

Organometallic Complexes in Synthesis. Part 9.¹ Tricarbonyliron Derivatives of Dihydroanistic Esters

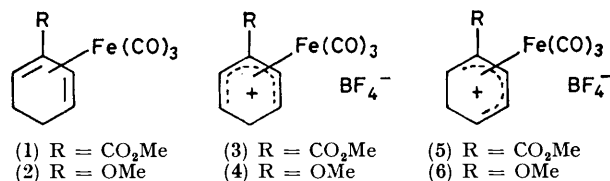
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Tricarbonyliron complexes of a number of dihydroanistic esters have been prepared and characterised, and their reactions with triphenylmethyl tetrafluoroborate studied. Only three of the complexes undergo hydride abstraction. The resulting dienyl complexes were found to react cleanly with dimethyl sodiomalonate in the expected manner.

PREVIOUS work from this laboratory described the preparation and some of the chemistry of several tricarbonyliron complexes of cyclohexadienecarboxylic esters, including a number of methyl-substituted derivatives.² We were subsequently interested in the preparation and characterisation of some tricarbonyliron derivatives of dihydroanistic esters, since these are of interest from the point of view of (a) the greater functionality present in the molecules, and (b) the structures of dienyl complexes derived by reaction with triphenylmethyl tetrafluoroborate. The latter subject is important since it is these types of dienyl complexes which are most likely to find application in organic synthesis.

In the monosubstituted series, hydride abstraction from tricarbonyl-(2-methoxycarbonylcyclohexa-1,3-diene)iron (1) results in tricarbonyl-(3-methoxycarbonylcyclohexadienyl)iron tetrafluoroborate (3) as the major product, the 2-substituted isomer (5) being the minor

product.^{1,2} On the other hand, the methoxy-substituted analogue (2) gives rise to tricarbonyl-(2-methoxycyclohexadienyl)iron tetrafluoroborate (6) as major, and



tricarbonyl-(3-methoxycyclohexadienyl)iron tetrafluoroborate (4) as minor products.^{3,4} A major factor in determining which dienyl complex is formed may be a thermodynamic one, and in consequence it is of interest to determine how these substituents interact in the dihydroanistic ester complexes and whether the hydride abstraction results are predictable on the basis of those for the mono-substituted compounds.

¹ Part 8, A. J. Birch, P. W. Westerman, and A. J. Pearson, *Austral. J. Chem.*, 1976, 29, 1671.

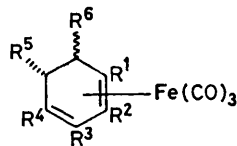
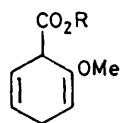
² A. J. Birch and D. H. Williamson, *J.C.S., Perkin I*, 1973, 1892.

³ R. E. Ireland, G. G. Brown, jun., R. H. Stanford, jun., and T. C. McKenzie, *J. Org. Chem.*, 1974, 39, 51.

⁴ A. J. Birch, P. E. Cross, J. Lewis, D. A. White, and S. B. Wild, *J. Chem. Soc. (A)*, 1968, 332.

RESULTS AND DISCUSSION

Preparation of Complexes.—2-Methoxycyclohexa-2,5-dienecarboxylic acid (7), prepared according to the literature procedure,⁵ was treated with dimethyl sulphate to give the corresponding ester (8). Reaction of this



