Organometallic Compounds in Organic Synthesis. Part 10.[1] Preparations and Some Reactions of Tricarbonyl-1,3- and -1,4-dimethoxycyclohexa-1,3-dieneiron and Related Compounds: the Preparation of the Tricarbonyl-3-methoxycyclohexadienyliumiron Cation

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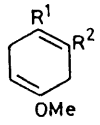
Tricarbonylcyclohexadienyliumiron cations can be regarded as synthetic equivalents, depending on the reaction sequence, either of specific aryl cations or, in the case of methoxy-derivatives, of cations derived from cyclohex-2-enones. An important series can be entered through the symmetrical 3-methoxy cation (32, $R^1 = R^2 = H$, $R^3 = OMe$) made efficiently for the first time from tricarbonyl-1,3-dimethoxycyclohexa-1,3-dieneiron (18). It is synthetically equivalent to a *meta*-methoxy-benzene cation or to a 5-cation of cyclohex-2-enone. Another series of aromatic equivalents can be defined based on nucleophilic reactions at the 1-position of derivatives of tricarbonylcyclohexa-2,4-dienoneiron (33), and efficient syntheses of (33) and its 3-methoxy (35) and 4-methoxy (37) derivatives are described. The precursors for these reactions require the efficient complexation of the 1,3- or 1,4-dimethoxycyclohexadienes, which can be carried out using the conjugated, but not the unconjugated, 1,4-dienes where loss of OMe occurs. Related processes are described in preparations and uses of complexes of some 1-morpholinocyclohexa-1,3-dienes. Some mechanisms are discussed.

SPECIFICALLY substituted tricarbonylcyclohexa-1,3-dienyliumiron cations are synthetically equivalent to either aryl cations or to cyclohex-2-enones with a positive charge in the 4- or 5-position, according to the substituents and to sequence of processes in which they are used.[2] To make synthetic use of this equivalence requires the availability of methods for making pure defined complexes. Some aspects have been discussed,[3] including regiospecific and stereospecific reactions with a range of nucleophiles, particularly those leading to new sterically defined C–C bonds. A particularly useful example is the symmetrical 3-methoxy cation, which is equivalent, as discussed below, to a cyclohexenone with the capability to react as a sterically defined cation at the 5-position. There are no known general classical methods of producing a new C–C bond at such a situation by nucleophilic processes.

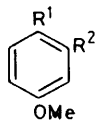
Preparations of the cations in general begin with neutral substituted tricarbonylcyclohexa-1,3-dieneiron complexes. One particularly useful conversion method is the action of sulphuric acid on the 1-OMe or the 2-OMe complexes, accompanied by rearrangement and loss of OMe. The mechanism has been discussed.[4]

If this type of procedure is to be used to form OR substituted cations, the diene precursors must contain two OR groups, or possibly OR and a group such as NR_2 which might be similarly removed. We have accordingly first examined the formations of such complexes, and their conversions into cations of potential synthetic applications.

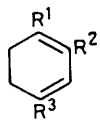
Diene precursors are obtainable by Birch reductions of the available substituted aromatic compounds (1)—(6). These are initially 1,4-dienes, which are therefore more readily available than 1,3-dienes, into which they can be converted. It is known [5] that the initial dienes (9) and (10), containing NR_2, usually undergo conjugation to some extent during isolation from the reduction, and (9) was as expected mixed with (13), and (10) with (14) and (15). Distillation converted (9) fully into (13), but distillation of (10) resulted in a mixture containing about 40% of (14) and (15), unaffected further by Wilkinson's catalyst.[6]



(1) $R^1 = OMe$, $R^2 = H$
(2) $R^1 = H$, $R^2 = OMe$
(3) R^1 = morpholino, $R^2 = H$
(4) $R^1 = H$, R^2 = morpholino
(5) $R^1 = Pr^iO$, $R^2 = H$
(6) $R^1 = H$, $R^2 = Pr^iO$



(7) $R^1 = H$, $R^2 = OMe$
(8) $R^1 = OMe$, $R^2 = H$
(9) R^1 = morpholino, $R^2 = H$
(10) $R^1 = H$, R^2 = morpholino
(11) $R^1 = Pr^iO$, $R^2 = H$
(12) $R^1 = H$, $R^2 = Pr^iO$



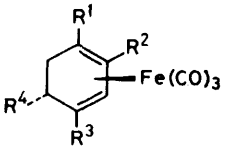
(13) R^1 = morpholino, $R^2 = H$, $R^3 = OMe$
(14) $R^1 = H$, R^2 = morpholino, $R^3 = OMe$
(15) $R^1 = H$, $R^2 = OMe$, R^3 = morpholino
(16) $R^1 = H$, $R^2 = OMe$, $R^3 = OMe$
(17) $R^1 = OMe$, $R^2 = H$, $R^3 = OMe$

Unconjugated cyclohexa-1,4-dienes can be treated with iron carbonyls, with isomerisation occurring, to yield complexes of 1,3-dienes. Because of their availability the dienes (7) and (8) were first treated directly with pentacarbonyliron for the preparation of (18) and (19). However, the desired products (Table), as well as those from the related isopropoxy-dienes (11) and (12), were obtained in poor yields mixed with the products of OR loss. Hypotheses [7] of isomerisation occurring in this type of complexation are consistent with the formation of a complex of type (27) (Scheme 1) followed by reductive removal of OR. Support for this view was obtained by reaction of the tricarbonyl-2-methoxycyclo-

Diene	% Yield [a] of dialkoxy product (structure)	% Yield [a] of monoalkoxy products (structure)			
		1-MeO	2-MeO	1-Pr^{i}O	2-Pr^{i}O
(7)	8.4 (18)	5.9 (23)	6.0 (24)		
(8)	11.5 (19)	2.6 (23)	2.3 (24)		
(11)	25.7 (20)	0.4 (23)	0.2 (24)	3 (25)	1 (26)
(12)	1.5 (21) [b] 1.5 (22) [b]	None	0.5 (24)	None	1.7 (26)

