A Novel Approach to the Formation of Quaternary Centres and the Introduction of Angular Substituents by using Tricarbonyldieneiron Complexes

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Tricarbonyl-(4-methoxy-1-methylcyclohexadienylium)iron hexafluorophosphate (2) undergoes exclusive addition of carbanions derived from 1.3-dicarbonyl compounds at the methylated ring position. The directing effect of the methoxy-substituent in the cation of (2) has been applied successfully to the bicyclic analogues tricarbonyl-1.3—6-η-4-methoxybicyclo[4.4.0]deca-3.5-dienylium)iron hexafluorophosphate (8). and tricarbonyl-(1,3-6-η-4-methoxybicyclo[4.3.0]nona-3.5-dienylium)iron hexafluorophosphate (17). reactions of which with similar carbanions provide an efficient method of introduction of angular substituents.

It has been previously noted [1] that the addition of the readily available nucleophiles hydroxide, morpholine, and hydride ion to tricarbonyl-(4-methoxy-1-methylcyclohexadienylium)iron [as (2)] occurs predominantly at C-1, the methylated and presumably most sterically hindered terminus of the dienylium system. In a preliminary communication [2] it was shown that cyanide anion also reacts in this manner, and that this behaviour could be extended to the bicyclic dienylium complex (8) to produce angularly substituted compounds in good yield. This study has now been extended to the reactions of these types of dienylium complexes with stable carbanions derived from 1,3-diketones, and the present paper describes these reactions together with

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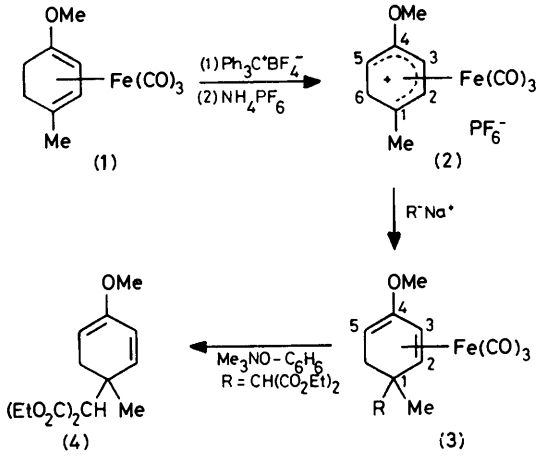
[1] A. J. Birch, K. B. Chamberlain, M. A. Haas, and D. J. Thompson, *J.C.S. Perkin I*, 1973, 1882; A. J. Birch, P. E. Cross, J. Lewis, D. A. White, and S. B. Wild, *J. Chem. Soc.* (*A*), 1968, 332.

[2] A. J. Pearson, *J.C.S. Chem. Comm.*, 1977, 339.

details of the preparation and spectral properties of the bicyclic diene complex precursors.

RESULTS AND DISCUSSION

Reaction of Tricarbonyl-(4-methoxy-1-methylcyclohexadienylium)iron Hexafluorophosphate with Stable Carbanions.—In the earlier preparation of the tetrafluoroborate analogue of the complex (2),[1] yields were limited



SCHEME 1

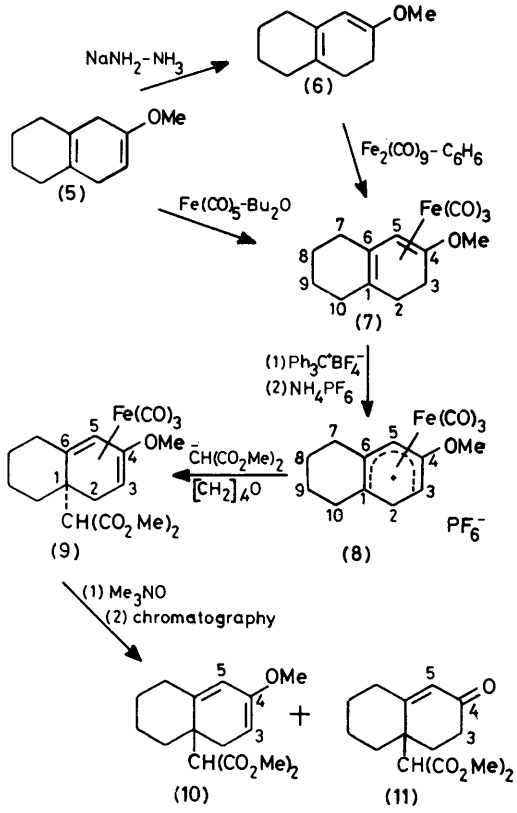
by the fact that the diene complex precursor (1), required for reaction with triphenylmethyl tetrafluoroborate, is obtained as a 1 : 1 mixture with the isomer (3; R = *endo*-H). These two compounds are readily separated chromatographically, and pure (3; R = *endo*-H) thus obtained may be reconverted into the equilibrium mixture by refluxing in di-n-butyl ether for 24 h. In this way, the yield of the complex (1) may be increased. The tetrafluoroborate analogue of (2) was difficult to handle, since it did not readily form stable crystals, so in all the preparations it was immediately converted into the hexafluorophosphate by precipitation from aqueous solution.