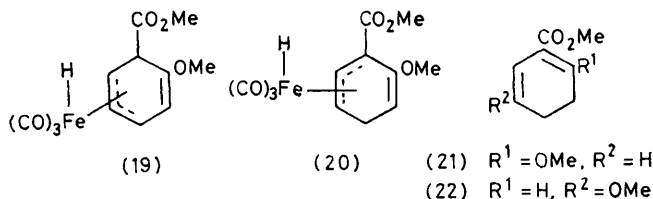
- (7) R = H (9) R¹ = OMe, R² = R³ = R⁴ = R⁵ = H, R⁶ = CO₂Me
 (8) R = Me (10) R¹ = R² = R³ = R⁴ = R⁵ = H, R⁶ = CO₂Me
 (11) R¹ = OMe, R² = CO₂Me, R³ = R⁴ = R⁵ = R⁶ = H
 (12) R¹ = R⁴ = R⁵ = R⁶ = H, R² = OMe, R³ = CO₂Me
 (13) R¹ = CO₂Me, R² = OMe, R³ = R⁴ = R⁵ = R⁶ = H
 (14) R¹ = OMe, R² = R⁴ = R⁵ = R⁶ = H, R³ = CO₂Me
 (15) R¹ = CO₂Me, R² = R⁴ = R⁵ = R⁶ = H, R³ = OMe
 (16) R¹ = R³ = R⁴ = R⁶ = H, R² = OMe, R⁵ = CN
 (17) R¹ = OMe, R² = R³ = R⁵ = R⁶ = H, R⁴ = CO₂Me
 (18) R¹ = OMe, R² = R³ = R⁵ = R⁶ = H, R⁴ = Me

compound with iron pentacarbonyl in the usual way produced a diene-Fe(CO)₃ complex which gave a single band on chromatography and was isolated as a yellow oil but which nevertheless contained two isomeric compounds as shown by the ¹H n.m.r. spectrum. Repeated recrystallisation from light petroleum at -78 °C and finally at -20 °C produced a pure sample of the major component which had spectral properties consistent with the structure (9). Thus, the OMe resonance at δ 3.42 showed this group to be on the terminal diene carbon atom (2-methoxy substituents resonate at δ ca. 3.6 and 1-methoxy substituents at δ ca. 3.4^{3,4,6}) and the signals at δ 2.90, 5.14, and 5.45 due to the diene protons 4-, 3-, and 2-H unambiguously define this structure.

Removal of solvent from the mother liquors gave a product the major component of which was the isomer of (9), which could not be obtained pure. From the ¹H n.m.r. spectrum of (9) and its isomer it was apparent that the isomer had the same substitution pattern as (9) and differed only in the stereochemistry at C-6. The n.m.r. spectral details are shown in Table 1, and we have assigned to the pure component isolated the structure (9) with an *exo*-CO₂Me group [occupying the opposite face of the diene to that occupied by Fe(CO)₃], the minor component being the *endo*-CO₂Me isomer. This conclusion is based on the observation that the CO₂Me

proton resonance of (9, *exo*-CO₂Me) is at higher field than that of (9, *endo*-CO₂Me), as is observed for *exo* and *endo* protons in other tricarbonyliron complexes.^{7,8} This behaviour is in contrast to that observed for the complexation of methyl cyclohexa-2,5-dienecarboxylate which has been reported to give the *endo* derivative (10, R⁶ = *endo*-CO₂Me) indicating that the ester unit directs the Fe(CO)₃ group to the same face.⁹ Birch and Williamson reported the formation of two complexes, tricarbonyl-(2-methoxycarbonylcyclohexa-1,3-diene)iron and tricarbonyl-(5-methoxycarbonylcyclohexa-1,3-diene)iron, the latter being the major isomer and of undefined stereochemistry.² We have repeated this work using the reaction conditions employed for the dihydroanisic esters, and the distilled complexes obtained did indeed correspond to the reported mixture, except the presence of a third minor compound was shown by the ¹H n.m.r. spectrum. This complex gave a singlet in the CO₂Me region which was 0.07 p.p.m. upfield from that corresponding to the major component. Since the olefinic region of the spectrum indicated the presence only of the aforementioned two isomers, we conclude that the third component is the diastereoisomer of (10) and is therefore the *exo*-CO₂Me complex. These observations support the conclusion that the lower-field signal corresponds to the *endo*-CO₂Me isomer and thereby show that the major product obtained from (8) is indeed the *exo*-CO₂Me complex. The reason for this difference in behaviour is not known at present.

The observation that the methoxycarbonyl group remains bonded to an *sp*³ hybridised carbon atom during reaction is consistent with a conjugation mechanism involving transfer of hydride anion to iron giving allyl-complex intermediates such as (19), which has a formal positive charge on the allyl ligand.¹⁰ This is clearly destabilised by the methoxycarbonyl group in the isomeric intermediate (20), which would be necessary



for the formation of complexes such as (11)–(13). Consequently, this pathway and these complexes are not observed in the preparation.