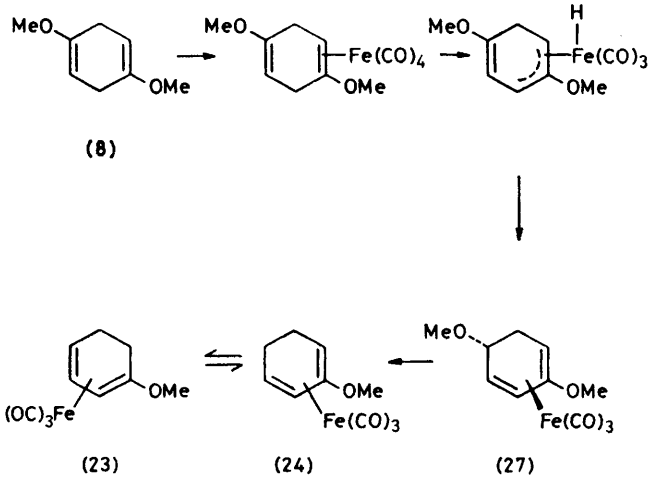
[a] Based on diene consumed. [b] Complexes (21) and (22) were not separated.

hexadienyl salt with methoxide, and reaction of the neutral product (27) with $Fe(CO)_5$ under the same conditions. A yield of about 30% of a mixture of the mono-substituted 1-OMe and 2-OMe complexes was obtained,



(18) $R^1 = R^4 = H$, $R^2 = R^3 = OMe$
(19) $R^1 = R^3 = OMe$, $R^2 = R^4 = H$
(20) $R^1 = Pr^iO$, $R^2 = R^4 = H$, $R^3 = OMe$
(21) $R^1 = R^4 = H$, $R^2 = Pr^iO$, $R^3 = OMe$
(22) $R^1 = R^4 = H$, $R^2 = MeO$, $R^3 = Pr^iO$
(23) $R^1 = OMe$, $R^2 = R^3 = R^4 = H$
(24) $R^1 = R^3 = R^4 = H$, $R^2 = OMe$
(25) $R^1 = Pr^iO$, $R^2 = R^3 = R^4 = H$
(26) $R^1 = R^3 = R^4 = H$, $R^2 = Pr^iO$
(27) $R^1 = R^3 = H$, $R^2 = R^4 = OMe$
(28) R^1 = morpholino, $R^2 = R^3 = R^4 = H$
(29) R^1 = morpholino, $R^2 = R^4 = H$, $R^3 = OMe$
(30) $R^1 = R^4 = H$, R^2 = morpholino, $R^3 = OMe$
(31) $R^1 = R^4 = H$, R^3 = morpholino, $R^2 = OMe$

identified by g.l.c. and n.m.r. spectroscopy. Low yields and mixed products render the unconjugated dienes unattractive and attention was turned to conjugation of the dienes by other methods before complexation, which is known to occur without rearrangement under conditions where the temperatures and the times of reaction are appropriately controlled. The 1-NR_2 series can usually be conjugated thermally.[5] Catalytic equilibration of 1-methoxycyclohexa-1,4-diene with the 1,3-diene



(8) (23) (24) (27)

SCHEME 1

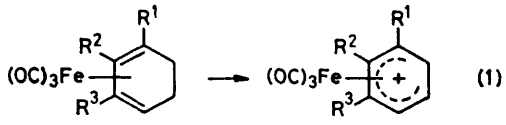
(*ca.* 75%) using potassium in liquid ammonia yields[8] only the 1-OMe conjugated isomer. Other conjugation catalysts which can be used include Wilkinson's catalyst[6] or dichloromaleic anhydride.[9] Frequently only about 70—80% of the conjugated isomer is present in the induced equilibrium,[10] but the complexation product formed under mild conditions corresponds to the same reactive conjugated isomer present.

The unusual difficulty encountered in conjugating the amine (10), as compared to (9), was also encountered with other '*meta*'-substituted dienes, and (7), for example, required potassium t-butoxide in dimethyl sulphoxide or potassium amide in liquid ammonia to produce about 70% of the conjugated isomer (16) in the product.

By this process of pre-conjugation followed by complexation, the dienes (7) and (8) gave the desired complexes (18) and (19) respectively as sole products, contrasting with the direct complexation of the unconjugated dienes under usual conditions[11] to give (18) and (19), together with (23) and (24), separable by chromatography (silica gel–petrol). Likewise the diene (11), when treated directly with $Fe(CO)_5$, gave a mixture consisting of (20) together with the monoalkoxy complexes (23)—(26) again separable by chromatography. The diene (12), by direct complexation, gave rise to the complexes (21) and (22) (not separated) as well as (24) and (26). The yields shown in the Table indicate the poor nature of the direct complexation approach where non-conjugated 1,3- or 1,4-dialkoxy-1,4-dienes are used.

The complex (28) is best prepared in 65—80% yields by irradiation of the diene for 2 h in pentane in the presence of $Fe(CO)_5$. The diene (13) similarly produced (29) (54%) as rather unstable crystals. Attempted complexation of the non-conjugated diene (10) was unsuccessful, but the mixture containing about 40% of the conjugated isomers (14) and (15) gave two complexes separable by solubility in hexane. The less soluble was identified by spectroscopy as (31) and the more soluble as (30). The ratio was 1.2 : 1 which may represent relative concentrations of dienes in the mixture. The spectra agree with observations on the linear and cross-conjugated morpholino-complexes derived from isophorone.[12]

Neutral complexes such as (23) or (24) lead in two ways to cations, those still containing OMe (32, R^1 or R^2 or R^3 = OMe) by hydride removal [equation (1)], or those



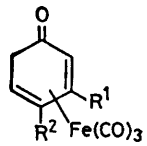
(1)