Reaction of the complex (2) with the diethyl sodiomalonate in tetrahydrofuran at 0 °C yielded a yellow oil. Chromatography produced a single yellow product in 89% yield. A sample further purified by preparative layer chromatography had a ^{1}H n.m.r. spectrum consistent with the structure [3; R = *exo*-CH(CO_2Et)$_2$], the malonyl substituent being assigned the *exo*-orientation relative to Fe(CO)$_3$ by analogy with other similar reactions.[3] Thus, the H-3 signal appears as a doublet of doublets ($J_{3.5}$ 2, $J_{2.3}$ 7 Hz) at δ 5.04, that of H-5 as a multiplet at 3.35, and that of H-2 as a doublet ($J_{2.3}$ 7 Hz) at 2.58. The single proton of the malonate resonates as a singlet at δ 3.13, showing this to be adjacent to a quaternary carbon atom. Had reaction occurred at the unsubstituted terminus C-5 of (2), this resonance would have been a doublet. The methoxy-singlet at δ 3.66 is typical of a tricarbonyl-(2-methoxycyclohexadiene)iron complex,[1,3] and the similarity of this and the diene proton signals to those of (3; R = *endo*-H) further supports the structural assignment.

The ethyl groups of the malonyl substituent of [3; R = *exo*-CH(CO_2Et)$_2$] give rise to two sets of closely overlapping signals owing to the diastereotopic nature of this moiety (it is bonded to an asymmetric centre).

Addition of the malonate carbanion exclusively at the most hindered terminus (Scheme 1) is at least partly due to the deactivation of C-5 by mesomeric interaction with the methoxy-substituent. Thus, the ^{13}C n.m.r. spectrum of (2) (Experimental section) shows C-1 (δ 91.3 p.p.m. downfield from tetramethylsilane) to have much greater positive charge than C-5 (δ 42.9), so that if electronic control predominates during reaction the kinetic product would be [3; R = *exo*-CH(CO_2Et)$_2$], as is observed. However, the extent to which thermodynamic factors are involved is unknown, so this behaviour may not necessarily extend to other types of carbanion or carbanion equivalents. In the present case of reaction with a 'soft' carbanion the transition state may be product-like, leading to some degree of thermodynamic control.

The directing effects displayed in the reactions with anions of 1,3-dicarbonyl compounds are sufficient to overcome varying degrees of steric hindrance. Thus,



SCHEME 2

reaction of (2) with diethyl methyl(sodio)malonate, ethyl sodioacetoacetate, and t-butyl sodioacetoacetate led to compounds of structure (3) in each case.

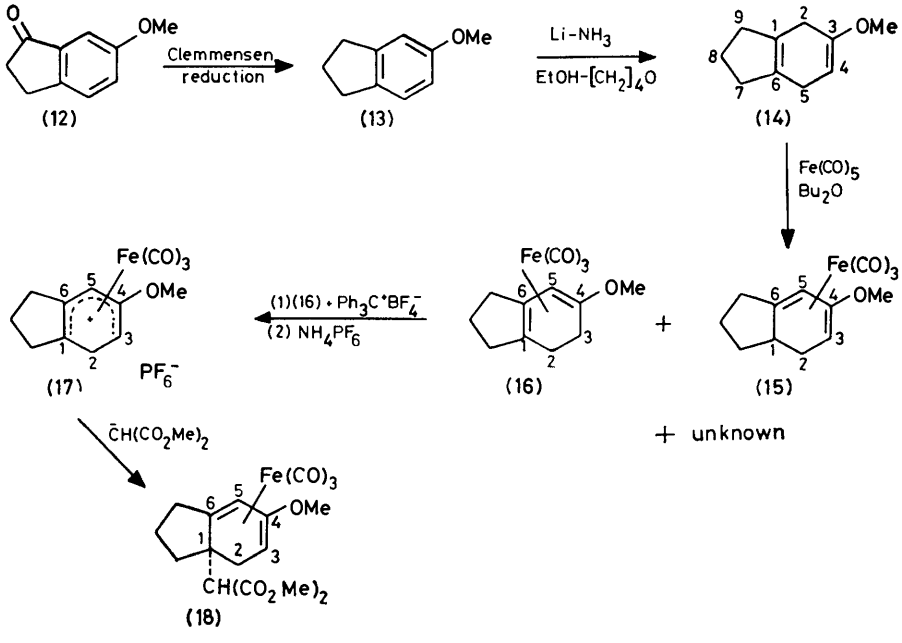
[3] R. E. Ireland, G. G. Brown, jun., R. H. Stanford, jun., and T. C. McKenzie, *J. Org. Chem.*, 1974, **39**, 51.
[4] Y. Shvo and E. Hazum, *J.C.S. Chem. Comm.*, 1975, 829.