When the reduction of *o*-methoxybenzoic acid was carried out without acidification and isolation of (7), but followed by direct methylation in the presence of the lithium ethoxide produced during reduction, the ester isolated contained a major proportion of the

⁹ T. H. Whitesides, R. W. Slaven, and J. C. Calabrese, *Inorg. Chem.*, 1974, **13**, 1895.

¹⁰ H. Alper, P. C. Le Port, and S. Wolfe, *J. Amer. Chem. Soc.*, 1969, **91**, 7553; F. G. Cowherd and J. L. von Rosenberg, *ibid.*, p. 2157; W. T. Hendrix, F. G. Cowherd, and J. L. von Rosenberg, *Chem. Comm.*, 1968, 97; R. Pettit and G. F. Emerson, *Adv. Organometallic Chem.*, 1964, **1**, 1.

⁵ I. Alfaro, W. Ashton, L. D. McManus, R. C. Newstead, K. L. Rabone, N. A. J. Rogers, and (in part) W. Kernick, *Tetrahedron*, 1970, **26**, 201.

⁶ A. J. Birch, K. B. Chamberlain, M. A. Haas, and D. J. Thompson, *J. C. S. Perkin I*, 1973, 1882.

⁷ A. J. Pearson, *Austral. J. Chem.*, 1976, **29**, 1101.

⁸ A. L. Burrows, B. F. G. Johnson, J. Lewis, and D. G. Parker, *J. Organometallic Chem.*, 1977, **127**, C22.

conjugated diene (21). Treatment of this compound with pentacarbonyl iron produced a yellow oil which gave the major product (11) on crystallisation from light petroleum at -78°C . Again, the OMe resonance at δ 3.46 is consistent with this group being on the diene terminus (C-1), and the methoxycarbonyl singlet at δ 3.78 shows it to be on C-2, by comparison with the simple monosubstituted analogues.² The occurrence of a doublet at δ 5.57 (3-H), in the region associated with 2- and 3-H of a 1,3-diene complex,^{4,11} rules out the structure (12).

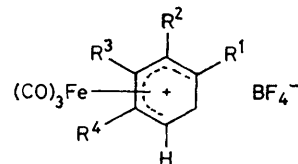
The mixture of *endo*- and *exo*-isomers (9) obtained above was refluxed in 10% methanolic sulphuric acid and gave the isomer (13), as expected from the results of isomerisation of the analogous monosubstituted complex.² This compound still contained a minor amount of (9, *exo*-CO₂Me), which could not be removed by chromatography, and we were unable to crystallise (13). Prolonged refluxing with methanolic sulphuric acid led to higher losses without increasing the proportion of the desired compound (13). The ¹H n.m.r. spectrum of this compound showed the methoxy singlet at δ 3.70 and the methoxycarbonyl resonance at δ 3.76, as expected (these assignments may be reversed, but this does not affect the structural implications). The ester carbonyl i.r. stretching frequencies for compounds (11) and (13) compare well with the unsubstituted ester analogues. Thus, it has been shown² that the i.r. band for a 1-CO₂Me substituent occurs at 1698 cm⁻¹, that for a 2-CO₂Me substituent being at 1717 cm⁻¹. Complexes (11) and (13) give bands at 1720 and 1700 cm⁻¹, respectively, again consistent with the assigned substitution patterns (Table 2).

Reaction of the ester (22)¹² with nonacarbonyliron in refluxing diethyl ether gave the expected complex (14) which could be purified by crystallisation from light petroleum, as above. Treatment of this compound with refluxing methanolic sulphuric acid produced the isomeric complex (15) in 78% yield, which was homogeneous on t.l.c., and appeared >95% pure from its ¹H n.m.r. spectrum, but which could not be induced to crystallise. The structures of (14) and (15) were again readily deduced from their n.m.r. and i.r. spectral data (Tables 1 and 2).

