt, shown by ^{1}H n.m.r. spectrum to be (9). This salt has not previously been obtained free from other isomers, and is presumably formed by hydride shift in the primary carbonium ion generated. A solution of (8) in trifluoroacetic acid showed the ^{1}H n.m.r. spectrum of (9). Similar treatment of the other hydroxymethyl complexes gave mixtures of products which were not examined.

It has been shown [1,2] that removal of hydride, by the

action of triphenylmethyl fluoroborate, occurs from one or both of two non-equivalent positions allylic to a complexed diene system, to yield tricarbonyl-π-cyclohexadienyl salts. Which of two possible products is

X = Fe(CO)₃
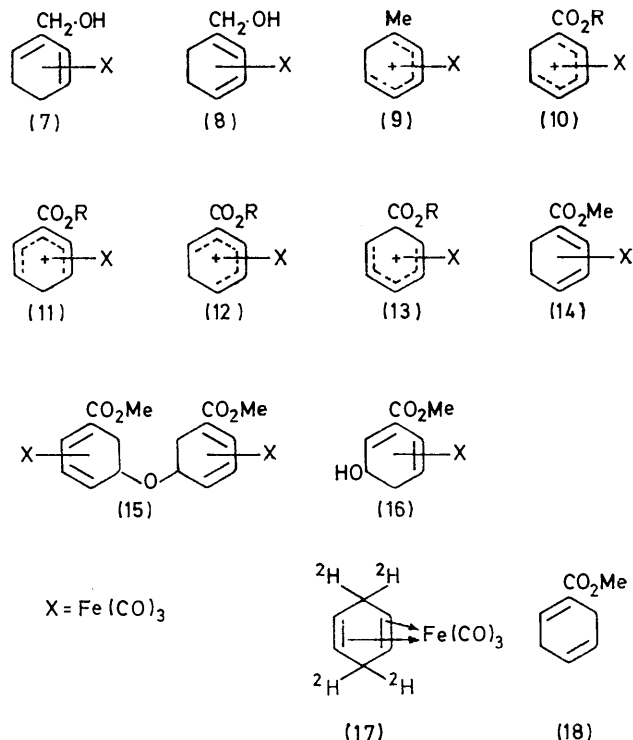
formed is of considerable interest in the series containing CO_2R substituents (R = Me or H) compared with those containing other substituents of different electronic character previously examined.[1,2] Little difference was observed between the series with R = Me and R = H. The ester (2; R = Me) gave (10) as the major product, the structure (Experimental section) being supported by the ^{1}H n.m.r. spectrum. The ester (3; R = Me) gave a mixture of the two salts (11; R = Me) and (12; R = Me) in the ratio of about 4 : 1, which could not be separated, the nature of the mixture being defined by the ^{1}H n.m.r. spectrum (Experimental section). The mixture of (1; R = Me) and (3; R = Me) gave a mixture of (10) and (13) in the ratio 21 : 79 from the former; a ratio deducible from spectra since the starting materials cannot give rise to common products except by hydrogen migration, which has not been noted in this series. The structures of the cations were determined for their ^{1}H n.m.r. spectra (solutions in trifluoroacetic acid), the chemical shifts and spin–spin splitting of protons clearly distinguishing various isomers.[2,9]

The situation with structure (1) is complicated by the uncertainty of the configuration. According to precedent, only an exo-H should be abstracted by triphenylmethyl cation; the ratio of products could therefore be determined by the ratio of stereoisomers of (1). How-

[9] D. Jones, L. Pratt, and G. Wilkinson, J. Chem. Soc., 1962, 4458.

ever if (1) consists of only the *exo*-CO_2Me isomer it is surprising that any removal of 5-H occurs. Possibly the abstraction mechanism is an indirect one, involving reaction of the triphenylmethyl cation initially with the ester carbonyl oxygen atom. The matter is under further examination.

The results may be summarised by noting that the 1-CO_2Me compound undergoes abstraction only from the 5-position, the 2-CO_2Me compound from the 6-position (major) and the 5-position (minor), and the 5-CO_2Me compound from the 6-position (major) and the 5-position (minor). The position of hydride removal is not greatly affected by change from ester to acid.

The fluoroborate salts of the esters were reactive towards water, qualitatively observed rates of reaction decreasing in the order (10; R = Me) $\gg$ (11; R = Me), (12; R = Me) > (13; R = Me). The reactivity of the carbonium ion is presumably affected by electron withdrawal by CO_2Me, this being most effective with (10; R = Me). The expected product from (10; R = Me), tricarbonyl-5-hydroxy-1-methoxycarbonylcyclohexa-1,3-dieneiron (14), accounted for only *ca.* 50% of a mixture; a second, less polar product contained no OH (i.r. spectrum). This was shown to be μ-[bis-(5-methoxycarbonylcyclohexa-2,4-dienyl) ether]bis(tricarbonyliron) (15). The mass spectrum contained no molecular ion, but the peaks m/e 294 ($C_{11}H_{10}FeO_6$) and 278 ($C_{11}H_{10}$-FeO_5) accord with fission of the ether linkage with hydrogen transfers. The ion m/e 278 was not present in the spectrum of the hydroxy-compound (14). The structure (15) was supported by the [1]H n.m.r. spectrum [δ 1·29 (t, J 8 and 4 Hz, 6,6′-H), 2·67 (m, 6-, 6′-H), 3·10 (m, 2-, 2′-H), 3·67 (s, 2 × CO_2Me), 4·00 (d, finely split, 1-, 1′-H), 5·44 (dd, 3-, 3′-H), and 6·16 (d, 4-, 4′-H)]. The compound did not crystallise and some broadened peaks in the foregoing spectrum suggest the presence of stereoisomers. A solution of the ether in trifluoroacetic acid showed the [1]H n.m.r. spectrum of the salt (10).

The methyl and ethyl ethers of (14) were formed by treatment with the appropriate alcohol in acid; the production of the ether (15) may be due to similar reaction of (14) with (10) catalysed by fluoroboric acid. In a series of equilibria the production of (15) may be favoured by its relative insolubility in water.

The reaction of (11) with water similarly gave (16) and the related dimeric ether; 20% of (12) in the starting material apparently produced the analogous compounds simultaneously. Chromatography and crystallisation gave pure (16). A similar series of products appears to be derived from (13) but since the latter has not been obtained free from isomeric salts the product of reaction with water was a complex mixture.

