Organoiron Complexes in Organic Synthesis. Part 2.[1] Conformational and Steric Effects of Methyl Substituents in Tricarbonyliron Derivatives of Bicyclo[4.4.0]decadienes

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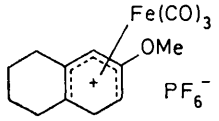
The reactions of cyanide and dimethyl sodiomalonate with 7- and 10-methyl-substituted derivatives of tricarbonyl-[1,3—6-η-4-methoxybicyclo[4.4.0]deca-3,5-dienylium]iron hexafluorophosphate have been studied. The presence of *exo*-methyl groups suppresses the addition of nucleophile to the angular terminus, C-1, and *endo*-methyl groups cause the formation of mixtures of angularly and non-angularly substituted products.

I have recently shown[2] that reactions of nucleophiles having synthetic potential with tricarbonyliron complexes of appropriately methoxylated bicyclic dienylium cations, such as (1), result in stereospecific, regiospecific



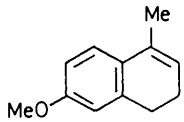
(1)

addition of the nucleophile to the angular terminal carbon atom of the dienyl system. With a view to testing the generality of this reaction, particularly with regard to steric effects, an examination of the synthesis and reactions of some methylated analogues of (1) was undertaken; the results are described in the present paper.

RESULTS AND DISCUSSION

Preparation of Complexes.—3-Methoxy-7-methylbicyclo[4.4.0]deca-1(6),3-diene (3) was prepared by lithium–ammonia reduction of the tetraene (2), obtained by standard procedures (Experimental section) and was treated with pentacarbonyliron in refluxing dibutyl ether as previously described.[2,3] After removal of solvent and unchanged (3), the residues were chromatographed on silica to give minor products of demethoxylation[2] and a small amount (0.3%) of complex (4) readily identified from its ^{1}H n.m.r. spectrum by comparison with those of previously prepared related compounds. The desired major product was obtained as a mixture of diastereoisomers (5) and (6), having *exo*- and *endo*-methyl substituents,‡ in the ratio *ca.* 3 : 1, estimated by ^{1}H n.m.r. spectroscopy of this and the mixture obtained from later hydride abstraction.

On the assumption that the preponderance of the



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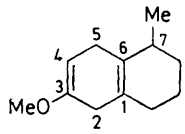

(3)

exo-compound (5) is due to steric hindrance from the methyl group during complex formation, an attempt was made to improve the stereoselectivity of this reaction. Accordingly, the diene (3) was treated with sodamide in liquid ammonia[4] to afford the conjugated diene (7). I envisaged that reaction of this compound under mild

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‡ *exo*- and *endo*-, although not entirely satisfactory, are used to denote substituents on the face of the diene opposite to and the same as, respectively that occupied by $Fe(CO)_3$. This is consistent with current literature.

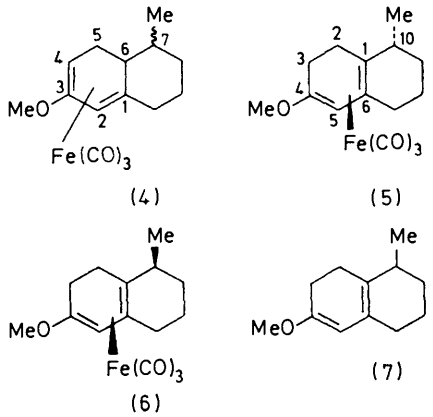
[1] Part 1 ref. 2*b*.

[2] A. J. Pearson, (*a*) *J.C.S. Chem. Comm.*, 1977, 339; (*b*) *J.C.S. Perkin I*, 1977, 2069.

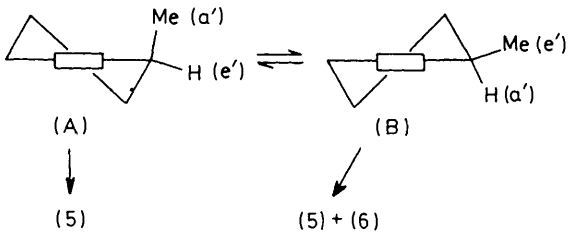
[3] A. J. Birch, K. B. Chamberlain, M. A. Haas, and D. J. Thompson, *J.C.S. Perkin I*, 1973, 1882.