(32)

lacking OMe by the action of sulphuric acid. Only the 2-OMe cation can be prepared in good yields by hydride removal from the 2-OMe complex;[13] the 1-OMe cation is formed as an intermediate from the 1-OMe complex but is unstable to water during isolation and yields the cyclohexadienone complex of type (33).[13] The desirable

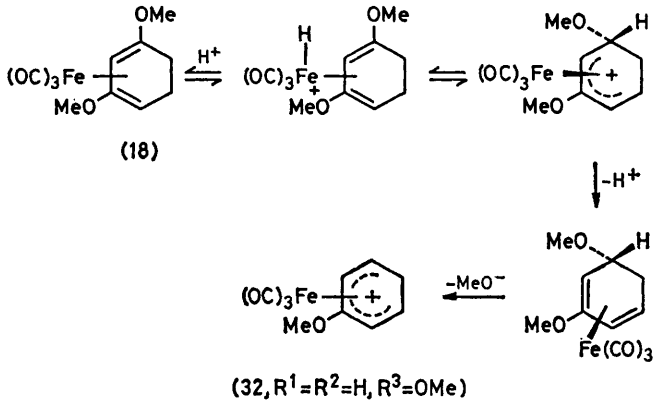
3-OMe cation (32, R^1, R^2 = H, R^3 = OMe) has hitherto been available only as a minor side-product.[14]

Reaction of sulphuric acid with (18) gave an 80% yield of (32, R^1 = R^2 = H, R^3 = OMe) isolated as the



(33) R^1 = R^2 = H
(34) R^1 = H, R^2 = D
(35) R^1 = OMe, R^2 = H
(36) R^1 = OPr^i, R^2 = H
(37) R^1 = H, R^2 = OMe
(38) R^1 = H, R^2 = OPr^i

PF_6 salt but contaminated (5—10%) with the 2-OMe isomer (32, R^1 = R^3 = H, R^2 = OMe). Use of trifluoroacetic acid at 0 °C gave the desired 3-OMe salt only. In conjunction with the ready preparation of (18) from the



SCHEME 2

conjugated diene this salt now becomes readily available. A postulated mechanism is shown in Scheme 2.

Previous studies of the product from the use of D_2SO_4[4] support the view that the first irreversible addition of H^+ or D^+ to carbon in this series is to a terminus of the η-4 system, in this case at the end bearing OMe.

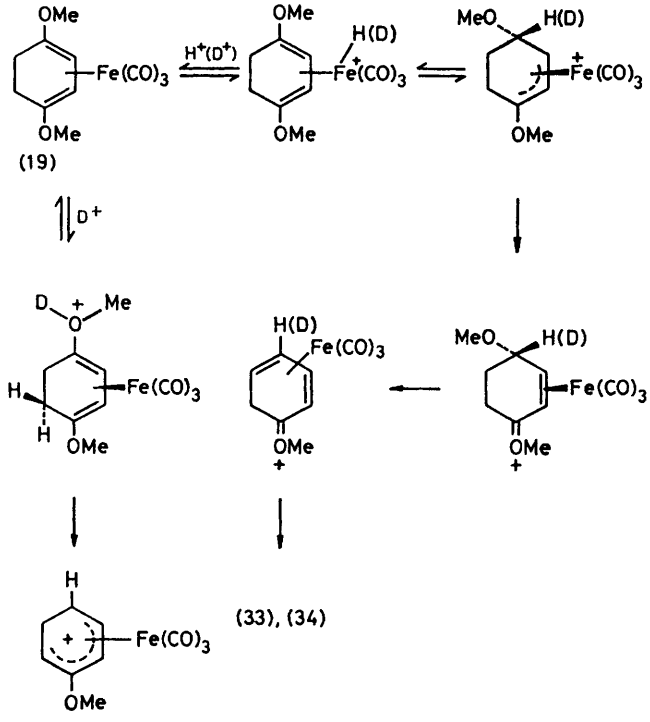
The 1,4-substituted complexes (19) or (20) gave a 70—80% yield of (33) with sulphuric acid, together with a small proportion (2—10%) of a 2-alkoxy cation salt. Using D_2SO_4 (97% D; 30 mol. equiv.) the ketone contained deuterium (60%), and the salt contained none. The ^1H n.m.r. spectrum indicated that deuterium was in the position shown in (34). The discrepancy between the extent of deuterium incorporation into the acid and into (34) can be attributed to high kinetic isotope effects in two successive steps. Use of D_2SO_4 containing 90% D led to a decrease in incorporation into the ketone to 30%. A large effect has been observed [15] with a related system. The steps probably consist of addition to $Fe(CO)_3$ (equilibrium) and then transfer of H^+ or D^+ to the terminus of the complexed carbon system. It was shown that use of D_2O in work-up had no effect on incorporation, and the C-4 proton of (33) did not exchange with D_2SO_4.

The Scheme 3 shows the possible courses of reaction, the usual nature being due to involvement of the p-electrons of OR at an intermediate stage. This overall sequence is probably the best experimental procedure to make the dienone (33).

The minor but significant proportion of the 2-OMe cation in the product is puzzling because of lack of incorporation into it of D. By the mechanism already discussed, incorporation should occur at the position originally occupied by the OMe lost. If it is not, then the formation of the ' allylic ' OMe required for loss must be by H transfer from elsewhere in the molecule. A possible mechanism, being explored, is by ' *meta* ' migration as shown, which would generate the required intermediate (Scheme 3).