In contrast to the ester analogues, the cations containing a carboxy-group were stable in water at room temperature, possibly as pseudo-zwitterions.

The foregoing work provides information concerning

the effects of a CO_2R substituent in directing conjugation of 1,4-dienes to produce the 1,3-diene complexes, and the effects on the positions of hydride abstraction and acid-catalysed rearrangement in the substituted complexes.

The conjugation process has been examined [7] and an allylic hydrogen shift has been confirmed in the photochemical reaction of 3,3,6,6-tetradeuteriocyclohexa-1,4-diene with iron pentacarbonyl, with specific formation of tricarbonyl-2,5,5,5-tetradeuteriocyclohexa-1,3-dieneiron. A possible mechanism involves migration of hydrogen with intermediate attachment to the iron after initial formation of an unstable unconjugated complex such as (17). In view of the possibility of ready rearrangement of electrons through the bonds, it is perhaps not very meaningful to ask whether the hydrogen shifts as a proton, an atom, or an anion. The small differences due to substituents of differing electronic character seem to show that there is little if any charge separation in a transition state of the reaction. For example, the electron-repelling substituent CH_2·OR and the electron-accepting substituent CO_2Me on the 3-position of a cyclohexa-1,4-diene both lead to conjugation principally in the same direction away from the substituent. There is no evidence at present that the uncomplexed conjugated dienes are intermediates, but even if they were the conjugation mechanism would probably involve a complex of type (17).

Some further dihydrobenzoic esters have now been examined. Treatment of methyl cyclohexa-1,4-diene-carboxylate (18) [3] with iron pentacarbonyl gave a mixture of (2; R = Me) (85% of the product) and (3; R = Me) (15% of the product) in 26% yield. The different nature of this mixture from that produced in the reaction of methyl cyclohexa-2,5-dienecarboxylate appears to rule out equilibration of the products once formed; they are therefore kinetically controlled, presumably by the conjugation process. Non-equilibration of the complexes is confirmed by the production of pure (3) when the corresponding 1,3-diene is used as starting material.

Another set of experiments involved the disubstituted dienes (19—21; R = Me). A Diels–Alder reaction between butadiene and tetrolic acid [10] gave (19; R = H) and similar reaction between penta-1,3-diene and propiolic acid [11] gave (20; R = H). Birch reduction of o-toluic acid [12] gave (21; R = H).

Although it has been reported [11] that the acid (20; R = H) is the sole product of the Diels–Alder reaction, dehydrogenation of our crude product with DDQ gave a mixture of o-toluic (91%) and m-toluic acids (9%), identified by [1]H n.m.r. spectra. This contamination of the Diels–Alder product was not sufficient to interfere with interpretation of the results. The results of [1]H n.m.r. spectral examinations of the complexes are shown in the Scheme. The details are given in the Experimental section and analyses are considered to be subject

[10] E. R. H. Jones, G. H. Mansfield, and M. C. Whiting, *J. Chem. Soc.*, 1956, 4073; R. Grewe and I. Hinrichs, *Chem. Ber.*, 1964, **97**, 443.

[11] A. A. Petrov and K. B. Rall, *J. Gen. Chem. U.S.S.R.*, 1956, **26**, 1779.

[12] A. J. Birch, *J. Chem. Soc.*, 1950, 1551.

to an absolute error of not more than $\pm 5\%$, although the smaller figures are almost certainly more accurate than this and there is no doubt that the compounds listed are present. Kinetic control can again be assumed from the results. The configurations of the CHMe systems present in some of the isomers were not examined. Although there was no evidence from spectra for more than one isomer being present, some similar cases [1,6] result in mixtures of *endo*- and *exo*-isomers.

$X = Fe(CO)_3$
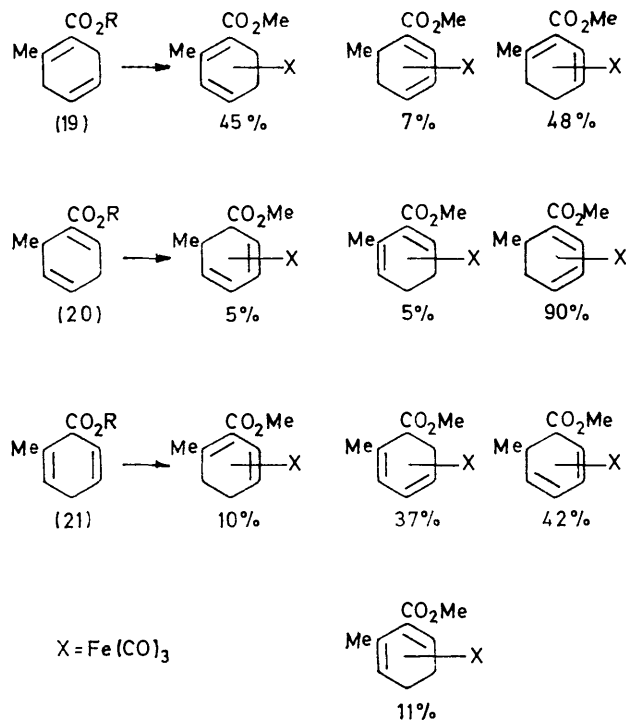
SCHEME

In view of the poor overall yields, the ratios of the products may not necessarily represent relative rates of formation and may be partly determined by decomposition rates. However, on the assumption that they do indicate roughly the rates of formation of the various isomers, the foregoing results, and the previous ones, are largely explicable on the basis of steric effects. In the conjugation process it seems to be more difficult to remove a hydride ion from a substituted position, whether the substituent is CO_2Me or Me. Migration of a hydride ion to an occupied position is also less favoured. There is no obvious correlation with electronic factors, or with the thermodynamic stability of the product. There is also no evidence in this series of further isomerisation of the complex once it is formed, although in some other examples to be reported this has been observed by further action of iron pentacarbonyl.

The positions of hydride abstraction from (1—3; R = Me) are probably determined by the effects of steric hindrance. As already noted, however, the configuration of (1; R = Me) is not known, and the situation may be complicated by the possibility of indirect attack of

triphenylmethyl cation involving CO_2Me. A further possibly relevant point is that the carbonium ion is more 'conjugated' with the destabilising CO_2Me dipole in (10) than in (13), the major product. The reaction of (2; R = Me) is more surprising since although the hydrogen atom abstracted is the less hindered the product is the 'conjugated' complex (10), but abstraction *via* reaction with CO_2Me would give this observed product. Abstraction from (3; R = Me) is presumably not affected by steric factors to any large extent and it is not clear why a 3-CO_2Me is preferred to a 2-CO_2Me in the cation formed; abstraction in this case is presumably direct.