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

conditions with the presumably more sterically demanding $Fe_2(CO)_9$ would result in complex formation predominantly at the unsubstituted face of the diene, leading to a greater proportion of (5) in the products. This was not so, however, and when the reaction was performed in refluxing diethyl ether the complex obtained was shown to be an *equimolar* mixture of (5) and (6) by its ^1H n.m.r. spectrum. However, treatment of (7) with pentacarbonyliron in refluxing dibutyl ether



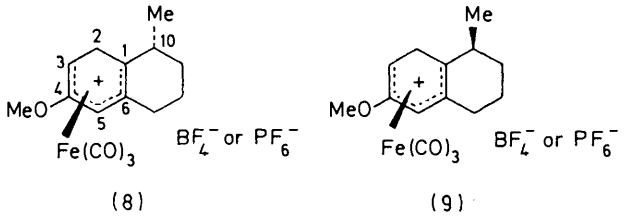
resulted in a mixture containing *ca.* 80% of (5). The most acceptable explanation for these observations is that at high temperatures (refluxing dibutyl ether) the equilibrium shown in (1) gives an equimolar mixture of conformers (A) and (B) (depicted as cyclohexene derivatives for simplicity). Molecules in conformation (A) react with the iron carbonyl only at the unsubstituted face, producing (5), whereas B may complex on either



(1)

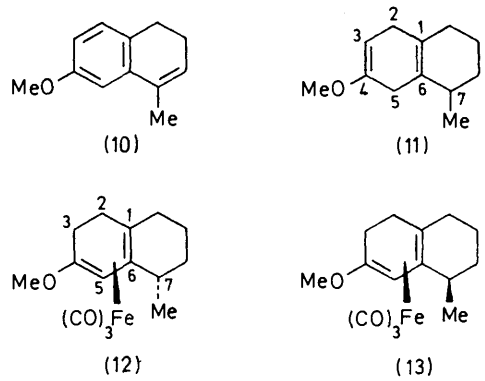
face. Therefore, for an equimolar equilibrium composition, we should expect to obtain a mixture containing 75% of (5) and 25% of (6), which is close to the observed ratios. At lower temperatures (diethyl ether), equilibrium will lie in favour of conformation (B), which can react at either face and which will therefore produce the observed equimolar mixture of complexes (5) and (6).

Reaction of the mixture of (5) and (6) with triphenylmethylium tetrafluoroborate proceeded in the expected manner [2] to give the dienylium complexes (8) and (9) containing 75—80% of the *exo*-isomer (8) (by ^1H n.m.r.). The tetrafluoroborates thus obtained were converted into the more stable hexafluorophosphates, and careful selective precipitation of these from dichloromethane solution, by addition of diethyl ether, produced a mixture containing 90—95% of (8). It was not possible to obtain pure (8) by this method. Complete precipitation of the mother liquors from this procedure gave

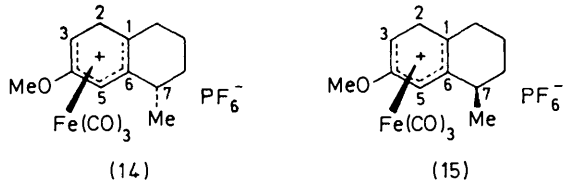


an approximately equimolar mixture of (8) and (9) which was used to study the reactions of (9) with nucleophiles.

Birch reduction of (10) gave the diene (11) and reaction of this with pentacarbonyliron produced, upon chromatography, the major product consisting of a mixture of diastereoisomers (12) (80%) and (13) (20%),



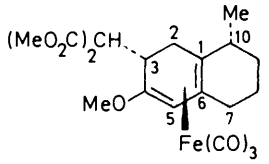
as determined by ^1H n.m.r. spectroscopy (Experimental section). Treatment of this mixture with triphenylmethylium tetrafluoroborate in the usual way did not give a clean reaction, and addition of ether gave a dark oil. Extraction of this into water, followed by washing the aqueous extracts with ether, produced a clear yellow solution, and addition of aqueous ammonium hexafluorophosphate to this resulted in a yellow crystalline mixture of diastereoisomers (14) and (15) in lower yield than usual. Selective ether precipitation from dichloromethane produced (14) approximately 95% pure.