Removal of the tricarbonyliron group from [3; R = *exo*-$CH(CO_2Et)_2$] was readily achieved by using trimethylamine *N*-oxide in refluxing benzene,[4] and gave a 60% yield of diethyl 4-methoxy-1-methylcyclohexa-2,4-dienylmalonate (4), characterised spectroscopically (Experimental section).

Preparation of, and Introduction of, Angular Substituents into Dienylium Complexes derived from Bicyclic Systems.—Reactions of the unconjugated dienes (5) and (14), obtainable as shown in Schemes 2 and 3, with pentacarbonyliron led to moderate yields of the tricarbonyliron complexes (7) and (16), respectively, which were readily identified from their n.m.r. spectra. Minor products of demethoxylation, which were not identified, were also obtained in each case. The diene (14) also gave a minor amount of the isomeric dienol ether complex (15), identified from its n.m.r. spectrum, which proved useful for comparison with those of the later reaction products and confirmation of their structures. Pre-conjugation of the diene (5) with sodamide in liquid ammonia gave compound (6),[5] but treatment of this with enneacarbonyliron in refluxing benzene did not give a greatly improved yield of (7), so no attempt was made to repeat the procedure with the indane derivative (14). Reactions of the complexes (7) and (16) with triphenylmethyl tetrafluoroborate gave exclusively the dienylium complexes (8) and (17), again readily identified by comparison of their ^1H n.m.r. spectra with those of the monocyclic analogues[1,3] (Experimental section). The tetrafluoroborate salts of (8) and (17) deteriorated, and so were converted into the hexafluorophosphates, which could be stored unchanged indefinitely at room temperature.

The dienylium complexes (8) and (17) were treated with dimethyl sodiomalonate as described above (use of the diethyl ester led to overlaps in the product n.m.r. spectra). A single crystalline product was obtained in each case, and this could be purified by recrystallisation from light petroleum or preparative layer chromatography on silica. The pure products were shown to have structures (9) and (18) from their ^1H n.m.r. spectra. Thus, the malonate CH signal was a sharp singlet, as for the complex [3; R = *exo*-$CH(CO_2Et)_2$], and the H-5 signal appeared as a narrow doublet,[1,3,6c] owing to long-range coupling (2 Hz) to H-3, which resonated at the characteristic position, δ *ca.* 3.2. The singlet for the dienol ether methoxy-group occurred at the typical position (δ 3.6), which is downfield from the methoxy-signals of (7) and (16), and consistent with the trends observed for similarly substituted monocyclic complexes (above). The spectra of (9) and (18) are very similar to those of [3; R = *exo*-$CH(CO_2Et)_2$] and (15), so there is no doubt that reaction occurs at the terminal dienylium angular position, as shown in Schemes 2 and 3. By analogy with reactions of similar nucleophiles with monocyclic dienylium complexes it is assumed that reaction occurs stereospecifically at the face of the molecule opposite to the metal.[3]

The $Fe(CO)_3$ group was removed smoothly from (9) with trimethylamine *N*-oxide as above. The crude product had a ^1H n.m.r. spectrum consistent with the expected structure (10), and was *ca.* 80% pure. Attempts at purification by preparative layer chromatography on Florisil or alumina, as for the monocyclic analogue (4), gave two bands. The slower running



SCHEME 3

[5] A. J. Birch, E. M. A. Shoukry, and F. Stansfield, *J. Chem. Soc.*, 1961, 5376.

[6] (*a*) A. J. Birch, P. W. Westerman, and A. J. Pearson, *Austral. J. Chem.*, 1976, **29**, 1671; (*b*) A. J. Pearson, *ibid.*, p. 1679; (*c*) A. J. Pearson, *ibid.*, 1977, **30**, 407.

compound was identified from its spectral properties as the enone (11), the hydrolysis product of (10), and the broad less polar band contained *ca.* 50% of (11) (^{1}H n.m.r. spectrum), evidently owing to hydrolysis of (10) during chromatography, the remaining peaks being consistent with the structure (10). A pure sample of (10) was not obtained, but observation in the n.m.r. spectrum of the crude material of a multiplet at δ 4.44 (H-3), and of a narrow doublet (2.5 Hz) at δ 5.59 (H-5), together with the malonate CH signal as a sharp singlet, analogous to that in (4), is convincing evidence for the structures of these compounds.