The thermodynamic stability, which favours the system with a 1-CO_2Me group, can be rationalised in terms of 'conjugation', as shown by the spectral and chemical properties of the CO_2Me group. This contrasts with the alkyl systems.[1,2,5] where the 2-substituted isomers are predominant after acid-catalysed isomerisation. Explanations of these effects may be forthcoming from more detailed examination of the interactions of the groups with the bonding found in the complexed system.

EXPERIMENTAL

Routine i.r. spectra were recorded with Perkin-Elmer 257 and 457 spectrometers (solids as Nujol mulls and liquids as films unless otherwise noted). Precise measurements (Table) were obtained for solutions in $CHCl_3$ with a Perkin-Elmer 225 spectrometer. U.v. and visible spectra were examined with a Unicam SP 800 spectrometer. [1]H N.m.r. spectra were measured with a JEOLCO C-60HL or a Varian HA100 instrument, with tetramethylsilane as the internal standard (60 MHz) or internal lock signal (100 MHz), for solutions in $CDCl_3$ unless stated otherwise. Mass spectra were examined with an A.E.I. MS902 spectrometer.

All reactions involving complexes were carried out under nitrogen and all solvents were degassed under nitrogen.

Reactions of Cyclohexa-1,4-dienes with Iron Pentacarbonyl. —The diene and the carbonyl compound were refluxed in peroxide-free di-n-butyl ether in a slow stream of nitrogen for 16 h. The dark solution was cooled and filtered through Celite 535, which was washed with di-n-butyl ether (the solid product is frequently pyrophoric). Solvent and unchanged iron carbonyl were removed at 80° and 15 mmHg. Remaining solvent and unchanged diene were then removed at 25—60° and 0·05 mmHg. Method A involved distilling the complex and gave a higher purity product, but with greater loss than Method B, whereby the remaining liquid was taken up in light petroleum (b.p. 30—40°) and filtered through a short column of activity III acidic alumina; the solvent was then evaporated off. The liquid complexes were stored under nitrogen at −20°; the solid ones are more stable and can be kept at 4° in air for some months with only minor decomposition. A potentially more efficient method, not examined here, is described elsewhere.[1]

Reaction of Methyl Cyclohexa-2,5-dienecarboxylate.—The ester (14 g) (obtained by Birch reduction of benzoic acid [3] and methylation with diazomethane) and iron pentacarbonyl (25 ml, 36 g) in di-n-butyl ether (75 ml) were treated as in Method A. The mixed product consisted of tricarbonyl-2-methoxycarbonylcyclohexa-1,3-dieneiron (3; R =

Me) and *tricarbonyl-5-methoxycarbonylcyclohexa-1,3-diene-iron* (1; R = Me), b.p. 88° at 0·01 mmHg (7·4 g, 34%), as an orange oil (the ratio varied from 11 : 39 to 1 : 1), $\nu_{max.}$ 2050, 1718, and 1210 cm^{-1}; δ 6·07 [dd, 3-H of (3; R = Me)], 5·4 [m, 2-, 3-H of (1; R = Me)], 3·79 [s, CO$_2$Me of (3; R = Me)], 3·68 [s, CO$_2$Me of (1; R = Me)], and 3·5—1·5 (m, remaining H). The ratio of the integrals of the peaks at δ 6·07 and 5·4 permitted calculation of the ratio of isomers. The mass spectrum showed *m/e* 278 (*M*) (C$_{11}$H$_{10}$FeO$_5$) with losses of 3 × CO and Fe [*m/e* 250, 222, 194, and 138 (base peak)] (Found: C, 47·5; H, 3·8. Calc. for C$_{11}$H$_{10}$FeO$_5$: C, 47·5; H, 3·6%).

Reaction of Methyl Cyclohexa-1,5-dienecarboxylate.—The ester (10 g) (obtained by base-catalysed conjugation of the 1,4-diene [3] and esterification with diazomethane) reacted with iron pentacarbonyl (Method A) to give pure *tricarbonyl-2-methoxycarbonylcyclohexa-1,3-dieneiron* (3; R = Me) (7·7 g, 38%), b.p. 78° at 9·05 mmHg, which crystallised from light petroleum (b.p. 40—60°) at −20° as yellow needles, m.p. 40—41°, $\nu_{max.}$ 2053, 1983, 1717, and 1250 cm^{-1}; δ 6·07 (dd, 3-H), 3·79 (s, CO$_2$Me); 3·70 (d, finely split, 1-H), 3·36 (d, finely split, 4-H), and 1·9—1·5 (m, 5-, 6-H, $J_{1,3}$ 2, $J_{3,4}$ 7 Hz) (Found: C, 47·6; H, 3·9. C$_{11}$H$_{10}$FeO$_5$ requires C, 47·5; H, 3·6%).

Acidic Methanolysis of Tricarbonyl-5-cyanocyclohexa-1,3-dieneiron (4).—The nitrile complex (380 mg) was refluxed with methanol (50 ml) and sulphuric acid (5 ml) for 24 h. Ether (20 ml) was added, followed by ice–water. Evaporation of the ether layer gave *tricarbonyl-1-methoxycarbonyl-cyclohexa-1,3-dieneiron* (2; R = Me) (360 mg 80%) as an orange oil which solidified at −20°, but melted at room temperature (Found: C, 47·8; H, 3·6. C$_{11}$H$_{10}$FeO$_5$ requires C, 47·5; H, 3·6%); $\nu_{max.}$ 2056, 1987, 1698, and 1250 cm^{-1}; δ 6·05 (d, 2-H), 5·36 (dd, 3-H), 3·70 (s, CO$_2$Me), 3·36 (d, finely split, 4-H), and 2·4—1·3 (m, 5-, 6-H, $J_{2,3}$ 4, $J_{3,4}$ 6 Hz); *m/e* 278 (C$_{11}$H$_{10}$FeO$_5$) with loss of CO and Fe as for (3; R = Me).

Isomerisation of Tricarbonyl-2- and -5-methoxycarbonyl-cyclohexa-1,3-dieneiron [(3; R = Me) *and* (1; R = Me)] *with Acid.*—The mixture of complexes (200 mg) was re-fluxed for 24 h, in methanol (25 ml) containing sulphuric acid (2·5 ml). Worked up as before, the product was pure (2; R = Me), with the properties reported. The pure 2-methoxycarbonyl isomer gave the same product.