Reactions of Dienylium Complexes with Nucleophiles.— In order to make a direct comparison with the reactions already observed for the non-methylated analogues of (8), (9), (14), and (15), the reactions of these compounds with dimethyl sodiomalonate and cyanide anion were examined. Reaction of both (8) and (14) with dimethyl

sodiomalonate resulted in exclusive addition of the carbanion to the methoxy-deactivated terminus of the dienylium cation, C-3, so that in both cases the presence of the *exo*-methyl group prevents addition at the angular position. For the complex (8) the presence of a methyl group *cis*-α to the approaching nucleophile directly hinders attack at C-1 and the observed product is (16). Although the methyl substituent of (14) appears to be relatively remote from C-1, the process of axial addition of the nucleophile to this angular position brings the methyl group also into an axial conformation. This results in an unfavourable 1,3-diaxial interaction in the transition state, so that reaction occurs preferentially at the more remote, but less reactive terminus, giving (17).

Treatment of the equimolar mixture of (8) and (9) with dimethyl sodiomalonate led to a mixture of three isomeric products in ratio 2 : 1 : 1, which were inseparable on t.l.c. The major component had ^{1}H n.m.r. signals corresponding to (16) and therefore arises from (8). Further examination of the n.m.r. spectrum led to the assignment of structures (18) and (19) to the remaining compounds, both of these being formed from (9). In particular, (19) showed the typical singlet at δ 3.92 due to the angular malonyl methine proton, and a narrow doublet ($J_{3,5}$ 2 Hz) at 4.63 corresponding to H-5, directly comparable with data for the angularly substituted compounds obtained in the previous studies.[2] The presence of the complex (18) was revealed by the sharp singlet at δ 5.07 (H-5) and a methyl doublet at 1.02, both upfield (0.08 and 0.12 p.p.m., respectively) from the corresponding signals for (16). The formation



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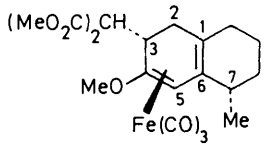

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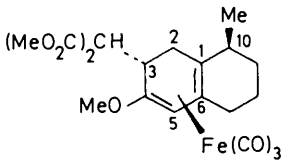

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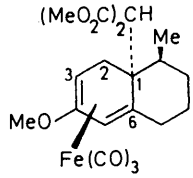
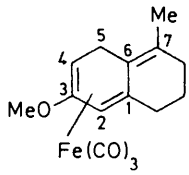


(19)

of (18) may be due to interaction between the methyl substituent and malonate anion, or the adoption of axial conformation by the *trans*-methyl group on formation of (19) [and therefore unfavourable interaction with $Fe(CO)_3$].

In all of these reactions the carbanion is assumed to add stereospecifically to the *exo*-face of the dienylium complex, as has been established for the simpler, monocyclic analogues.[5]

Next the reactions of the cations with cyanide anion were studied, this nucleophile being sterically less demanding than the malonyl anion. The reaction with the cation (8) produced a single unstable compound which could be purified by careful preparative layer chromatography under nitrogen. It showed no CN i.r. absorption, but the ^{1}H n.m.r. spectrum showed it to possess the same diene–$Fe(CO)_3$ structural unit as (4), and the mass spectrum gave a molecular ion at *m/e* 316 (the nitrile requires *M* 343). Since none of the angular nitriles prepared previously or in the present study showed loss of HCN in the mass spectrum, it is evident that this compound is the η^4-triene complex (20). This



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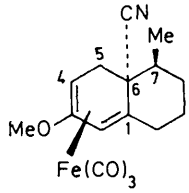
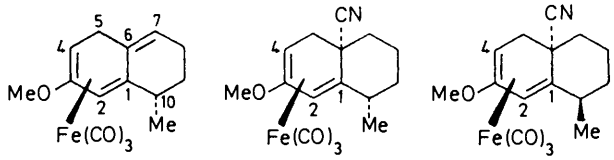