Thus, tricarbonyldieneiron complexes derived from bicyclic dienes and having a methoxy-substituent in the appropriate position may be used as a means of obtaining angularly substituted compounds. The potential of this reaction in steroid conversions is being investigated.

EXPERIMENTAL

I.r. spectra were determined with a Perkin-Elmer 257 and mass spectra with an A.E.I. MS9 spectrometer. ^{1}H N.m.r. spectra (100 MHz) were obtained for solutions in deuteriochloroform unless otherwise stated with a Varian HA100 or JEOL Minimar spectrometer, and ^{13}C n.m.r. spectra were determined with a JEOL FT-60 spectrometer, operating at 15.1 MHz and 304 K, by the pulsed Fourier transform method. Assignments of ^{13}C n.m.r. signals were made by inspection of proton-decoupled and gated-proton-decoupled spectra and comparison with our own and other previously reported assignments for related compounds.[2,6] The malonate and acetoacetate esters, pentacarbonyliron and enneacarbonyliron were obtained from commercial sources. All chromatographic operations were conducted under argon or nitrogen.

Tricarbonyl-(4-methoxy-1-methylcyclohexadienylium)iron Hexafluorophosphate (2).—Birch reduction of 4-methylanisole provided 1-methoxy-4-methylcyclohexa-1,4-diene, b.p. 170—172 °C. This compound (50 g) was refluxed under nitrogen with pentacarbonyliron (100 g) in dibutyl ether (300 ml) for 18 h. The mixture was filtered through Celite and the solvent and pentacarbonyliron collected at aspirator pressure. Distillation of the product gave starting material (30 g), followed by a mixture of the complexes (1) and (3; R = *endo*-H), b.p. 78—82° at 0.3 mmHg (26 g). The recovered starting material was added to the residual pentacarbonyliron and dibutyl ether and treated as before. This led to a total of 45 g (42%) of complexes after distillation, together with unchanged starting material, so that in principle good yields of the complexes may be obtained by repetition of this procedure. Chromatography of the mixture (8 g) on silica gave three bands. The first (*ca.* 200 mg), eluted with light petroleum, was not identified. The second, eluted with light petroleum, was compound (3; R = *endo*-H) (3.6 g), and the third, eluted with benzene, and which was very susceptible to aerial oxidation, was compound (1) (3.8 g). The complex (3; R = *endo*-H) was refluxed under nitrogen in dibutyl ether for 24 h; chromatography as above then gave (3; R = *endo*-H) (1.2 g) and (1) (1.1 g). In this way, the desired isomer (1) could be obtained in higher yields than previously reported.[1] Treatment of (1) with triphenylmethyl tetrafluoroborate (published procedure [1]) gave tricarbonyl-(4-methoxy-1-methylcyclohexadienylium)iron tetrafluoroborate in 90% yield, and this was immediately converted into the more stable hexafluorophosphate (2) quantitatively by precipitation from a saturated aqueous solution with a 20% excess of ammonium hexafluorophosphate. All compounds had spectral properties consistent with those previously reported,[1] and (2) showed δ_C (CD_3CN; referred to Me_4Si) 23.8 (q, *J* 129 Hz, Me), 33.6 (t, *J* 141 Hz, C-6), 42.9 (d, *J* 172 Hz, C-5), 58.0 (q, *J* 149 Hz, MeO), 73.0 (d, *J* 184 Hz, C-3), 91.3 (s, C-1), 96.2 (d, *J* 174 Hz, C-2), 150.4 (s, C-4), and 201.5 [s, $Fe(CO)_3$].

Preparation of, and Hydride Abstraction from, Tricarbonyl-{1,4—6-η-4-methoxybicyclo[4.4.0]deca-1(6),4-diene}iron (7).—*Method A*. Birch reduction of 2-methoxytetralin provided the corresponding 1,4-diene (5).[5] This compound (2 g) was refluxed under nitrogen with pentacarbonyliron (10 ml) and dry, peroxide-free dibutyl ether (40 ml), for 20 h. The product was filtered through Celite and the excess of pentacarbonyliron and dibutyl ether were removed at aspirator pressure. The excess of starting material was removed by heating at 100—110 °C and 0.05 mmHg; the diene (5) (1 g, 50%) was collected at 0 °C and could be recycled as described above for monocyclic compounds. (It has previously been observed that this recycling procedure leads to better yields than prolonged refluxing, owing apparently to autocatalytic decomposition of the complexes.[1]) The residues were then chromatographed on a silica column, development with light petroleum giving two bands (90 and 150 mg, respectively), obtained as yellow oils showing $Fe(CO)_3$ i.r. absorptions, but having no methoxy-signals in the ^{1}H n.m.r. spectrum. They were not identified. The third band, eluted with light petroleum–benzene (1 : 1), gave the complex (7) (800 mg, 53% based on diene consumed).