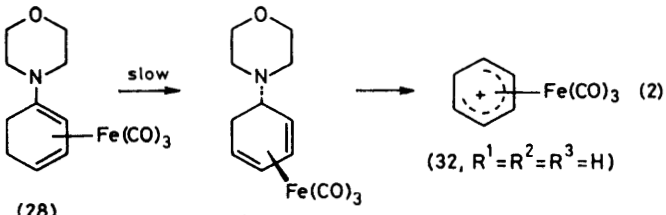
The morpholino-complexes underwent protonation with sulphuric acid, the salts being isolable as crystalline PF_6 derivatives.[16] No demethoxylation occurred using the complexes (29)—(31). Reaction of (28) for a prolonged period (20 h) gave a 34% yield of (32, R^1 = R^2 = R^3 = H), which contrasts with the rapid conversion of the presumed intermediate (39) into the same salt [equation (2)]. The conclusion is that protonation of the nitrogen of (28) converts this base into the cation, with resultant inhibition of further addition of a proton to C-1 carrying the cationic nitrogen, and therefore of conversion into (32, R^1 = R^2 = R^3 = H).

Because of the potential usefulness of the functionalised



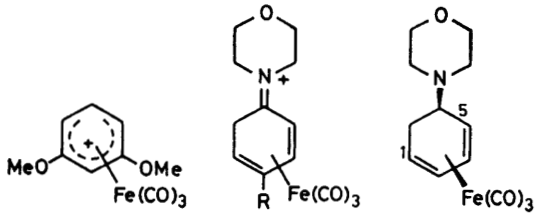
SCHEME 3

products, the reactions of characteristic disubstituted complexes with trityl fluoroborate were explored. The 1,3-dimethoxy complex is of particular interest, since in the monomethoxy series a 1-OMe directs abstraction



(28) (39)

mainly to the 5-position, and a 2-OMe (equivalent here to the 3-OMe) into the 4-position. These effects are here in competition. A mixture of salts resulted, in which the 1-OMe salt was converted by hot water [13] into tricarbonyl-3-methoxycyclohexa-2,4-dienoneiron (35) separable from (40) because of its very weakly basic nature. The ratio of (35) to (40) is about 1 : 1 indicating equal rate of hydride removal from the two possible positions. Nevertheless, because of the ease of separation, the reaction has preparative value for either component. Also, the dienone (35) can be converted by borohydride into the alcohol and then by HBF_4 into the 3-methoxy cation salt as an alternative preparative sequence. The symmetrical nature of (40) leads to a uniform product



(40) (41) (42)

when it is treated with malonate ion, and the salt is equivalent to a dihydroresorcinol with a cation in the 4-position.

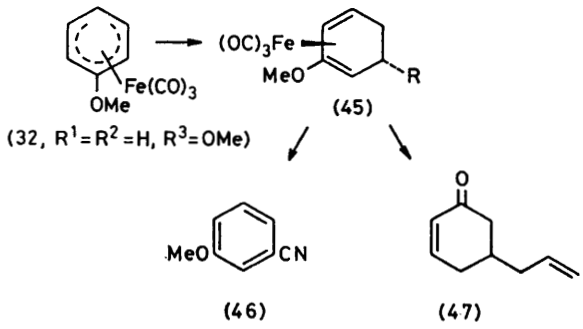
Hydride extraction from (19) has been reported,[17] yielding the dienone (37) after aqueous work-up. To see whether use could be made of substituent specificities involving the ether groups, the complex (20) was examined, but the products were (37) and (38) in about equal ratios, separable by chromatography.

A rather unexpected feature is the fact that the bulky trityl group is not directed predominantly to the position adjacent to the smaller OMe, since competition between Me and $CHMe_2$, in the α-terpinene complex, leads to abstraction only adjacent to Me.[18] There must be here a balance of steric and electronic effects, the ability of $OCHMe_2$ to stabilise a developing cation being greater than that of OMe.

The effect of p-electrons on the nitrogen in the morpholino-complexes (28) and (29) is clearly shown by the sole extraction of hydride from the 5-position to give the stable quaternary iminium salt (41, R = H or OMe). Reaction of (30) and (31) resulted only in decomposition.

Attempted hydrolysis of (41, R = H) to the dienone or reaction with a number of nucleophiles resulted only in production of the aryl morpholine by deprotonation and loss of $Fe(CO)_3$. However, borohydride at −40 °C gave what seems to be the unstable β-morpholino complex (42) by comparison of its spectra with the α-isomer obtained by reaction of morpholine with the cation. The lower stability of (42) may be due to steric crowding compared with the α-complex.

(43) (44)



(45) (46) (47)

The cation (32, $R^1 = R^2 = H$, R^3 = OMe) has at least two synthetic equivalents (43) and (44), according to the treatment accorded to the product of reaction with a nucleophile. Removal of the complexing group with dehydrogenation leads to the former, and removal of the complexing group with hydrolysis of the enol-ether to the latter. The symmetrical nature of (32, $R^1 = R^2 = H$, R^3 = OMe) makes the α-stereospecificity of nucleophilic attack irrelevant here, but it is worth noting that any further substituent on this cation will render it resolvable, with formation of a new asymmetric centre in the C–C bond formation. Reaction of (32, $R^1 = R^2 = H$, R^3 = OMe) with allyltrimethylsilane [19] gives (45, R = $CH_2CH{=}CH_2$) which on conversion into (47) completes the equivalency represented by structure (44). Similarly conversion of (45, R = CN) into *m*-methoxybenzonitrile implies the synthetic equivalent (43).

It is hardly necessary to point out the potential value of what is equivalent to a direct alkylation process *meta*- to OMe, with the ease which would be associated in classical organic chemistry with a reactive halide.

Dienones of type (33), if submitted to nucleophilic reactions on carbonyl, followed by removal of the complexing group, are equivalent to aryl cations with the charge on the position occupied by the carbonyl. Reagents utilisable include amines [20] and metal alkyls.[21]

EXPERIMENTAL

Distillations were carried out using a kugelrohr bulb-to-bulb distillation apparatus. I.r. spectra were measured for

carbon tetrachloride solutions unless otherwise stated, using a Perkin-Elmer 257 grating spectrophotometer. U.v. spectra were recorded for hexane solutions using a Pye–Unicam SP 800 spectrophotometer. ^{1}H N.m.r. spectra were measured on a Varian HA-100 spectrometer and ^{13}C n.m.r. spectra on a Jeol FT 60 spectrometer using Me_4Si as internal standard. Mass spectra were measured on an A.E.I. MS 902 mass spectrometer. Solvents used were reagent grade, ether referring to diethyl ether and petroleum spirit implying the 60—80 °C boiling fraction.