The corresponding *para*-disubstituted diene complex (23) cannot be produced *via* Birch reduction of *p*-anisic acid since this compound is known to be demethoxylated under metal-ammonia reducing conditions.¹³ Consequently, we treated tricarbonyl-(2-methoxycyclohexadienyl)iron hexafluorophosphate (6, PF₆⁻ salt) with aqueous sodium cyanide to produce exclusively the nitrile (16).⁴ Since this compound was quite unstable it was not purified, and the crude complex was subjected to acid methanolysis in the usual way² to give, after crystallisation from light petroleum, the ester complex (17), again easily identified from its n.m.r. and i.r. spectra.

¹¹ M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1959, 3753.

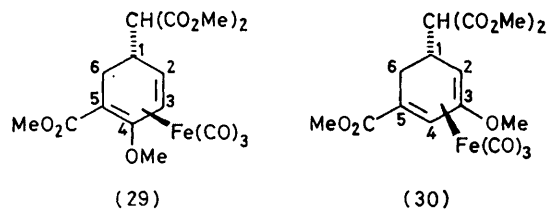
Reaction of Complexes with Triphenylmethyl Tetrafluoroborate.—Only three of the complexes were found to undergo hydride abstraction on treatment with trityl fluoroborate: (13)—(15). No dienyl complexes could be obtained from (9, *exo*-CO₂Me), (11), and (17) and unchanged starting material was recovered in each case. Compounds (13), (14), and (15) all lost hydride from the position remote from the terminal substituent, giving the dienyl complexes (23), (24), and (25), respectively.



- (23) R¹ = CO₂Me, R² = OMe, R³ = R⁴ = H
 (24) R¹ = OMe, R² = R⁴ = H, R³ = CO₂Me
 (25) R¹ = CO₂Me, R² = R⁴ = H, R³ = OMe
 (26) R¹ = R⁴ = H, R² = OMe, R³ = CO₂Me
 (27) R¹ = CO₂Me, R² = R³ = H, R⁴ = OMe
 (28) R¹ = Me, R² = R³ = H, R⁴ = OMe

These were identified from their ¹H n.m.r. spectra, by comparison with the appropriate monosubstituted compounds. Thus, (23) shows singlets at δ 3.73 and 4.10, typical of 2-OMe³ and 1-CO₂Me² dienyl substituents, respectively, whilst 3-H appears as a doublet at the characteristically low field of δ 7.0, 4-H as a triplet at δ 5.86, and 5-H as a triplet, owing to coupling with 4- and *endo*-6-H, at δ 4.53. The remaining spectral details for this compound, (24) and (25) are given in Table 3. The changes in chemical shift difference between *exo*- and *endo*-H probably reflect the influence of 1- or 3-CO₂Me substituents on the conformation of the molecule.

The lack of reactivity of complex (9, *exo*-CO₂Me) is readily rationalised in terms of steric hindrance by the methoxycarbonyl group, as is the case with analogous alkyl substituted complexes.⁷ However, we should have expected (11) and (17) to give rise to the cations (26) and (27), respectively, in which the substituents occupy positions which are stable in the mono-substituted compounds, *e.g.* (2) and (5). Prolonged treatment with trityl fluoroborate led only to extensive decomposition, but no salt formation. That this lack of reactivity is not due to steric hindrance by the methoxy-substituent



is adequately demonstrated by the ready hydride abstraction from (18), an analogue of (17), to give the salt (28). It would appear then that the stabilising

¹² M. E. C. Biffin, A. G. Moritz, and D. B. Paul, *Austral. J. Chem.*, 1972, **25**, 1329.

¹³ A. J. Birch, A. R. Murray, and H. Smith, *J. Chem. Soc.*, 1951, 1945.