Method B. Treatment of the diene (5) with sodamide in liquid ammonia [5] gave a mixture of conjugated and unconjugated dienes containing *ca.* 70% of the desired isomer (6). Since such contaminant material does not react with enneacarbonyliron under mild conditions (unpublished work from this laboratory) yields of complex are based on the amount of (6) present in the reaction. The mixture containing 2 g of (6) was refluxed under nitrogen in dry benzene (25 ml) with enneacarbonyliron (5 g) for 4 h. The cooled mixture was filtered through Celite and worked up as in method A to give unchanged diene (1 g, 50%), which was treated with a further 2.5 g of enneacarbonyliron. The combined complexes from this procedure produced, upon chromatography, a minor amount (50 mg) of non-polar complex identical with the faster running compound obtained in method A. Elution with light petroleum–benzene (1 : 1) gave the *complex* (7) (2.1 g, 57%) as a yellow crystalline solid, m.p. 37—39 °C; $\nu_{max.}$ (CCl_4) 2 030 and 1 940 cm^{-1}; δ_H 1.4—3.0 (12 H, 6 × CH_2), 3.44 (3 H, s, MeO), and 5.16 (1 H, s, H-5), *M* 304 (Found: C, 55.4; H, 5.3. $C_{11}H_{16}FeO_4$ requires C, 55.3; H, 5.3%).

Triphenylmethyl tetrafluoroborate (2.1 g) was dissolved in the minimum volume of dry dichloromethane and mixed with a solution of (7) (1.9 g) in a similar volume of dichloromethane. After 30 min in a stoppered flask at ambient temperature, the solution was poured into an excess of ether, and the precipitated tetrafluoroborate salt (2.0 g, 82%) was collected at the pump, washed well with ether and dried. This compound could be used directly for subsequent reaction, but slowly deteriorated, and so for storage was converted into the stable *hexafluorophosphate* as described above; δ_H (CD_3CN) 1.2—3.1 (10 H, 5 × CH_2),

3.80 (3 H, s, MeO), 3.9 (1 H, m, H-3), and 6.75 (1 H, d, $J_{3,5}$ 2.5 Hz, H-5) (Found: C, 37.8; H, 3.7; Fe, 12.9. $C_{14}H_{15}F_6FeO_4P$ requires C, 37.9; H, 3.3; Fe, 12.3%).

Preparation of, and Hydride Abstraction from, Tricarbonyl-{1,4—6-η-4-methoxybicyclo[4.3.0]nona-1(6),4-diene}iron (16).—Clemmensen reduction of the ketone (12)[7] gave 2-methoxyindane as a liquid (95%), b.p. 114—118 °C at 20 mmHg. This compound (8.7 g) was reduced with lithium (2.0 g) in ammonia (400 ml), using ethanol (30 ml) as proton source and tetrahydrofuran (30 ml) as cosolvent. Evaporation of the ammonia, followed by addition of water sufficient to dissolve lithium salts, and extraction with light petroleum afforded the diene (6.5 g, 74%) as a liquid, b.p. 105 °C at 15 mmHg; $\nu_{max.}$ 1 700 and 1 660 cm^{-1}; δ_H 1.9 (2 H, m), 2.25 (4 H, m), and 2.7br (4 H, s) (5 × CH_2), 3.54 (3 H, s, MeO), and 4.64br (1 H, olefinic). This diene (4 g) was treated with pentacarbonyliron as in method A above; 2 g of starting material was recovered. The residual crude complexes were chromatographed in the usual way giving a minor compound displaying no methoxy-signal in the n.m.r. spectrum (250 mg), as for the previous complexes, followed by the complex (15) (150 mg), obtained as a yellow oil, $\nu_{max.}$ 2 040 and 1 955 cm^{-1}; δ_H 1.6—2.4 (9 H, 4 × CH_2 and H-1), 3.42 (1 H, m, H-3), 3.60 (3 H, s, MeO), and 4.75 (1 H, d, $J_{3,5}$ 2 Hz, H-5); *M* 290. The third major band was eluted with light petroleum–benzene (1 : 1), and gave the desired complex (16) (1.8 g, 57% based on diene consumed) as a yellow oil, $\nu_{max.}$ 2 030 and 1 940 cm^{-1}; δ_H 1.5—2.9 (10 H, 5 × CH_2), 3.44 (3 H, s, MeO), and 5.38 (1 H, s, H-5); *M* 290. Minor impurities (≤5%) could not be removed by preparative layer chromatography, and so this compound was used directly for reaction with triphenylmethyl tetrafluoroborate.