Preparation of Complexes.—Tricarbonyl-1,3-dimethoxycyclohexa-1,3-dieneiron (18). A solution of 1,5-dimethoxycyclohexa-1,4-diene (7) (20 g, 0.14 mol) in dimethyl sulphoxide (200 ml; dried with 3 A molecular sieve) containing potassium t-butoxide (16 g, 0.14 mol) was stirred during 1 h at an oil bath temperature of 65—75 °C. Water (200 ml) was added to the cooled solution and the mixture extracted with petroleum spirit in the usual way. The organic phase was washed with dilute sodium hydrogen carbonate solution and dried (K_2CO_3). Evaporation left a colourless oil (18 g) which was shown by ^{1}H n.m.r. spectroscopy to contain the starting diene and its conjugated isomer (16) in the ratio 1 : 3. The mixture could be stored for short periods in the presence of K_2CO_3 but was generally used immediately in the complexation reaction; (16) in the mixture showed ^{1}H n.m.r. resonances at δ ($CDCl_3$) 4.85br (1 H, s, 2-H), 4.30 (1 H, m, 4-H), 3.53 (6 H, s, OMe), and 2.20br (4 H, s, 5- and 6-H). A portion of the crude conjugated diene containing 6.5 g of (16) was dissolved in di-n-butyl ether (150 ml; freshly filtered through a column of activity I basic alumina) and pentacarbonyliron (18 ml) was added. The yellow solution was stirred in a nitrogen atmosphere at a bath temperature of 135—145 °C for 18 h. After cooling, the dark solution was filtered through a pad of dry Celite and the solvent removed at aspirator pressure (70 °C). The residue was chromatographed (SiO_2; hexane) and the resulting yellow oil distilled to give the *complex* (18), 5.73 g (44%), b.p. 90—100 °C (at 0.001 mmHg), which solidified on cooling, m.p. 40—41 °C; $\nu_{max.}$ 2 055 and 1 960 cm^{-1}; δ (CCl_4) 5.02 (1 H, d, *J* 2 Hz, 2-H), 3.56 (3 H, s, 3-OMe), 3.36 (3 H, s, 1-OMe), 3.12 (1 H, m, 4-H), 2.00 (1 H, m, 6-H), and 1.85—1.35 (3 H, m, 5- and 6-H); *m/e* 280 (M^+), 252, 224, and 196 (Found: C, 47.0; H, 4.3. $C_{11}H_{12}FeO_5$ requires C, 47.2; H, 4.3%).

Tricarbonyl-1,4-dimethoxycyclohexa-1,3-dieneiron [17] (19). The complex (19) was prepared from the crude mixture (18 g) of (8) and (17) [obtained [6] by Rh-catalysed isomerisation of (8)] in a manner similar to that just described; yield, 48%; $\nu_{max.}$ 2 055 and 1 960 cm^{-1}; δ (CCl_4) 5.02 (2 H, s, 2- and 3-H), 3.40 (6 H, s, OMe), and 2.35—1.70 (4 H, m, 5- and 6-H); *m/e* 280 (M^+), 252, 224, and 196.

Tricarbonyl-1-isopropoxy-4-methoxycyclohexa-1,3-dieneiron (20). Complex (20) was prepared by the conventional [11] method employing the diene (11) (10 g). Chromatography (t.l.c. grade SiO_2; hexane) gave three distinct bands. The first two contained products of de-alkoxylation (see Table) while the third (slowest) contained only complex (20) (25.7%); $\nu_{max.}$ 2 050 and 1 955 cm^{-1}; δ (CCl_4) 4.90 (2 H, s, 2- and 3-H), 4.00 (1 H, sept., *J* 7 Hz, OCH), 3.40 (3 H, s, OMe), 2.35—1.70 (4 H, m, 5-, 6-H), and 1.25 (6 H, d, *J* 7 Hz, Me); *m/e* 308 (M^+), 280, 252, 250, and 222.

Tricarbonyl-1-morpholinocyclohexa-1,3-dieneiron (28). This complex was prepared by irradiation (medium-pressure Hg lamp) of 1-morpholinocyclohexa-1,3-diene (3.22 g) in petroleum spirit (1 500 ml) containing pentacarbonyliron (3.8 g) during 2 h. Filtration through Celite followed by evaporation gave the crude *morpholino derivative* (28) as yellow-orange crystals, which readily crystallised from hexane (87%), m.p. 97—98 °C, $\nu_{max.}$ 2 028 and 1 960 cm^{-1}; δ (CCl_4) 5.27 (1 H, d, *J* 4 Hz, 2-H), 5.04 (1 H, dd, *J* 4 and 4 Hz, 3-H), 3.73 (4 H, t, *J* 5 Hz, morpholino), 2.94 (3 H, m, 4-H, morpholino), 2.56 (2 H, m, morpholino), 2.30—1.95 (2 H, m, 5- and 6-H), and 1.85—1.50 (2 H, m, 5-, 6-H); *m/e* 305 (M^+), 277, 249, 247, and 219 (Found: C, 51.3; H, 5.2; N, 4.6. $C_{13}H_{15}FeNO_4$ requires C, 51.2; H, 5.0; N, 4.6%).