(21)

assignment is supported by the observation in the ^{1}H n.m.r. spectrum of the methyl resonance at δ 1.45 as a broadened singlet (long-range coupling), and a C=C i.r. absorption at 1 612 cm^{-1}. The mixture of salts (8) and (9) gave, as expected, the deprotonation product (20), together with a second compound which could be separated by preparative layer chromatography. This product must arise from (9) (32% yield); the spectral and analytical data showed it to be an angular nitrile which must therefore have the stereochemistry shown in (21). The yield was lower than that from the unsubstituted salt (1),[2] and it is probable that some deprotonation of (9) also occurs. Again, this may be due to direct interaction between the Me group and CN^- or the interaction between Me and $Fe(CO)_3$ on forming (21) making addition to C-1 unfavourable. These data, and the above observations of reactions of (8) and (9) with the malonyl anion, also support the structural assignments made for the dienylium salts, since it is more likely that the *endo*-compound (9) will give rise to nucleophile addition at the angular position. Complex (14) reacted with CN^- in a similar manner to give, by proton loss, the triene complex (22), the ^{1}H n.m.r. spectrum of which showed the vinyl proton signal as a multiplet at δ 5.0, thus confirming the structure of this and of (20). These two compounds showed similar behaviour on t.l.c. Also obtained from this reaction as a pale yellow solid, m.p. 77—80°, after preparative layer chromatography, was a diastereoisomeric mixture of nitriles, analytically pure. The ^{1}H n.m.r. spectrum indicated this to be a 2 : 1 mixture of (23) and (24) (the former compound has the lower field Me resonance, as for all other *exo*-Me compounds reported herein). Since the total yield of this mixture was 15%, and the dienylium complex used contained *ca.* 5% of

[5] R. E. Ireland, G. G. Brown, jun., R. H. Stanford, jun., and T. C. McKenzie, *J. Org. Chem.*, 1971, **39**, 51.

(15), compound (15) must react with cyanide to give exclusive angular addition, whereas (14) reacts mainly by loss of proton, angular addition being only a minor pathway. Again these results are explained on the basis of steric interaction with the *exo*-methyl group,



(22) (23) (24)

except that CN^- prefers to act as base rather than add to the deactivated dienylium terminus α to the methoxy substituent.

Organic reactions seldom show complete generality, and it is useful to know as many as possible of the controlling factors at the outset. In the present case I have demonstrated that the directing ability of the methoxy substituent in these dienylium complexes is insufficient to overcome steric hindrance presented by *exo*-methyl groups α or β to the reaction centre. The applicability of electronic control in the synthesis of spirocyclic compounds and gibberellin intermediates and 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. ^1H N.m.r. spectra (100 MHz) were obtained with Varian HA100 or JEOL Minimar spectrometers. M.p.s were determined on a Reichert apparatus. Pentacarbonyliron and enneacarbonyliron were obtained from commercial sources. All chromatographic operations were conducted under nitrogen.