TABLE 1

¹H N.m.r. spectral data for tricarbonyl(dihydroanisic ester)iron complexes; δ values for solutions in CDCl₃; Me₄Si internal reference; J values in Hz

| Compound | 2-H | 3-H | 4-H | 5-H | 6H | OMe | CO ₂ Me |
|--------------------------------------|------------------------------------|---------------------------------------|-----------------------------------|-------------|-----------|-------------------|--------------------|
| (9, <i>exo</i> -CO ₂ Me) | 5.45,d $J_{2,3}$ 6 | 5.14,t $J_{2,3} = J_{3,4} = 6$ | 2.90,m | 1.68—2.28,m | 3.3,m | 3.42 | 3.60 |
| (9, <i>endo</i> -CO ₂ Me) | 5.36,d $J_{2,3}$ 5 | 4.94,dd $J_{3,4}$ 6 $J_{2,3}$ 5 | 2.85,t $J_{3,4} = J_{4,5} = 6$ | | | 3.42 | 3.63 |
| (11) | | 5.57,d $J_{3,4}$ 7 | 3.0,m | 1.64—2.36 | 1.64—2.36 | 3.46 | 3.78 |
| (13) | | 5.05,d $J_{3,4}$ 7 | 2.9,m | 1.2—2.3 | 1.2—2.3 | 3.70 ^a | 3.76 ^a |
| (14) | 5.96,s(br) ^b | | 3.49 ^c | 1.6—2.5 | 1.6—2.5 | 3.49 | 3.79 |
| (15) | 5.70,d $J_{2,4}$ 2 ^d | | 3.55,m | 1.2—2.2 | 1.2—2.2 | 3.65 ^a | 3.68 ^a |
| (23) | 5.28,d $J_{2,3}$ 5 | 5.68,d $J_{2,3}$ 5 | | 1.4—2.5 | 1.4—2.5 | 3.44 | 3.60 |

^a Assignments may be reversed. ^b Long-range coupling of *ca.* 0.7 Hz resolvable. ^c Coincident with methoxy resonance (integral 4 H). ^d This coupling is characteristic of complexes having 2-MeO substituents.⁶

factors of the methoxy and methoxycarbonyl substituents are not additive, and their mode of interaction with each other and the complexed dienyl ligand are at present unknown.

TABLE 2

I.r. spectral data for tricarbonyl(dihydroanisic ester)iron complexes (CCl₄ solution)

| Compound | $\nu_{\text{Fe}(\text{CO})_3}/\text{cm}^{-1}$ | $\nu_{\text{C-O}}/\text{cm}^{-1}$ |
|-------------------------------------|---|-----------------------------------|
| (9, <i>exo</i> -CO ₂ Me) | 2 040, 1 960 | 1 725 |
| (11) (2-CO ₂ Me) | 2 050, 1 975 | 1 720 |
| (13) (1-CO ₂ Me) | 2 055, 1975 | 1 700 |
| (14) (2-CO ₂ Me) | 2 045, 1970 | 1 720 |
| (15) (1-CO ₂ Me) | 2 060, 1 980 | 1 702 |
| (23) (1-CO ₂ Me) | 2 055, 1 980 | 1 708 |

Predictably, the dienyl complexes obtained above reacted with nucleophiles at the unsubstituted terminus. Thus, the salts (23) and (25) reacted with dimethyl

Tricarbonyl-(1-methoxy-6-methoxycarbonylcyclohexa-1,3-diene)iron (9).—The acid (7)⁵ was methylated in the usual way with dimethyl sulphate in refluxing acetone, in the presence of excess of potassium carbonate, to give the ester (8) in 70% yield, δ 6.1 (2 H, m, vinyl H), 4.90 (1 H, t, vinyl H), 3.92 (3 H, s, CO₂Me), 3.74 (3 H, s, OMe), 3.9 (1 H, m, 1-H), and 3.0 (2 H, m, methylene). The crude compound (4.0 g) was treated with pentacarbonyliron (10 g) in refluxing dibutyl ether (50 ml) in the usual way^{3,6} and excess of solvent and pentacarbonyliron were removed at aspirator pressure. Excess of ester (8) was removed at *ca.* 80 °C and 0.05 mmHg and the residual complexes were chromatographed on silica. Minor products were eluted with benzene, and a major band was eluted with benzene-ethyl acetate (10 : 1) to give the complexes (9) (4.0 g, 55%) as a mixture of *endo*- and *exo*-CO₂Me isomers. This mixture was dissolved in light petroleum (150 ml) at room temperature and the solution was cooled to -78 °C. The