Tricarbonyl-4-methoxy-1-morpholinocyclohexa-1,3-dieneiron (29). Complex (29) was prepared (54%) by the same method as just described from the diene (13) (2.15 g), m.p. 83—84 °C; $\nu_{max.}$ 2 025 and 1 960 cm^{-1}; δ (CCl_4) 5.06 (2 H, s, 2- and 3-H), 3.73 (4 H, t, *J* 5 Hz, morpholino), 3.45 (3 H, s, OMe), 2.95—2.30 (4 H, m, morpholino), and 2.26—1.60 (4 H, m, 5- and 6-H); *m/e* 335 (M^+), 307, 279, 277, and 249. This compound was rather unstable even when stored under nitrogen at low temperature (−20 °C).

Tricarbonyl-3-methoxy-1-morpholinocyclohexa-1,3-dieneiron (31) *and tricarbonyl-4-methoxy-2-morpholinocyclohexa-1,3-dieneiron* (30). Treatment of a mixture (4 g) of the conjugated isomers (14) and (15) derived from the diene (10) (containing 40% of conjugated material) with pentacarbonyliron as already described gave initially a red oil which was chromatographed (SiO_2; benzene–ethyl acetate, 1 : 1) to give a yellow oil (31%). Crystallisation from hexane gave yellow crystals identified as (31), m.p. 94—96 °C (decomp.); $\nu_{max.}$ 2 022 and 1 955 cm^{-1}; $\lambda_{max.}$ 209, 260 (w), and 302 (w) nm; δ (CCl_4) 5.36br (1 H, s, 2-H), 3.75 (4 H, t, *J* 5 Hz, morpholino), 3.63 (3 H, s, OMe), 3.33 (1 H, d, *J* 2 Hz, 4-H), 2.93—2.50 (4 H, m, morpholino), and 1.86—1.66 (4 H, m, 5- and 6-H); *m/e* 335 (M^+), 307, 279, 277, and 249. The mother liquors obtained from the foregoing procedure were concentrated to leave an orange oil which solidified when kept for a long time at −20 °C, m.p. 50—56 °C. This oil was shown to be complex (30), $\nu_{max.}$ 2 030 and 1 950 cm^{-1}; $\lambda_{max.}$ 212 and 307 nm; δ (CCl_4) 4.93 (1 H, d, *J* 2 Hz, 3-H), 3.80 (4 H, t, *J* 5 Hz, morpholino), 3.45 (3 H, s, OMe), 3.12 (1 H, d, *J* 2 Hz, 1-H), 2.83 (4 H, t, *J* 5 Hz, morpholino), 2.10 (1 H, m, 5-H), and 2.00—1.50 (3 H, m, 5- and 6-H); *m/e* 335 (M^+), 307, 279, 277, and 249.

Reactions of the Complexes with Acid.—Tricarbonyl-1,3-dimethoxycyclohexa-1,3-dieneiron (18). Complex (18) (5 g) was stirred in trifluoroacetic acid (10 ml) at 0 °C for 1 h and then at 10 °C for 10 min. The mixture was cooled to −50 °C and an ice-cold solution of ammonium hexafluorophosphate (5 g) in water (10 ml) was added. After the mixture had reached ambient temperature, the precipitated yellow salt was filtered off, washed with cold water, and air-dried. The solid was purified by precipitation (acetone–ether; acetonitrile should not be used) to give tricarbonyl-3-methoxycyclohexadienyliumiron hexafluorophosphate (32, $R^1 = R^2 = H$, $R^3 = OMe$), 4.9 g (70%); $\nu_{max.}$ (CH_2Cl_2) 2 110 and 2 060 cm^{-1}; δ_H (CD_3COCD_3) 6.36 (2 H, d, *J* 6 Hz, 2- and 4-H), 4.28 (3 H, s, OMe), 4.20 (2 H, t, *J* 6 Hz, 1- and 5-H), 3.02 (1 H, m, 6-H); and 2.04 (1 H, d, *J* 15 Hz, 6-H); δ (^{13}C) (CF_3CO_2H) 202.97 (CO), 144.02 (C-3), 89.96 (C-2 and -4), 59.74 (OMe), 56.23 (C-1 and -5), and 25.97 (C-6) p.p.m. (Found: C, 30.6; H, 2.4; $C_{10}H_9F_6FeO_4P$ requires C, 30.5; H, 2.3%).

Tricarbonyl-1,4-dimethoxycyclohexa-1,3-dieneiron (19) *and tricarbonyl-1-isopropoxy-4-methoxycyclohexa-1,3-dieneiron* (20). Complexes (19) or (20) (1.5 g) and sulphuric acid [4] gave the dienone (33) (80%), identified by comparison of its

spectral data with those of the known compound,[13] and a small amount of the 2-alkoxy salts (32, $R^1 = R^3 = H$, R^2 = OMe or Pr^{i}O) (2—10%). Use of D_2SO_4 (97% D) gave the dienone (34), the extent of deuteriation being assessed by integration of the ^1H n.m.r. resonance at δ 5.72 and by the ratio of the intensities of the molecular ions in the mass spectrum [*m/e* 234 (M^+) and 235 ($M^+ + 1$)] after allowing for natural-abundance contributions.

Hydride Abstraction from the Complexes.—Using the standard procedure [13] tricarbonyl-1,3-dimethoxycyclohexa-1,3-dieneiron (18) (5 g) gave a mixture of salts (95%) which was treated with water (80 °C; 1 h) to yield after extraction with ether, tricarbonyl-3-methoxycyclohexa-2,4-dien-1-one-iron (35) (28%); $\nu_{max.}$ 2 050, 1 970, and 1 665 cm^{-1}; δ (CCl_4) 5.50 (1 H, dd, *J* 6, 2 Hz, 4-H), 3.76 (3 H, s, OMe), 3.56 (1 H, d, *J* 2 Hz, 2-H), 2.80 (1 H, m, 5-H), and 2.20 (2 H, m, 6-H); *m/e* 264 (M^+), 236, 208, and 180. Addition of ammonium hexafluorophosphate (10% aq. solution) to the aqueous phase caused a yellow solid to precipitate. The solid was washed with water and air-dried. Recrystallisation (acetone–ether) gave *tricarbonyl-2,4-dimethoxycyclohexadienyliumiron hexafluorophosphate* (40) (37%); $\nu_{max.}$ (MeCN) 2 110 and 2 060 cm^{-1}; δ_H (CD_3COCD_3) 7.18 (1 H, s, 3-H), 4.18 (2 H, d, *J* 3 Hz, 1- and 5-H), 3.92 (6 H, s, OMe), 3.16 (1 H, m, 6-H), and 2.28 (1 H, m, 6-H); δ (^{13}C) (CD_3CN) 147.36 (C-2 and -4), 66.79 (C-3), 56.91 (OMe), 42.62 (C-1 and -5), and 27.28 (C-6) p.p.m. (Found: C, 40.0; H, 2.6. $C_{11}H_{11}F_6FeO_5P$ requires C, C, 31.2; H, 2.6%).