The complex (16) (1.37 g) was treated with triphenylmethyl tetrafluoroborate in the usual way to give the crude tetrafluoroborate (1.22 g) which was not sufficiently pure for direct reaction or characterisation. It was dissolved in the minimum volume of water and filtered into a flask containing aqueous ammonium hexafluorophosphate to produce a yellow precipitate of the *hexafluorophosphate* (17) which was filtered off, washed with water, ethanol, and then ether and dried in air. More could be obtained by concentrating the filtrate, cooling, and filtering *etc.* (total yield 1.4 g, 68%); δ_H (CD_3CN) 2.0—3.4 (8 H, 4 × CH_2), 3.8 (3 H, s, MeO), 3.9 (1 H, m, H-3), and 6.96 (1 H, d, $J_{3,5}$ 2 Hz, H-5) (Found: C, 35.7; H, 2.9. $C_{13}H_{13}F_6FeO_4P$ requires C, 35.9; H, 2.9%).

Reactions with Sodio-derivatives of 1,3-Dicarbonyl Compounds.—The procedure is described for diethyl malonate and the dienylium complex (2), that for all other reactions being identical. Sodium hydride dispersion in mineral oil [72 mg (3 mmol) of NaH] was introduced into a three-necked flask equipped with rubber septum, argon supply, and stirrer, and was washed with dry pentane (5 × 5 ml). Dry, oxygen-free tetrahydrofuran (10 ml) was introduced *via* the septum, and a solution of diethyl malonate (480 mg, 3 mmol) in tetrahydrofuran (5 ml) was introduced slowly at room temperature; a clear solution of its sodio-derivative was obtained. In a similar flask was placed the hexafluorophosphate (2) (500 mg, 1.22 mmol) and this was flushed with argon and cooled to 0 °C while tetrahydrofuran (10 ml) was introduced through the septum. To the stirred suspension so obtained was added dropwise with a syringe the solution of sodiomalonic ester until all the hexafluorophosphate had dissolved. A small excess of malonate anion was then added to ensure complete reaction, and the mixture was poured into water and extracted with light petroleum in the usual way. The products were purified by chromatography on silica with benzene as developer, followed by recrystallisation from light petroleum.

With tricarbonyl-(4-methoxy-1-methylcyclohexadienylium)-iron hexafluorophosphate (2). Diethyl malonate gave *tricarbonyl-(diethyl 4-methoxy-1-methylcyclohexa-2,4-dienylmalonate)iron* [3; R = *exo*-$CH(CO_2Et)_2$] as a yellow oil (500 mg, 89%); $\nu_{max.}$ (film) 2 050, 1 970, 1 750, and 1 730 cm^{-1}; δ_H 1.19 (3 H, s, partly obscured, 5-Me), 1.26 (6 H, two closely overlapping triplets, *J* 7 Hz, ester 2 × Me), 1.55 (1 H, dd, J_{gem} 16, $J_{5,6}$ 3 Hz) and 2.4 (1 H, dd, J_{gem} 16, $J_{5,6}$ 3 Hz) (6-H_2), 2.58 (1 H, d, $J_{2,3}$ 7 Hz, H-2), 3.13 (1 H, s, malonate CH), 3.35 (1 H, m, H-5), 3.66 (3 H, s, MeO), 4.20 and 4.23 (total 4 H, two overlapping q, *J* 7 Hz, ester 2 × CH_2), and 5.04 (1 H, dd, $J_{2,3}$ 7, $J_{3,5}$ 2 Hz, H-3); *M* 422 (Found: C, 49.8; H, 5.1. $C_{18}H_{22}FeO_8$ requires C, 51.2; H, 5.2%).