Deuteriation of the Complexes (1—3; R = Me).—Pure (2; R = Me) or (3; R = Me), or the mixture of (3; R = Me) and (1; R = Me) was refluxed in a solution of [^{2}H$_2$]sulphuric acid (0·3 ml) in methan[^{2}H]ol (5 ml) for 24 h. An identical product was obtained in each case, with the physical properties already described for tricarbonyl-1-carbomethoxycyclohexa-1,3-dieneiron. No differences were observed between the i.r. spectrum and that of undeuteriated material. Spectra indicated that the product is essentially the 6-deuterio-isomer. The ^{1}H n.m.r. spectrum was identical with that of (2; R = Me) except that the resonances due to CH$_2$ occupied the smaller range δ 2·0—1·3 p.p.m., and integration indicated the presence of slightly more than three protons instead of four. The mass spectrum had peaks *m/e* 278, 279, 280, 281 with relative intensities 22 : 100 : 18·5 : 3·2, as indicated by spectra run at 12, 15, 70 eV, which differed little in intensities. The percentages of non-, mono-, di-, and tri-deuteriated material could be calculated as 17, 79, 2·8, and 0·9%, respectively. For this calculation it was noted that the *M* − 1 peak from the undeuteriated compound is negligible; therefore that at

m/e 278 was taken to be due entirely to nondeuteriated material. Allowances were made for isotopic contributions by the respective molecular ions to *M* + 1 and *M* + 2 peaks of 14·9 and 1·4% (calculated from the known abundances of C, H, Fe, and O).

Hydrolysis of Tricarbonyl-5-cyanocyclohexa-1,3-dieneiron (4; R = CN) *by Base.*—The nitrile complex (1 g) was heated under reflux for 5 h with potassium hydroxide (25 g) in methanol (225 ml) and water (25 ml). Extraction of the cooled, diluted solution with ether gave 1-*carbamoylcyclohexa-1,3-dienetricarbonyliron* (320 mg, 28%), m.p. 140° (from aqueous ethanol), $\nu_{max.}$ 3480, 3150, 2060, 1970, 1650, and 1600 cm^{-1}; δ 6·10 (dd, 2-H), 5·90br (exchanges slowly in D$_2$O, CO·NH$_2$), 5·38 (dd, 3-H), 3·29 (d, finely split, 4-H), 2·1—1·4 (m, 5-, 6-H, $J_{2,3}$ 4, $J_{3,4}$ 6, $J_{2,4}$ 1 Hz); *m/e* 263 (C$_{10}$H$_9$FeNO$_4$), 235, 207, 177, and 121 (loss of 3 × CO, 1 × Fe, 2 × H); the compound also lost water to give the ion of the nitrile complex (*m/e* 245) which showed the further losses as above (Found: C, 45·8; H, 3·4. C$_{10}$H$_9$FeNO$_4$ requires C, 45·7; H, 3·4%).

The mother liquors of the neutral fraction (soluble in light petroleum) contained about 30% of tricarbonyl-1-cyano-cyclohexa-1,3-dieneiron, identified by spectra: $\nu_{max.}$ 2210, 2060, and 1980 cm^{-1}; δ 5·34 (dd, 3-H), 4·21 (d, 2-H), and 3·46 (d, finely split, $J_{2,3}$ 6, $J_{3,4}$ 4 Hz). Some uncomplexed material (diene and aromatic) appeared to be present. Acidification of the alkaline solution and extraction with ether gave tricarbonyl-5-carboxycyclohexa-1,3-dieneiron, δ 5·58 (m, 2-, 3-H), 3·28 (m, 1-, 4-H), and 2·91 (m, 5-H).

Conjugation of Tricarbonyl-2- and -5-methoxycarbonyl-cyclohexa-1,3-dieneiron in Basic Solution.—The mixture of complexes (3 : 1) was heated and refluxed for 5 h in dry methanol (7 ml) containing sodium methoxide (300 mg). The ^{1}H n.m.r. spectrum of the neutral product showed it to consist of tricarbonyl-1-methoxycarbonylcyclohexa-1,3-dieneiron with *ca.* 20% of benzoic ester (by comparison with authentic specimens). The small acidic fraction was shown by ^{1}H n.m.r. comparisons with the known compounds to contain tricarbonyl-2- and -5-carboxycyclohexa-1,3-diene-iron in the ratio 4 : 13 (virtually identical with that of the ester starting material).

Basic Hydrolysis of Esters.—Tricarbonyl-2-methoxycarb-onylcyclohexa-1,3-dieneiron (2 g) was treated at room temperature for 2 h with potassium hydroxide (8 g) in water (50 ml) and methanol (150 ml). The acidic product, crystallised from aqueous ethanol as yellow needles, m.p. 157—158° was *tricarbonyl-2-carboxycyclohexa-1,3-dieneiron* (3; R = H) (1·8 g, 84%) (Found: C, 45·4; H, 3·2. C$_{10}$H$_8$FeO$_5$ requires C, 45·5; H, 3·1%); δ 6·5br (exchanges in D$_2$O, CO$_2$H), 6·16 (dd, 3-H), 3·76 (d, finely split, 1-H), 3·51 (d, finely split, 4-H), and 1·65 (m, 5-, 6-H, $J_{3,4}$ 7, $J_{1,3}$ 2 Hz); *m/e* 264 (C$_{10}$H$_8$FeO$_5$) with losses of 3 × CO, Fe, 2 × H (*m/e* 236, 208, 180, and 122). The base peak at *m/e* 105 represented further loss of water.

A mixture of tricarbonyl-5- and -2-methoxycarbonyl-cyclohexa-1,3-dieneiron in the ratio 77 : 23 was similarly treated with potassium hydroxide. The corresponding acids were produced in unchanged ratio as an oil; ratios were calculated from the ^{1}H n.m.r. peak, for example those at δ 6·16 (3-H of the 2-isomer) and 5·5 (2-, 3-H of the 5-isomer).