Sodium borohydride (0.2 g) was added in one portion to a stirred solution of the dienone (35) (1.4 g) in dry 1,2-dimethoxyethane (15 ml) at 0 °C. The mixture was stirred at 4 °C during 12 h and then poured into water. Extraction with ether followed by usual work-up gave a dark oil which was dissolved in propionic anhydride (3 ml) and then treated with aqueous HPF_6 (2 ml; 65%) at 0 °C. This mixture was stirred for a further 15 min and then diluted with ether (100 ml). Filtration and washing with ether left a pale-yellow solid which was purified (acetone–ether) and shown by comparison of its ^1H n.m.r. spectrum with a known sample to be (32, $R^1 = R^2 = H$, R^3 = OMe); 0.8 g (39%).

Tricarbonyl-1-isopropoxy-4-methoxycyclohexa-1,3-dieneiron (20) (1.5 g), using the standard procedure,[13] gave a mixture of salts which were converted (H_2O; 50 °C; 1 h) into the ketones. Chromatography (SiO_2; hexane–ether, 1 : 3) gave two bands identified (faster band) as tricarbonyl-4-isopropoxycyclohexa-2,4-dien-1-oneiron (38) (54%), m.p. 110—112 °C; $\nu_{max.}$ 2 050, 1 960, and 1 670 cm^{-1}; δ (CCl_4) 5.50 (1 H, dd, *J* 7 and 3 Hz, 3-H), 4.33 (1 H, sept., *J* 7 Hz, OCH), 3.43 (1 H, q, *J* 3 Hz, 5-H), 2.76 (1 H, d, *J* 7 Hz, 2-H), 2.25 (2 H, m, 6-H), 1.33 and 1.46 (6 H, two overlapping d, *J* 7 Hz, Me); *m/e* 292 (M^+), 264, 236, and 208; the second (slower) band was identified as tricarbonyl-4-methoxycyclohexa-2,4-dien-1-oneiron (37) (58%), m.p. 104—105 °C; $\nu_{max.}$ 2 050, 1 960, and 1 670 cm^{-1}; δ (CCl_4) 5.56 (1 H, dd, *J* 7 and 3 Hz, 3-H), 3.75 (3 H, s, OMe), 3.46 (1 H, m, 5-H), 2.75 (1 H, d, *J* 7 Hz, 2-H), and 2.23 (2 H, m, 6-H); *m/e* 264 (M^+), 236, 208, and 180.

Tricarbonyl-1-morpholinocyclohexa-1,3-dieneiron (28) (3.0 g) gave *tricarbonyl-5-(morpholin-1-ylidenium)cyclohexa-1,3-dieneiron hexafluorophosphate* (41, R = H) in 95% yield; $\nu_{max.}$ (Nujol), 2 070, 2 020, 1 990, and 1 590 cm^{-1}; δ_H (CD_3COCD_3) 6.60 (1 H, dt, *J* 5 and 1 Hz, 3-H), 6.24 (1 H, t, *J* 5 Hz, 2-H), 3.96 (4 H, t, *J* 5 Hz, morph.), 3.90—3.42 (7 H, m, 1-, 4-, 6-H, and morph.), and 2.84 (1 H, d, *J* 17 Hz, 6-H) (Found: C, 35.1; H, 3.4; N, 2.9. $C_{13}H_{14}F_6FeNO_4P$ requires C, 34.8; H, 3.1; N, 3.1%).

Sodium Borohydride Reduction of the Iminium Salt (41, R = H). Sodium borohydride (0.03 g) was added in one portion to a stirred solution of the salt (41, R = H) (0.33 g) in dry dimethoxyethane (7 ml) at −40 °C under nitrogen. After 5 min the cooling bath was removed and the mixture allowed to reach *ca.* 0 °C before dilution with ether. The solution was then partitioned between ether and cold water in the usual way. The organic phase was dried and evaporated to yield a pale yellow oil which was dissolved in benzene–ethyl acetate (1 : 1) and quickly filtered through a short column of neutral alumina. Evaporation left an unstable yellow oil (0.14 g, 63%), the spectral information of which suggested it to be (42); $\nu_{max.}$ 2 040 and 1 975 cm^{-1}; δ (CCl_4) 5.20 (2 H, m, 2- and 3-H), 3.68 (4 H, t, *J* 5 Hz, morpholino), 3.10 (2 H, m, 1- and 4-H), 2.40 (4 H, m, morpholino), 2.18 (1 H, m 5-H), and 1.88—1.32 (2 H, m, 6-H); *m/e* 305 (M^+).