TABLE 3

¹H N.m.r. spectral data for dienyl-Fe(CO)₃ complexes; δ values; Me₄Si internal reference; J values in Hz

| Compound | Solvent | 2-H | 3-H | 4-H | 5-H | <i>endo</i> -6-H | <i>exo</i> -6-H | CO ₂ Me | OMe |
|----------|-----------------------------------|--------------|-----------------------|------------------------------------|---|---------------------------------------|-------------------------|--------------------|------|
| (24) | CD ₃ CN | | 7.0 d, $J_{3,4}$ 7 | 5.86 t, $J_{3,4} = J_{4,5} = 7$ | 4.53 t, $J_{4,5} = J_{5,6,endo} = 7$ | 3.14 dd, J_{gem} 11, $J_{5,6}$ 7 | 2.16 d, J_{gem} 11 | 4.10 | 3.73 |
| (25) | CF ₃ CO ₂ H | 4.90 s,br | | 7.76 d, $J_{4,5}$ 7 | 4.3 ^a m, | 3.4 dd, J_{gem} 15, $J_{5,6}$ 4 | 2.86 d, J_{gem} 15 | 4.18 | 4.02 |
| (26) | CF ₃ CO ₂ H | 7.62 s,br | | 7.06 d, $J_{4,5}$ 7 | 4.64 t, $J_{4,5} = J_{5,6,endo} = 7$ | 3.42 dd, J_{gem} 16, $J_{5,6}$ 7 | 1.98 d, J_{gem} 16 | 4.30 | 3.98 |

^a Partly obscured by CO₂Me.

sodiummalonate in tetrahydrofuran to give (29) and (30), respectively, again readily identified from their ¹H n.m.r. and i.r. spectra (Experimental section).

EXPERIMENTAL

M.p.s points were determined on a Reichert hot stage apparatus and are uncorrected. I.r. spectra were measured for solutions in carbon tetrachloride, unless otherwise stated, using a Perkin-Elmer 257 instrument, mass spectra with an A.E.I. MS9, and 100 MHz ¹H n.m.r. spectra with Varian HA 100 or JEOL Minimar spectrometers. The anisic acids, dimethyl malonate, pentacarbonyliron, and nonacarbonyliron were obtained from commercial sources. All chromatographic operations were conducted under a nitrogen atmosphere. Light petroleum refers to the fraction of b.p. 40—60 °C unless otherwise stated.

pale yellow solid was filtered off, using previously cooled apparatus, to give a compound which melted at room temperature. This was redissolved in light petroleum (70 ml), again cooled to -78 °C, and the solid thus obtained was finally recrystallised from light petroleum (b.p. 30—40 °C) by cooling to -20 °C, to give yellow crystals, m.p. 44—45 °C (1.0 g). Concentration of the combined washings did not allow any further isolation of crystalline material. The compound thus obtained was shown to be (9, *exo*-CO₂Me) by i.r. and n.m.r. spectroscopy and had *M* 308 (Found: C, 46.5; H, 4.1. C₁₂H₁₂FeO₆ requires C, 46.8; H, 3.9%). The compound obtained from the mother liquors was set aside for the preparation of complex (13).

Tricarbonyl-(1-methoxy-2-methoxycarbonylcyclohexa-1,3-diene)iron (11).—Removal of ammonia from the Birch reduction product of *o*-anisic acid, followed by refluxing the

alkaline material for 5 h in methanol with dimethyl sulphate and potassium carbonate afforded a crude ester in 50% yield, in which the major component was (21), formed by the metal alkoxide-catalysed conjugation of the cyclohexa-1,4-diene derivatives. Treatment of the crude ester (7.0 g) with pentacarbonyliron in the above manner gave a single major complex (5.0 g, 39%) on chromatography, shown to be almost pure (11) from its n.m.r. spectrum. An analytical sample was obtained by crystallisation from light petroleum as for complex (9) and gave *M* 308 (Found: C, 46.6; H, 4.1%), m.p. 64–66 °C. Spectral details are given in Tables 1 and 2.