Acidic Hydrolysis.—Tricarbonyl-1-methoxycarbonyl-cyclohexa-1,3-dieneiron (2; R = Me) (700 mg) was heated under reflux for 24 h with aqueous sulphuric acid (15%) to produce a suspended orange solid. Extraction gave

tricarbonyl-1-carboxycyclohexa-1,3-dieneiron (2; R = H) (520 mg), m.p. 175° (from aqueous ethanol) (Found: C, 45·6; H, 3·1. $C_{10}H_8FeO_5$ requires C, 45·5; H, 3·1%); ν_{max} 2057, 1988, and 1666 cm^{-1}; δ 6·10 (d, 2-H), 5·57 (dd, 3-H); 5·5br (exchanges in D_2O, CO_2H), 4·37 (d, finely split, 4-H), and 2·4—1·3 (m, 5-, 6-H, $J_{2,3}$ 4, $J_{3,4}$ 6 Hz); *m/e* 264 ($C_{10}H_8FeO_5$) and other losses of CO, *etc.*, similar to those already described.

Similar treatment of a mixture of the 2- and the 5-methoxycarbonyl complexes, or the pure 2-ester complex, gives the same product in 70—80% yield.

Reactions of Cyclohexadienecarboxylic Esters with Iron Pentacarbonyl.—Methyl cyclohexa-1,4-dienecarboxylate (19; R = H) (from butadiene and propiolic acid [10]) (5 g) and iron pentacarbonyl (8 ml, 12 g) were refluxed in di-n-butyl ether (50 ml). Method A (see before) gave an oil, b.p. 92° at 0·1 mmHg (2·6 g, 26%), shown to be a mixture of tricarbonyl-1- and -2-methoxycarbonylcyclohexa-1,3-dieneiron (85 : 15), identified by ^{1}H n.m.r. intensities and positions: δ 6·12 (part of dd due to 3-H of the 2-isomer) which overlaps with 6·04 (d, 2-H of the 1-isomer), 5·36 (dd, 3-H of the 1-isomer), 4·36 (d, H-4 of both isomers), and 2·4—1·2 (m, CH_2 of both isomers). The ratio of the peak due to 3-H of the 2-isomer and 2-H of the 1-isomer (δ 6·2—6·0) to that corresponding to 3-H of the 1-isomer (5·36 p.p.m.) was 13 : 11. Ratios quoted later are not all discussed in detail, but the methods of evaluation were similar.

Methyl 2-methylcyclohexa-1,4-dienecarboxylate (from butadiene and tetrolic acid [10] followed by methylation) (2·4 g) and iron pentacarbonyl (5 ml, 7·3 g) were treated as before. Method B gave an orange oil (2·2 g, 48%), which was a mixture of tricarbonyl-2-methoxycarbonyl-1-methyl- (48%), tricarbonyl-1-methoxycarbonyl-2-methyl- (45%), and tricarbonyl-1-methoxycarbonyl-6-methyl-cyclohexa-1,3-dieneiron (7%) (A, B, and C, respectively), ν_{max} 2060, 1980, 1730, and 1710 cm^{-1}; δ 6·05 (d, 2-H of C), 5·85 (d, 3-H of A), 5·42 (t, 3-H of C), 5·18 (d, 3-H of B), 3·83 (s, CO_2Me of A), 3·68 (s, CO_2Me of B), 3·22 (m, 4-H of A, B, and C), 2·47 (s, Me of B), 1·88 (s, Me of A), 0·86 (Me of C), and 2·4—1·2 (m, CH_2 of A, B, and C); A, $J_{3,4}$ 7; B, $J_{3,4}$ 6; C, $J_{2,3} = J_{3,4} = 6$ Hz. The integrated ratios of peaks at δ 6·05, 5·85, 5·42, and 5·18 were 2 : 14 : 2 : 13, giving the ratios A : B : C as 14 : 13 : 2.

Methyl 6-methylcyclohexa-1,4-dienecarboxylate (20; R = H) (92% of the mixture obtained from Diels–Alder reaction of penta-1,3-diene and propiolic acid,[11] followed by esterification) (5·5 g) and iron pentacarbonyl (11·4 g), treated as before (Method B) gave an orange oil (1·13 g, 11%) consisting of tricarbonyl-5-methoxycarbonyl-6-methyl- (D; less than 10%), tricarbonyl-2-methoxycarbonyl-3-methyl (E; less than 10%), and tricarbonyl-1-methoxycarbonyl-6-methylcyclohexa-1,3-dieneiron (C; 90%), identical (spectra) with that already described; δ 5·6—5·2 (m, 2-, 3-H of D), 4·39 (s, CO_2Me of E), 3·62 (s, CO_2Me of D), 2·36 (s, Me of E), and 1·13 (d, Me of D). The ratios could not be estimated accurately, but the mixture probably contains about 90% C.

Methyl 2-methylcyclohexa-2,5-dienecarboxylate (21; R = H) (from Birch reduction of *o*-toluic acid [12] and methylation) (21 g) and iron pentacarbonyl (35 g) were treated as before (Method A) to give an orange oil (4·95 g, 12%), b.p. 100—104° at 0·3 mmHg, ν_{max} 2060, 1980, and 1730 cm^{-1}. The ^{1}H n.m.r. spectrum was complex and difficult to analyse, although one component was obviously tricarbonyl-2-methoxycarbonyl-1-methylcyclohexa-1,3-dieneiron, δ 5·86

(d, 'inner' proton 3-H). Comparisons of spectra eliminated the possibility of the presence of the 1-methoxycarbonyl-2-methyl- and the 1-methoxycarbonyl-6-methyl isomers, leaving four other possible isomers. Those present were estimated by integral ratios of 'inner' diene proton peaks (δ 5·5—5·0), CO_2Me peaks (δ 3·83, 3·80, 3·70, and 3·64), and 'outer' diene proton peaks (δ 3·4—2·9) (47 : 90 : 46). The doublet at δ 5·86 for 3-H has a value of 3 on this scale; by subtracting the contributions of this isomer to the other peaks we concluded that the isomers present were tricarbonyl-2-methoxycarbonyl-1-methyl- (10%), tricarbonyl-6-methoxycarbonyl-1-methyl- (37%), tricarbonyl-5-methoxycarbonyl-6-methyl- (42%), and tricarbonyl-2-methoxycarbonyl-3-methyl-cyclohexa-1,3-dieneiron (11%).