3-*Methoxy*-7-*methylbicyclo*[4.4.0]*deca*-1(6),3-*diene* (3) *and* 4-*Methoxy*-10-*methylbicyclo*[4.4.0]*deca*-1(6),4-*diene* (7).—Reaction of 6-methoxy-1-tetralone with methylmagnesium iodide followed by dehydration by the method described by Elsner and Parker[6] for the analogous indanones, gave 6-methoxy-1-methyl-3,4-dihydronaphthalene (70—80%), b.p. 150° at 15 mmHg, δ 7.16 (1 H, d, *J* 10 Hz) and 6.7 (2 H, m) (aromatic), 5.72 (1 H, m, vinyl), 3.73 (3 H, s, MeO), 2.71 (2 H, t, *J* 8 Hz, 4-H_2), 2.2 (2 H, m, 3-H_2), and 2.0 (3 H, s,br, Me); $\nu_{max.}$ (film) 1 603 cm^{-1}; *M* 174. This compound (10 g) was treated with lithium wire (2.5 g) in liquid ammonia (500 ml) containing tetrahydrofuran (40 ml) and ethanol (40 ml) and gave, after aqueous work-up and extraction with light petroleum in the usual way, the diene (3) (9.5 g, 93%), b.p. 125—129° at 15 mmHg, δ 4.64 (1 H, m, vinyl), 3.56 (3 H, s, MeO), 2.8—1.3 (11 H), and 1.0 (3 H, d, *J* 8 Hz, Me), $\nu_{max.}$ (film) 1 700, 1 675, and 1 612 cm^{-1}; *M* 178. Treatment of this compound with sodamide in liquid ammonia according to the procedure described for non-methylated analogues, gave a quantitative yield of 4-methoxy-10-methylbicyclo[4.4.0]deca-1(6),4-diene, b.p. 120—125° at 20 mmHg, containing only minor amounts (<5%) of the unconjugated starting material. Prolonged reaction times (>24 h) led to some decomposition and poorer recovery; δ 4.70 (1 H, s, vinyl), 3.56 (3 H, s, MeO), 2.4—1.3 (11 H), and 0.98 (3 H, d, *J* 8 Hz, Me); *M* 178.

4-*Methoxy*-7-*methylbicyclo*[4.4.0]*deca*-1(6),3-*diene* (11).—7-Methoxy-1-tetralone[7] (25 g) was treated with methylmagnesium iodide; dehydration[6] gave 7-methoxy-1-methyl-3,4-dihydronaphthalene (10) (17 g, 69%), b.p. 140—142° at 15 mmHg, δ 6.95 (1 H, d, *J* 8 Hz), 6.75 (1 H, d, *J* 2 Hz), and 6.59 (1 H, dd, *J* 8 and 2 Hz) (aromatic), 5.78 (1 H, m, vinyl), 3.66 (3 H, s, MeO), 2.60 (2 H, t, CH_2), 2.15 (2 H, m, CH_2), and 1.96 (3 H, s,br, Me); *M* 174. Lithium–liquid ammonia reduced this compound (17 g) to the desired diene (11) (14 g, 81%), b.p. 124—128° at 18 mmHg; δ 4.62 (1 H, m, vinyl), 3.60 (3 H, s, MeO), 3.0—1.3 (11 H), and 1.04 (3 H, d, *J* 7 Hz, Me); $\nu_{max.}$ (film) 1 700, 1 673, and 1 620 cm^{-1}; *M* 178.

exo- *and* endo-*Tricarbonyl*{1,4—6-η-4-*methoxy*-10-*methylbicyclo*[4.4.0]*deca*-1(6),4-*diene*}*iron* (5) *and* (6).—*Method A*. The diene (3) (5.0 g) and pentacarbonyliron (7 ml) were refluxed in dibutyl ether (35 ml) under nitrogen for 18 h. The mixture was filtered through Celite and solvent and pentacarbonyliron were removed at aspirator pressure. Diene was removed at oil-pump pressure, combined with the residual solvent and $Fe(CO)_5$, and refluxed under nitrogen for a further 18 h. Work-up as before gave unchanged diene (1.5 g, 30%) and a residue of $Fe(CO)_3$ complexes which were chromatographed on silica. Minor products corresponding to loss of OMe (150 mg) were eluted with light petroleum. Further elution with light petroleum gave tricarbonyl{1—4-η-3-methoxy-7-methylbicyclo[4.4.0]deca-1,3-diene}iron (20 mg, 0.3%) as a yellow oil; δ 5.0 (1 H, d, $J_{2,4}$ 2 Hz, H-2), 3.60 (3 H, s, MeO), 3.20 (1 H, m, H-4), 2.2—0.9 (10 H), and 0.78 (3 H, s,br, Me); $\nu_{max.}$ (film) 2 035 and 1 970 cm^{-1}; *M* 318. A third yellow band was eluted with benzene–petroleum (1 : 1) which corresponded to the mixture of (5) (70%) and (6) (30%), obtained as a yellow oil (2.0 g, 32% based on diene consumed), and which was contaminated by minor amounts (<10%) of aromatic impurity. Since this did not interfere with hydride abstraction, further purification was not attempted; δ 5.18 (1 H, s, H-5), 3.40 (3 H, s, MeO), 1.16 (d, *J* 7 Hz, *exo*-Me), 1.0 (d, *J* 7 Hz, *endo*-Me), and 2.6—1.3 (11 H); *M* 318.