Diethyl methylmalonate gave *tricarbonyl-[diethyl 4-methoxy-1-methylcyclohexa-2,4-dienyl(methyl)malonate]iron* [3; R = *exo*-$CMe(CO_2Et)_2$] as a pale yellow crystalline solid, m.p. 58—59 °C (450 mg, 85%); $\nu_{max.}$ ($CHCl_3$) 2 050, 1 970, and 1 720 cm^{-1}, δ_H 1.26 [3 H, s, and 6 H, m (diastereotopic), 5-Me and ester 2 × Me], 1.43 (3 H, s, methylmalonate Me), 1.65 (1 H, dd, J_{gem} 16, $J_{5,6}$ 3 Hz, H-6), 2.54 (2 H, m, H-2 and H-6), 3.26 (1 H, m, H-5), 3.6 (3 H, s, MeO), 4.14 [4 H, m (diastereotopic), 2 × CH_2 ester], and 4.97 (1 H, dd, *J* 7 and 2 Hz, H-5); *M* 436 (Found: C, 52.1; H, 5.6. $C_{19}H_{24}FeO_8$ requires C, 52.3; H, 5.5%).

Ethyl acetoacetate gave *tricarbonyl[ethyl (4-methoxy-1-methylcyclohexa-2,4-dienyl)acetoacetate]iron* [3; R = *exo*-$CH(COMe)CO_2Et$] as a pale yellow crystalline diastereoisomeric mixture, m.p. 57—61 °C (376 mg, 79%); $\nu_{max.}$ ($CHCl_3$) 2 050, 1 970, and 1 725 cm^{-1}; δ_H 1.16 (3 H, s, 1-Me), 1.28 (3 H, 2 t overlapping, *J* 7 Hz, ester Me), 1.54 (1 H, dd, J_{gem} 15, $J_{5,6}$ 2 Hz), and 2.3 (1 H, dd, J_{gem} 15, $J_{5,6}$ 3 Hz) (6-H_2), 2.18 (s) and 2.20 (s) [total 3 H, Ac (diastereoisomers)], 2.54 (1 H, d, $J_{2,3}$ 7 Hz, H-2), 3.28 (2 H, m, H-5 and acetoacetate CH), 3.68 (3 H, s, MeO), 4.20 (2 H, 2q overlapping, *J* 7 Hz, ester CH_2), and 5.06 (1 H, m, H-3); *M* 392 (Found: C, 51.9; H, 5.0. $C_{17}H_{20}FeO_7$ requires C, 52.1; H, 5.1%).

t-Butyl acetoacetate gave *tricarbonyl-[t-butyl (4-methoxy-1-methylcyclohexa-1,4-dienyl)acetoacetate]iron* [3; R = *exo*-$CH(COMe)CO_2Bu^t$] as a yellow crystalline diastereoisomeric mixture, m.p. 79—84 °C (367 mg, 71%); $\nu_{max.}$ ($CHCl_3$) 2 050, 1 970, and 1 715 cm^{-1}; δ_H 1.18 (3 H, s, 1-Me), 1.52 (s) and 1.46 (s) [total 9 H, Bu^t (diastereoisomers)], 1.5 (1 H, m, partly obscured) and 2.2 (1 H, m) (6-H_2), 2.16 (s) and 2.20 (s) (3 H, Ac), 2.55 (1 H, H-2), 3.07 (s) and 3.18 (s) (1 H total, acetoacetate CH), 3.36 (1 H, m, H-5), 3.66 (3 H, s, MeO), and 5.04 (1 H, m, H-3); *M* 420 (Found: C, 53.4; H, 5.7. $C_{19}H_{24}FeO_7$ requires C, 54.3; H, 5.7%).

With tricarbonyl(1,3—6-η-4-methoxybicyclo[4.4.0]deca-3,5-dienylium)iron hexafluorophosphate (8). This salt (230 mg) with dimethyl sodiomalonate gave *tricarbonyl(dimethyl 3—6-η-4-methoxybicyclo[4.4.0]deca-3,5-dien-1-ylmalonate)-iron* (9) (170 mg, 77%), obtained pure by preparative layer chromatography on silica (benzene–ethyl acetate, 10 : 1) as a yellow solid, m.p. 135—136 °C; $\nu_{max.}$ (CCl_4) 2 045, 1 970, 1 760, and 1 730 cm^{-1}; δ_H 1.2—2.4 (9 H, 4 × CH_2 and *exo*-H-2), 2.96 (1 H, dd, J_{gem} 16, $J_{2,3}$ 3.5 Hz, *endo*-H-2), 3.24 (1 H, m, H-3), 3.60 (3 H, s, MeO) [assigned by comparison with product of addition of diethyl malonate anion to (8)], 3.64 (3 H, s) and 3.75 (3 H, s) (2 × CO_2Me), 4.10

[7] H. O. House and C. B. Hudson, *J. Org. Chem.*, 1970, **35**, 647.

(1 H, s, malonate CH), and 4.84 (1 H, d, $J_{3,5}$ 2 Hz, H-5); *M* 434 (Found: C, 52.6; H, 5.3; Fe, 12.9. $C_{19}H_{22}FeO_8$ requires C, 52.5; H, 5.1; Fe, 12.9%).