Isomerisation of Methyl-substituted Methyl Ester Complexes.—All the foregoing complexes, including mixtures, when treated with methanolic sulphuric acid as before gave a mixture of tricarbonyl-1-methoxycarbonyl-2-methyl- (B; 82%), tricarbonyl-1-methoxycarbonyl-6-methyl- (C; 16%), and tricarbonyl-2-methoxycarbonyl-1-methyl-cyclohexa-1,3-dieneiron (A; 2%), ν_{max} 2060, 1980, and 1705 cm^{-1}; δ 6·04 (d, 2-H of C), 5·84 (d, 3-H of A), 5·40 (t, 3-H of C), 5·16 (d, 3-H of B), 3·79 (s, CO_2Me of A), 3·68 (s, CO_2Me of B and C), 3·18 (m, 4-H of A, B, and C), 2·45 (s, Me of B), 0·86 (d, Me of C), and 2·4—1·3 (m, methylenes). The ratio of isomers was based on integrals of the peaks at δ 6·04, 5·84, 5·00, and 5·16 (18 : 2 : 18 : 93).

Complexes of Protected 5-Hydroxymethylcyclohexa-1,4-dienes.—The alcohols were obtained [3] by reduction of the corresponding acids. The acetates were made with acetic anhydride and pyridine; the tetrahydropyranyl ethers were formed in the usual way and purified by chromatography on silica gel.

5-(Acetoxymethyl)cyclohexa-1,4-diene (14 g) was treated with iron pentacarbonyl (31 g) as before. Method A gave tricarbonyl-5-acetoxymethylcyclohexa-1,3-dieneiron (8 g), b.p. 94° at 0·02 mmHg, ν_{max} 2060, 1950, 1735, and 1235 cm^{-1}; δ 5·5—5·1 (m, 2-, 3-H), 4·80 (t, CH_2), 3·3—3·9 (m, 1; 4-H), 2·40 (m, 5-H), 2·04 (s, COMe), and 2·2—1·2 (m, 6-H); *m/e* 292 ($C_{12}H_{12}FeO_5$) with the usual losses of CO and Fe; base peak *m/e* 134 (C_6H_6Fe).

The 5-(tetrahydropyran-2-yloxymethyl)cyclohexa-1,4-diene (7·5 g) (Method B) gave tricarbonyl-5-(tetrahydropyran-2-yloxymethyl)cyclohexa-1,3-dieneiron (3·3 g, 36%), ν_{max} 2060, 1950, 1130, and 1040 cm^{-1}; δ 5·5—5·1 (m, 2-, 3-H), 4·45 (m, O·CH), 4·0—2·9 (m, 1-, 4-H, O·CH_2), 2·6—2·2 (m, 5-H), and 2·2—1·1 (m, 6-H_2 and [CH_2]$_3$), *m/e* 334 ($C_{15}H_{18}FeO_5$).

The acetate was hydrolysed with methanolic potassium hydroxide in the cold to give tricarbonyl-5-(hydroxymethyl)cyclohexa-1,3-dieneiron, ν_{max} 3320, 2060, 1970, 1040 cm^{-1}; δ 5·5—5·1 (m, 2-, 3-H), 3·7—2·9 (m, 1-, 4-H and CH_2·O), and 2·5—0·8 (m, 5-, 6-H and OH), *m/e* 250 ($C_{10}H_{10}FeO_4$) with loss of 3CO, H_2O, and CH_2.

The tetrahydropyranyl ether was hydrolysed with 10N-hydrochloric acid (1 ml) in methanol (60 ml) and water (8 ml) for 80 min. The product was identical with that from the acetate. The acetate and tetrahydropyranyl ether could be re-formed from this product in the usual way.

Methylcyclohexa-1,5-dienecarboxylate, when reduced with lithium aluminium hydride, gave a mixture containing cyclohex-1-enecarbaldehyde (55%) and the desired 2-(hydroxymethyl)cyclohexa-1,3-diene (45%); the 2,4-dinitrophenylhydrazone of the former had m.p. 213—215° (from acetic acid), *m/e* 290, and the ^{1}H n.m.r. spectrum

agreed with the postulated structure. Separation on silica gel gave the pure products.

Reduction of Tricarbonylcarboxycyclohexa-1,3-dieneiron Derivatives with Diborane.—The complex (500 mg) was dissolved in tetrahydrofuran (20 ml) and a solution of diborane (1M in BH_3) in tetrahydrofuran (5 ml) was added under nitrogen, with a further 5 ml after 1 h. At the end of a further 1 h ethanol (2 ml) was cautiously added, followed by saturated aqueous sodium chloride (500 ml), and the product was extracted with ether and chromatographed on silica gel (20 g) in chloroform. The product from the 1-carboxy-derivative was crystallised from light petroleum at 20° to give *tricarbonyl-1-(hydroxymethyl)cyclohexa-1,3-dieneiron* (8), m.p. 63—64°, $\nu_{max.}$ 3220, 2050, 1970, and 1950 cm^{-1}; δ 5·39 (d, 2-H), 5·20 (dd, 3-H), 3·82 (d, collapsing to s with D_2O, CH_2·O), 3·19 (d, 4-H), and 2·0—1·4 [m, 5-, 6-H and OH (lost in D_2O)]; $J_{2.3}$ 4, $J_{3.4}$ 6, $J_{CH_2, OH}$ 3 Hz; m/e 250 ($C_{10}H_{10}FeO_4$) (Found: C, 48·1; H, 4·2. $C_{10}H_{10}FeO_4$ requires C, 48·0; H, 4·0%).

The 2-carboxy-complex similarly gave tricarbonyl-2-(hydroxymethyl)cyclohexa-1,3-dieneiron (7), m.p. 42—43°; $\nu_{max.}$ 3220, 2050, and 1970 cm^{-1}; δ 5·42 (dd, 3-H), 4·40 and 4·06 (each d forming ABq, CH_2·O), 3·23 (d, H-1), 3·14 (d, H-4), 2·18br (s, exchanged in D_2O, OH), and 2·0—1·3 (m, 5-, 6-H); $J_{1.3}$ 2, $J_{3.4}$ 6, $J_{gem\text{-}CH_2}$ 13 Hz; m/e 250 ($C_{10}H_{10}FeO_4$).

Reaction of the 1-Hydroxymethyl Complex with Acid.—Anhydrous fluoroboric acid was obtained by slowly adding aqueous fluoroboric acid (1·5 ml, 2 g) to cooled propionic anhydride (5 ml). The 1-hydroxymethyl complex (8) (100 mg) in propionic anhydride (0·12 ml) was treated with this fluoroboric acid solution (0·2 ml), giving an immediate yellow precipitate. Ice–water (1 ml) was added and the precipitate was filtered off and washed with ether to give tricarbonyl-1-methylcyclohexadienyliron fluoroborate (9) (70 mg, 55%); $\nu_{max.}$ 3100, 3070, 2120, 2080, and 1065 cm^{-1}; δ (CF_3·CO_2H) 7·11 (t, 3-H), 5·85 (t, 4-H), 5·46 (d, 2-H), 4·20 (t, 5-H), 3·02 (dd, *endo*-6-H), 3·30 (d, *exo*-6-H), and 1·28 (s, Me); $J_{2.3} = J_{3.4} = 5$, $J_{4.5} = J_{5,6\text{-}endo} = 6$, $J_{6\text{-}endo, 6\text{-}exo}$ 17 Hz.