Method B. The conjugated diene (7) (1.2 g) was stirred with enneacarbonyliron (3.0 g) in refluxing Na-dried diethyl ether (50 ml) under nitrogen for 16 h. Filtration through Celite followed by removal of solvent and treatment as in Method A gave unchanged diene (0.7 g, 58%), and an equimolar mixture of (5) and (6) (0.7 g, 78% based on diene consumed). Although the mixture is cleaner on chromatography, and the yield better by this method, it suffers from lesser stereoselectivity than Method A.

Method C. The diene (7) (12.0 g) was treated with pentacarbonyliron (20 ml) in refluxing dibutyl ether (100 ml) under nitrogen for 24 h. Work-up as in Method A gave unchanged (7) (3.2 g, 27%). Chromatography of the residual complexes gave two products of demethoxylation (300 mg each), and none of the complex (4). Complexes (5) (80%) and (6) (20%) were obtained as a yellow oil (7.0 g, 44% based on diene consumed) contaminated with minor amounts of aromatic impurity.

exo- *and* endo-*Tricarbonyl*{1,4—6-η-4-*methoxy*-7-*methylbicyclo*[4.4.0]*deca*-1(6),4-*diene*}*iron* (12) *and* (13).—The diene (11) (5.0 g) was treated with pentacarbonyliron (7 ml) in

[6] B. B. Elsner and K. J. Parker, *J. Chem. Soc.*, 1957, 592.
[7] D G. Thomas, and A. H. Nathan, *J. Amer. Chem. Soc.*, 1948, **70**, 331; R. L. Aubrey, and P. W. Scullard, *ibid.*, 1968, **90**, 4924.

dibutyl ether (35 ml) as in Method A to give unchanged diene (1.5 g, 30%). Chromatography of the complexes gave two demethoxylation products (60 and 30 mg) followed by a mixture of (12) (75%) and (13) (25%) as a yellow oil (2.5 g, 40% based on diene consumed) containing minor amounts of aromatic impurities (<10%); δ 5.24 [s, H-5 of (12)], 5.0 [s, H-5 of (13)], 3.42 [MeO of (12) and (13)], 1.26 [d, *J* 7 Hz, Me of (12)], 1.16 [d, *J* 7 Hz, Me of (13)], and 2.9—1.4 (11 H); $\nu_{max.}$ 2 040 and 1 970 cm^{-1}; *M* 318.

exo- *and* endo-*Tricarbonyl*{1,3—6-η-4-*methoxy*-10-*methylbicyclo*[4.4.0]*deca*-3,5-*dienylium*}*iron Hexafluorophosphates* (8) *and* (9).—Triphenylmethylium tetrafluoroborate (2.0 g) was dissolved in the minimum volume of dry dichloromethane, and the complexes (5) and (6) obtained from Method C above (1.6 g) were dissolved in a similar volume of dichloromethane. The two solutions were mixed and kept at ambient temperature for 20—30 min, after which the mixture was added to an excess of diethyl ether. The yellow precipitate was filtered off at the pump, washed well with ether, and dried in air to give the tetrafluoroborates (1.5 g, 74%). These salts deteriorated slowly and so were converted into the hexafluorophosphates (8) (80%) and (9) (20%) by precipitation from saturated aqueous solution with a 10% excess of ammonium hexafluorophosphate. This mixture (3.5 g) was dissolved in dichloromethane (50 ml) and the solution was filtered to remove impurities. Diethyl ether was added with gentle swirling until crystals commenced forming, and the solution was set aside at 0 °C to complete crystallisation. The solution was filtered at the pump to yield yellow crystals (2.0 g), shown to consist of (8) (90%) and (9) (10%) by ^1H n.m.r. spectroscopy. Addition of an excess of ether to the filtrate gave an equimolar mixture of (8) and (9). The enriched compound thus obtained could be re-treated by this procedure to yield 95% pure *hexafluorophosphate* (8), δ(CD_3CN) 6.68 (1 H, d, $J_{3,5}$ 2 Hz, H-5), 3.92 (1 H, m, H-3), 3.70 (3 H, s, MeO), 3.16 (1 H, dd, J_{gem} 16, $J_{2,3}$ 7 Hz, *endo*-H-2), 2.20 (1 H, d, J_{gem} 16 Hz, *exo*-H-2), 1.37 (3 H, d, *J* 6 Hz, Me), 3.0—2.3, and 1.9—1.5 (7 H); $\nu_{max.}$ (Nujol) 2 100 and 2 030 cm^{-1} (Found: C, 39.4; H, 3.85. $C_{15}H_{17}F_6FeO_4P$ requires C, 39.0; H, 3.72%). Comparison of the ^1H n.m.r. spectra of this and the equimolar mixture of (8) and (9) gave for (9); δ(CD_3CN) 6.68 (1 H, H-5), 3.88 (1 H, m, H-3), 3.72 (3 H, s, MeO), and 1.0 (3 H, d, *J* 7 Hz, Me).