Conversion of the Dimethoxy-compound (27) *into* (23) *and* (24).—Tricarbonyl-2-methoxycyclohexadienyliumiron tetrafluoroborate (32, $R^1 = R^3 = H$, R^2 = OMe) was left in methanol in the presence of anhydrous potassium carbonate for 2 days. Most of the methanol was removed under reduced pressure, water was added, and the neutral product extracted with ether and washed with water. This product (500 mg) was treated with pentacarbonyliron (1 g) in refluxing di-n-butyl ether for 6 h. Bulb-to-bulb distillation of the gummy product at 0.1 mmHg pressure gave an oil (160 mg) shown by g.l.c. and by n.m.r. measurements [13] to be a *ca.* 1 : 1 mixture of the 1-OMe (23) and the 2-OMe (24) derivative of tricarbonylcyclohexa-1,3-dieneiron.

Reactions of the Cations (40) *and* (32, $R^1 = R^2 = H$, R^3 = OMe) *with Nucleophiles*.—(a) Tricarbonyl-2,4-dimethoxycyclohexadienyliumiron hexafluorophosphate (40) (0.324 g) was treated with diethyl sodiomalonate in the usual manner [22] to give *tricarbonyl-6-(bisethoxycarbonyl)-methyl-1,3-dimethoxycyclohexa-1,3-dieneiron*, m.p. 51—53 °C (from pentane) (69%); $\nu_{max.}$ 2 055, 1 975, 1 750, and 1 730 cm^{-1}; δ (CCl_4) 5.20 (1 H, d, *J* 2 Hz, 2-H), 4.00 (4 H, q, *J* 7 Hz, CO_2CH_2Me), 3.60 (3 H, s, 3-OMe), 3.34 (3 H, s, 1-OMe), 3.10 (2 H, m, 4-H and EtO_2CCHCO_2Et), 2.10 (1 H, m, 6-H), 1.72 (1 H, m, 5-H), 1.26 (6 H, t, *J* 7 Hz, CO_2CH_2Me), and 0.90 (1 H, m, 5-H); *m/e* 438 (M^+), 410, 382, and 354 (Found: C, 49.65; H, 5.0. $C_{19}H_{22}FeO_9$ requires C, 49.3, H, 5.1%).

(b) To a stirred, ice-cooled solution of the cation (32, $R^1 = R^2 = H$, R^3 = OMe) (2.0 g) in acetone (20 ml) was added dropwise a cold saturated aqueous solution of sodium cyanide (10% excess). The resulting mixture was stirred for a further 10 min and evaporated, and the residue taken up into ether. Usual work-up gave a yellow oil which was purified by chromatography on silica gel (benzene). Crystallisation from hexane gave tricarbonyl-6-cyano-2-methoxycyclohexa-1,3-dieneiron (45, R = CN) as a rather unstable yellow solid, m.p. 125—127 °C (decomp.) (74%); $\nu_{max.}$ 2 240, 2 045, and 1 975 cm^{-1}; δ (CCl_4) 5.20 (1 H, dd, *J* 6 and 2 Hz, 3-H), 3.64 (3 H, s, OMe), 3.38 (1 H, m, 1-H), 2.95 (1 H, m, 6-H), 2.80 (1 H, m, 4-H), and 2.14—1.80 (2 H, m, 5-H); *m/e* 274.9881 (M^+); $C_{11}H_9FeO_4N$ requires *M* 274.9881. Removal of metal from this complex (1.5 g) with trimethylamine *N*-oxide (5 g) (toluene; 110 °C; 2 h) followed by treatment of the crude (filtered) solution with 2,3-dichloro-4,5-dicyanobenzoquinone (10% excess; 110 °C; 1 h) gave after the usual work-up 3-methoxybenzonitrile (0.45 g, 62%); δ (CCl_4) 7.6—6.9 (4 H, m, ArH) and 3.84

(3 H, s, OMe), which was converted into *m*-anisic acid by alkaline hydrolysis, m.p. 108 °C (lit.,[23] 110 °C).

(c) Tricarbonyl-3-methoxycyclohexadienyliumiron hexafluorophosphate (32, $R^1 = R^2 = H$, $R^3 = OMe$) (2 g) was heated in dry refluxing dichloromethane (50 ml) containing allyltrimethylsilane (8 ml) during 20 h. Evaporation of solvent and excess of silane left a yellow oil which was chromatographed on silica gel (petrol–ether; 20 : 1) to give *tricarbonyl-2-methoxy-6-prop-2-enylcyclohexa-1,3-dieneiron* (45, R = $CH_2CH{=}CH_2$) as a yellow oil (1.13 g, 77%); $\nu_{max.}$ 2 050, 1 975, and 1 640 cm^{-1}; δ (CCl_4) 5.86—4.78 (3 H, m, $CH{=}CH_2$), 5.08 (1 H, dd, *J* 6 and 2 Hz, 3-H), 3.60 (3 H, s, OMe), 3.34 (1 H, m, 1-H), 2.56 (1 H, m, 4-H), 2.00 (3 H, m, $=CHCH_2$ and 6-H), 1.80 (1 H, m, 5-H), and 1.15 (1 H, m, 5-H); *m/e* 290 (M^+), 2.62, 234, 206, and 204 (Found: C, 53.6; H, 5.1. $C_{11}H_{14}FeO_4$ requires C, 53.8; H, 4.9%). This complex (0.82 g) was dissolved in acetone (20 ml) and stirred at ambient temperatures while ceric ammonium nitrate (5 g) was added in portions. After a further 15 min the solution was diluted with water (20 ml) and poured into ether containing acetic acid (10 ml). The mixture was shaken for 10 min and the organic phase separated off and dried. Evaporation left an oil which was filtered through a pad of silica gel and then distilled, b.p. 80 °C (at 2.5 mmHg) to give 5-prop-2-enylcyclohex-2-enone (47) as a colourless oil, 0.3 g (78%); $\nu_{max.}$ 1 685 cm^{-1}; δ (CCl_4) 6.9 (1 H, m, 3-H), 6.00—4.90 (4 H, m, $CH{=}CH_2$, 2-H), and 2.60—1.90 (7 H, m, 4-, 5-, 6-H, and $=CHCH_2$); *m/e* 136 (M^+), 95, 68, and 66.

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