Direct dissolution of the alcohol in trifluoroacetic acid gave the same spectrum, indicating immediate complete conversion.

Hydride Abstraction from the Complexes.—This was carried out by use of triphenylmethyl fluoroborate in methylene chloride.[2] The 1-methoxycarbonyl complex (2; R = Me) (1 g) gave an orange gum (940 mg) on addition of ether; the the gum was washed with dry ether and kept at 0·05 mmHg. It had $\nu_{max.}$ 3070, 2130, 2090, 2070, 1715, 1275, and 1050 cm^{-1} and the ^{1}H n.m.r. spectrum of a solution in trifluoroacetic acid showed it to be tricarbonyl-1-methoxycarbonylcyclohexadienyliron fluoroborate (10), δ 7·54 (t, 3-H), 6·72 (d, 2-H), 6·00 (t, 4-H), 4·82 (t, 5-H), 3·98 (s, CO_2Me), 3·45 (dd, *endo*-6-H), and 2·65 (d, *exo*-6-H); $J_{2.3} = J_{3.4} = J_{4.5} = J_{5,6\text{-}endo} = 6$, $J_{6\text{-}endo, 6\text{-}exo}$ 15 Hz. The crude material contained some triphenyl methanol.

The 2-methoxycarbonyl complex (3; R = Me) gave a crystalline fluoroborate salt which was nevertheless a mixture of tricarbonyl-2- (20%) (F) and -3-methoxycarbonylcyclohexadienyliron fluoroborate (80%) (G); $\nu_{max.}$ 3080, 2130, 2105, 2090, 2065, 1725, 1310, and 1070 cm^{-1}; δ (CF_3·CO_2H) 7·95 (d, 3-H of F), 6·50 (d, 2-, 4-H of G), 6·03 (t, 4-H of F), 4·12 (d, 1-H of F), 4·63 (t, 1-, 5-H of G and 5-H of F), 4·24 (s, CO_2Me of G), 4·03 (s, CO_2Me of F), 3·4—3·0 (m, *endo*-6-H of F and G), and 2·16 (d, *exo*-6-H of F and G); for F $J_{3.4} = J_{4.5} = J_{1\text{-}6, endo} = 6$, $J_{6\text{-}endo, 6\text{-}exo}$ 16; for G:

$J_{1.2} = J_{4.5} = J_{1, 6\text{-}endo} = J_{5, 6\text{-}endo} = 7$, $J_{6\text{-}endo, 6\text{-}exo}$ 16 Hz. The ratio of intensities at δ 7·95 and 6·50 was 7·58 : 1, indicating the proportion of isomers.

The 5-methoxycarbonyl complex (1; R = Fe) gave a crystalline fluoroborate shown by ^{1}H n.m.r. spectra to be a mixture of the foregoing three fluoroborate salts, together with tricarbonyl-6-methoxycarbonylcyclohexadienyliron fluoroborate (H). Additional peaks in the ^{1}H n.m.r. spectrum for the new isomer, which were clearly discernible were δ (CF_3·CO_2H) 7·40 (t, 3-H), 6·04 (t, 2-, 4-H), 4·52 (t, 1-, 5-H), and 4·08 (s, CO_2Me); $J_{1.2} = J_{4.5} = J_{2.3} = J_{3.4} = J_{1, 6\text{-}endo} = J_{5, 6\text{-}endo} = 6$ Hz. The ratio of the 1-ester isomer to the 6-ester isomer was 21 : 79, given by integration of peaks at δ 6·72 and 7·40 (4 : 15).

Similar experiments with the acids gave the corresponding carboxy-salts. The tricarbonyl-1-carboxycyclohexadienyliron fluoroborate had $\nu_{max.}$ 3240, 3070, 2130, 2080, 1723, 1230, and 1090 cm^{-1}; δ (CF_3·CO_2H) 7·59 (t, 3-H), 6·78 (d, 2-H), 6·05 (t, 4-H), 4·88 (t, 5-H), 3·48 (dd, *endo*-6-H), and 2·08 (d, *exo*-6-H); $J_{2.3} = J_{3.4} = J_{4.5} = J_{5, 6\text{-}endo} = 6$; $J_{6\text{-}endo, 6\text{-}exo}$ 15 Hz. A *reineckate* was precipitated by ammonium reineckate as $[(C_6H_6CO_2H)Fe(CO)_3]$ $[Cr(SCN)_4(NH_3)_2]$ (Found: C, 28·3; H, 2·3; N, 14·3. $C_{14}H_{13}CrFeN_6O_5S_4$ requires C, 28·4; H, 2·2; N, 14·2%).

The 2-carboxy-complex gave a mixture of tricarbonyl-2- (14%) (J), and -3-carboxycyclohexadienyliron fluoroborate (86%) (K), $\nu_{max.}$ 3080, 2670, 2570, 2140, 2100, 1705, 1317, and 1065 cm^{-1}; δ 7·99 (d, 3-H of J), 6·50 (d, 2-,4-H of K), 6·04 (t, 4-H of J), 4·95 (m, 1-, 5-H of J), 4·67 (t, 1-, 5-H of K), 3·4—3·0 (m, *endo*-6-H of J, K), and 2·20 (d, *exo*-6-H of J, K); for J: $J_{3.4}$ 6; for K $J_{1.2} = J_{4.5} = J_{1, 6\text{-}endo} = J_{5, 6\text{-}endo} = 6$, $J_{6\text{-}endo, 6\text{-}exo}$ 17 Hz. The ratio J : K was calculated from the integrals of the peaks at δ 7·99 and 6·50 (4 : 50). A similar precipitate of a pink reineckate was obtained.

The 5-carboxy-complex in admixture with a minor proportion of the 2-carboxy-complex was treated similarly; the salt obtained contained the 2- and 3-carboxy-complexes to be expected from the latter as well as a major proportion of the tricarbonyl-6-carboxycyclohexadienyliron fluoroborate, δ 7·42 (3-H), 6·09 (2-, 3-H), and 4·50 (1-, 2-H); the peaks were broad and expected splittings were not well resolved.