Tricarbonyl-(2-methoxy-1-methoxycarbonylcyclohexa-1,3-diene)iron (13).—The mixture of *exo*- and *endo*-isomers of (9) (1.9 g) from the aforementioned crystallisation procedure was refluxed in 10% methanolic sulphuric acid (250 ml) under nitrogen for 24 h. The solution was poured into water (500 ml) and extracted with ether in the usual way to give the crude product (0.9 g, 47%). This was homogeneous on t.l.c. and attempts to crystallise the compound from light petroleum ether gave only a gum. ¹H N.m.r. spectroscopy showed the product to be (13) together with a small amount of unchanged (9). Spectral details are given in Tables 1 and 2. Prolonged refluxing gave rise to extensive decomposition without change in the proportion of residual (9).

Tricarbonyl-(1-methoxy-3-methoxycarbonylcyclohexa-1,3-diene)iron (14).—The ester (22) was prepared by reaction of the corresponding acid¹² with dimethyl sulphate in the usual way and gave n.m.r. resonances at δ 6.76 (1 H, m, vinyl H), 5.42 (1 H, s, vinyl H), 3.72 (3 H, s, CO₂Me), 3.62 (3 H, s, OMe), and 2.5–2.1 (4 H, m, CH₂). A stirred mixture of the crude ester (3.5 g) and nonacarbonyliron (8 g) in diethyl ether (100 ml) was refluxed for 4 h under nitrogen, the product filtered through Celite, and the solvent removed. Excess of ester (1.0 g, 29%) was removed at 70–80 °C and 0.05 mmHg, and the residual complexes were chromatographed on silica to give a single major compound, eluted with benzene. Two recrystallisations from light petroleum, at –78 and at –10 °C, gave 2.4 g (38%) of pure (14), m.p. 57.5–59 °C, *M* 308 (Found: C, 47.2; H, 4.0%). Further spectral details are in Tables 1 and 2.

Tricarbonyl-(3-methoxy-1-methoxycarbonylcyclohexa-1,3-diene)iron (15).—Complex (14) (900 mg) was treated with 10% methanolic sulphuric acid as above to give (15) (700 mg, 78%), which was homogeneous on t.l.c. and which could not be induced to crystallise from light petroleum. The ¹H n.m.r. spectrum showed no evidence of impurities and the compound gave *M* 308 (Found: C, 46.9; H, 3.8%).

Tricarbonyl-(1-methoxy-4-methoxycarbonylcyclohexa-1,3-diene)iron (17).—The nitrile complex (16)⁴ (980 mg) was treated with refluxing 10% methanolic sulphuric acid as above to give crude (17) (400 mg) which was recrystallised from light petroleum at –20 °C to give the pure complex (200 mg, 18%), m.p. 76–77 °C, *M* 308 (Found: C, 46.7; H, 4.2%).

Reaction of Complexes with Triphenylmethyl Tetrafluoroborate.—Triphenylmethyl tetrafluoroborate (530 mg) was dissolved in the minimum volume of dichloromethane and added to the dihydroanionic ester complex (500 mg) in a similar volume of dichloromethane. The solution was kept at room temperature for 30–40 min and sufficient 'wet' ether was added to cause complete precipitation of dienyl complexes (use of 'wet' ether removes any excess triphenylmethyl tetrafluoroborate by hydrolysis). The pro-

duct was filtered off under reduced pressure and washed with ether. Paramagnetic impurities resulting from decomposition were removed by dissolving the complex in acetonitrile, centrifuging, adding the clear supernatant liquid dropwise to stirred dry ether, and filtering as above. Any unchanged starting material was recovered by removing the ether from the washings, dissolving the product in light petroleum and filtering to remove triphenylmethanol (from 'wet' ether hydrolysis) which sometimes cochromatographed with the complexes, and finally purifying by preparative layer chromatography. The recovered diene complexes were identified by ¹H n.m.r. spectroscopy. The n.m.r. spectra of the salts obtained are given in Table 3.

Complexes (9, *exo*-CO₂Me), (11), and (17) gave only unchanged starting materials (60, 40, and 72%, respectively).