With tricarbonyl-(1,3—6-η-4-*methoxybicyclo*[4.3.0]*nona*-3,5-*dienylium*)*iron hexafluorophosphate* (17). This salt (250 mg) with dimethyl sodiomalonate gave a product showing a single yellow band on preparative layer chromatography (210 mg) but the n.m.r. spectrum still showed some impurities. Recrystallisation from light petroleum afforded pale yellow needles (150 mg, 57%) of pure *tricarbonyl-*(*dimethyl* 3—6-η-4-*methoxybicyclo*[4.3.0]*nona*-3,5-*dien*-1-*ylmalonate*)*iron* (18), m.p. 110.5—112.5 °C; $\nu_{max.}$ ($CHCl_3$) 2 040, 1 960, 1 740, and 1 720 cm^{-1}; δ_H 1.6—2.4 (7 H, 3 × CH_2 and *exo*-H-2), 2.8 (1 H, dd, J_{gem} 16, $J_{2,3}$ 3 Hz, *endo*-H-2), 3.22 (1 H, dd, $J_{2,3}$ 3, $J_{3,5}$ 2 Hz, H-3), 3.49 (1 H, s, malonate CH), 3.62 (3 H, s, MeO), 3.69 (3 H, s) and 3.76 (3 H, s) (2 × CO_2Me), and 5.25 (1 H, d, $J_{3,5}$ 2 Hz, H-5); *M* 420 (Found: C, 51.5; H, 4.7. $C_{18}H_{20}FeO_8$ requires C, 51.4; H, 4.8%).

Removal of Iron from Complexes.—The complex [3; R = *exo*-$CH(CO_2Et)_2$] (500 mg) was refluxed in dry benzene (15 ml) with trimethylamine *N*-oxide (1 g) for 30 h. The cooled mixture was filtered through Celite, the solvent removed, and the residue purified by t.l.c. on Florisil, developed with benzene, to afford *diethyl* 4-*methoxy*-1-*methylcyclohexa*-2,4-*dienylmalonate* (4) (225 mg, 68%) as an oil, $\nu_{max.}$ 1 755, 1 730, 1 685, 1 655, and 1 610 cm^{-1}; δ_H 1.28 (9 H total, 3 × Me), 2.16 (1 H, dd, J_{gem} 17, $J_{5,6}$ 5 Hz) and 2.58 (1 H, dd, J_{gem} 17, $J_{5,6}$ 5 Hz) (6-H_2), 3.59 (3 H, s, MeO), 3.66 (1 H, s, malonate CH), 4.25 (4 H, m, ethyl ester 2 × CH_2), 4.6 (1 H, m, H-5), 5.78 (1 H, dd, $J_{2,3}$ 10, $J_{3,5}$ 2.5 Hz, H-3), and 6.0 (1 H, d, $J_{2,3}$ 10 Hz, H-2) (Found: *M*, 282.1474. $C_{15}H_{22}O_5$ requires *M*, 282.1467).

The complex (9) (200 mg) was refluxed in dry benzene (7 ml) with trimethylamine *N*-oxide (500 mg) for 4 h and the product worked up as above, to give crude (10) in 90% yield, which appeared to be *ca.* 80% pure from its ^1H n.m.r. spectrum. Attempts to purify this compound by preparative t.l.c. on Florisil or alumina with sodium-dried benzene or benzene–ethyl acetate (10 : 1) gave two bands. Extraction of the more polar band produced *dimethyl* 4-*oxobicyclo*[4.4.0]*dec*-5-*en*-1-*ylmalonate* (11), m.p. 78—80 °C (23%); $\nu_{max.}$ ($CHCl_3$) 1 750, 1 730, 1 663, and 1 620 cm^{-1}; δ_H 1.4—3.0 (12 H, 6 × CH_2), 3.66 (3 H, s) and 3.77 (3 H, s) (2 × CO_2Me), 4.18 (1 H, s, malonate CH), and 5.92 (1 H, s, H-5); *M* 280 (Found: C, 64.7; H, 7.3. $C_{15}H_{20}O_5$ requires C, 64.3; H, 7.2%). Extraction of the broad less polar band gave a substance the ^1H n.m.r. spectrum of which showed the presence of *ca.* 50% (11), the remaining peaks being consistent with the structure (10); δ 1.3—2.5 (methylene region), 3.47 (3 H, s, MeO), 3.59 (3 H, s) and 3.73 (3 H, s) (2 × CO_2Me), 4.44 (1 H, m, H-3), and 5.59 (1 H, d, $J_{3,5}$ 2.5 Hz, H-5).

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