Reactions of the Methoxycarbonyl Salt Complexes with Water and Alcohols.—Addition of water to the gummy fluoroborate (1 g) obtained from tricarbonyl-1-methoxy-carbonylcyclohexa-1,3-dieneiron gave an immediate precipitate. Chromatography on neutral alumina (III) (20 g) in ethanol-free chloroform gave two fractions. The first was μ-[bis-(5-methoxycarbonylcyclohexa-2,4-dienyl) ether]-bis(tricarbonyliron) (15), obtained as a sticky oil (200 mg), $\nu_{max.}$ 2060, 1980, 1700, and 1250 cm^{-1}; δ 6·16 (d, 2-, 2′-H), 5·44 (dd, 3-, 3′-H), 4·00 (d, 5-,5′-H), 3·67 (s, 2 × CO_2Me), 3·10 (m, 4-,4′H), 2·67 (m, 6-, 6′-H, probably *endo*), and 1·29 (t, 6-, 6′-H, probably *exo*); $J_{2.3}$ 4, $J_{3.4}$ 8 Hz. The mass spectrum showed no molecular ion, but peaks at m/e 294 and 278, corresponding to ether fission with H transfer; the former peak showed a fragmentation pattern identical with the carbinol described later; both peaks showed the usual loss of 3CO, 2H, and Fe.

The second fraction crystallised from light petroleum at −20° to give *tricarbonyl-1-methoxycarbonyl-5-hydroxycyclohexa-1,3-dieneiron* (14) (215 mg), m.p. 84—85°, $\nu_{max.}$ 3400, 2060, 1980, 1705, and 1250 cm^{-1}; δ 6·26 (d, 2-H), 5·49 (t, 3-H), 4·43br (sharpening to dt on addition of D_2O, 5-H, probably *endo*), 3·70 (s, CO_2Me), 3·18 (t, 4-H), 2·79 (dd,

6-H, probably *endo*); 2·07br (d, lost in D_2O, OH), and 1·14 (dd, 6-H, probably *exo*); $J_{2,3} = J_{3,4} = 5$, $J_{4,5\text{-}endo}$ 3, $J_{5\text{-}endo,\text{OH}}$ 4, $J_{5\text{-}endo,6\text{-}exo}$ 4, $J_{5\text{-}endo,6\text{-}endo}$ 10, $J_{6\text{-}endo,6\text{-}exo}$ 15 Hz; m/e 294 ($C_{11}H_{10}FeO_6$) with the usual fragments (Found: C, 45·2; H, 3·5. $C_{11}H_{10}FeO_6$ requires C, 44·9; H, 3·4%).

In the presence of ethanol in the chloroform, the first fraction eluted was the ethyl ether, and the methyl ether was obtained by treatment of the alcohol with a trace of hydrochloric acid in methanol. The ethyl ether had $\nu_{max.}$ 2060, 1980, 1705, and 1250 cm^{-1}; δ 6·19 (d, 2-H), 5·48 (t, 3-H), 4·00 (dt, 5-H, probably *endo*), 3·67 (s, CO_2Me); 3·42 (q, $O\cdot CH_2$), 3·24 (m, 4-H), 2·68 (dd, 6-H, probably *endo*), 1·37 (dd, 6-H, probably *exo*), and 1·12 (t, Me); $J_{2,3}$ 4, $J_{3,4}$ 5, $J_{4,5\text{-}endo}$ 3, $J_{5\text{-}endo,6\text{-}endo}$ 10, $J_{5\text{-}endo,6\text{-}exo}$ 3, $J_{5\text{-}endo,6\text{-}exo}$ 15 Hz.

The mixture of salts (20 and 80%) obtained from the 2-methoxycarbonyl complex (1 g) was stirred in water (30 ml) with ether (30 ml) until all the yellow colour had passed into the ether. Chromatography gave an initial ether fraction (100 mg) probably consisting mainly of the ether of the 3-methoxycarbonyl complex joined through the 5-position with some of the 1-methoxycarbonyl complex joined by an ether linkage through the 6-position; unsymmetrical ethers cannot be excluded. The major fraction showed the following resonances δ 6·33 (d, 3-, 3′-H), 4·03 (dt, 6-, 6′-H, probably *endo*), 3·85 (s, 2 × CO_2Me), 4·70 ·

(m, 1-, 1′-H), 3·10 (m, 4-, 4′-H), 2·33 (m, 5-,5′-H, probably *endo*), and 1·42 (t, 5-,5′-H, probably *exo*); $J_{3,4}$ 6, $J_{1,6\text{-}endo}$ 3, $J_{6\text{-}endo,5\text{-}endo}$ 10, $J_{6\text{-}endo,5\text{-}exo}$ 3 Hz. The ratio of peaks at δ 6·33 and 5·50 was 13 : 3, representing about 23% of the second isomer.

The second fraction (240 mg) consisted of a mixture of tricarbonyl-2-methoxycarbonyl-6-hydroxy- (L) (85%) and -1-methoxycarbonyl-6-hydroxycyclohexa-1,3-dieneiron (M) (15%); $\nu_{max.}$ 3400, 2060, 1980, 1720, and 1250 cm^{-1}; δ 6·35 (d, 3-H of L), 6·14 (d, 2-H of M), 5·64 (t, 3-H of M), 4·40 (m, collapsing to dt on addition of D_2O, 6-H probably *endo* of L) 3·85 (s, CO_2Me of L), 3·72 (s, CO_2Me of M), 3·54 (dd, 1-H of L), 3·08 (m, 4-H of L), 2·37 (m, 5-H, probably *endo* of L), 2·30 (d, lost in D_2O, OH of L), and 1·50 (d, 5-H, probably *exo* of L); for L $J_{3,4}$ 7, $J_{1,3}$ 1·5, $J_{1,6\text{-}endo}$ 4, $J_{5\text{-}endo,6\text{-}endo}$ 10, $J_{5\text{-}exo,6\text{-}endo}$ 3, $J_{5\text{-}endo,5\text{-}exo}$ 15; for M $J_{2,3} = J_{3,4} = 5$ Hz. The ratio L : M was given by integrals of peaks at δ 6·35 and 6·14 (17 : 3). Several crystallisations from light petroleum at $-20°$ gave pure (L), confirming the ^{1}H n.m.r. assignments.