Complex (13) gave *tricarbonyl-(2-methoxy-1-methoxycarbonylcyclohexadienyl)iron tetrafluoroborate* (23) (73%), ν_{\max} (KBr) 2 120, 2 055, 1 970, and 1 710 cm^{–1} (Found: C, 37.0; H, 3.0%. C₁₂H₁₁BF₄FeO₆ requires C, 36.6; H, 2.8%).

Complex (14) gave *tricarbonyl-(1-methoxy-3-methoxycarbonylcyclohexadienyl)iron tetrafluoroborate* (24) (39%) which was hydrolysed very rapidly by atmospheric moisture, ν_{\max} (Nujol) 2 115, 2 080, 2 050, and 1 720 cm^{–1}. Unchanged (14) accounted for a further 40% of the starting material.

Complex (15) gave *tricarbonyl-(3-methoxy-1-methoxycarbonylcyclohexadienyl)iron tetrafluoroborate* (25) (32%) and unchanged (15) (50%). Prolonged treatment led to extensive decomposition of complexes, ν_{\max} (Nujol) 2 115, 2 065, 2 050, and 1 707 cm^{–1} (Found: C, 36.4; H, 3.2%).

Reaction of Dienyl Complexes with Dimethyl Sodiummalonate.—To a stirred suspension of the dienyl-Fe(CO)₃ salt (170 mg) in dry tetrahydrofuran (5 ml) at room temperature and under nitrogen was added a 10% molar excess of dimethyl sodiummalonate in tetrahydrofuran (previously prepared from sodium hydride and dimethylmalonate), using typical syringe techniques. When all the iron complex had dissolved the mixture was poured into water and the product extracted with light petroleum.

Complex (23) gave *tricarbonyl(dimethyl 4-methoxy-5-methoxycarbonylcyclohexa-2,4-dienylmalonate)iron* (29), obtained as pale yellow crystals from light petroleum (100 mg, 53%), m.p. 86–88 °C; ν_{\max} (CCl₄) 2 065, 1 990, 1 750, 1 738, and 1 707 (1-CO₂Me) cm^{–1}; δ (CDCl₃) 1.46 (1 H, dd, *J*_{gem} 14 Hz, *J*_{5,6} 2.5 Hz, *exo*-6-H), 2.46 (1 H, dd, *J*_{gem} 14 Hz, *J*_{5,6} 11 Hz, *endo*-6-H), 2.75 [1 H, m, 4-H (confirmed by spin decoupling: irradiation of 3-H leads to appropriate change)], 2.9 (1 H, m, 5-H), 3.07 (1 H, d, *J* 8 Hz, malonyl CH), 3.68 (6 H, s), 3.73 (3 H, s), and 3.77 (3 H, s) (3 × CO₂Me and OMe), and 4.97 (1 H, d, *J*_{3,4} 6.5 Hz, 3-H); *M* 438 (Found: C, 46.8; H, 4.1. C₁₇H₁₈FeO₁₀ requires C, 46.6; H, 4.1%).

Complex (25) gave *tricarbonyl-(dimethyl 3-methoxy-5-methoxycarbonylcyclohexa-2,4-dienylmalonate)iron* (30) which could not be crystallised from light petroleum and so was purified by preparative layer chromatography to give a yellow viscous oil (100 mg, 53%); ν_{\max} (CCl₄) 2 065, 1 990, 1 750, 1 735, and 1 705 (1-CO₂Me) cm^{–1}; δ (CDCl₃) 1.22 (1 H, dd, *J*_{gem} 14 Hz, *J*_{5,6} 4 Hz, *exo*-6-H), 2.40 (1 H, dd, *J*_{gem} 14 Hz, *J*_{5,6} 11 Hz, *endo*-6-H), 2.92 (1 H, m, 5-H), 3.14 (1 H, d, *J* 8 Hz, malonyl CH), 3.40 (1 H, m, 4-H), 3.62 (9 H, s), and 3.68 (3 H, s, 3 × CO₂Me and OMe), and 5.68 (1 H, d, *J*_{2,4} 2 Hz, 2-H); *M* 438.

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