exo- *and* endo-*Tricarbonyl*{1,3—6-η-4-*methoxy*-7-*methylbicyclo*[4.4.0]*deca*-3,5-*dienylium*}*iron Hexafluorophosphates* (14) *and* (15).—The complexes (12) and (13) (2.5 g) were treated in the above manner with triphenylmethylium tetrafluoroborate (3.1 g). Addition to ether produced a dark oil which was dissolved in the minimum volume of water, and the aqueous solution was washed with portions (10 ml) of ether till the organic layer was colourless. A solution of ammonium hexafluorophosphate (1.4 g) in water (10 ml) was added to the aqueous layer and the mixture set aside to complete precipitation. The yellow solid was removed at the pump and washed with ice-cold water, ethanol, and ether and dried in air to yield (14) (85%) and (15) (15%) (1.3 g, 36%). Recrystallisation as above gave 95% pure *hexafluorophosphate* (14) (0.90 g); δ[$(CD_3)_2CO$] 7.09 (1 H, d, $J_{3,5}$ 2 Hz, H-5), 4.2 (1 H, m, H-3), 3.88 (3 H, s, MeO), 3.10 (1 H, dd, J_{gem} 16, $J_{2,3}$ 5 Hz, *endo*-H-2), 2.56 (1 H, d, J_{gem} 16 Hz, *exo*-H-2), 1.52 (3 H, d, *J* 7 Hz, Me), 3.0—1.2 (7 H); $\nu_{max.}$ (Nujol) 2 100 and 2 050 cm^{-1} (Found: C, 38.9; H, 3.92. $C_{15}H_{17}F_6FeO_4P$ requires C, 39.0; H, 3.72%). The equimolar mixture of (14) and (15) obtained from precipitation of the mother liquors gave: δ(CD_3CN) 6.78 (1 H, H-5 of both), 4.0 (1 H, H-3 of both), 3.74 [s, MeO of (15)], 3.72 [s, MeO of (14)], 1.44 [d, *J* 7 Hz, Me of (14)], 1.42 [d, *J* 7 Hz, Me of (15)], and 3.5—1.1 (9 H). The ^1H n.m.r. spectrum of a solution in $(CD_3)_2CO$ showed greater separation of the H-5 doublets for (14) and (15) (δ 7.04 and 6.92, respectively), but in CD_3CN the MeO and Me resonances were resolved.

Reaction of Dienylium Salts with Nucleophiles.—Dimethyl sodiomalonate. The procedure previously described was used in all cases.[2b] Tricarbonyl{1,3—6-η-methoxy-10-*exo*-methylbicyclo[4.4.0]deca-3,5-dienylium}iron hexafluorophosphate (8) (150 mg) gave a yellow oil which, upon preparative layer chromatography (silica; benzene), produced a single compound (120 mg, 83%); m.p. 88.5—90 °C (from hexane); spectroscopic properties consistent with the structure (16);[2] δ 5.15 (1 H, s, H-5), 3.63 (3 H, s) and 3.61 (3 H, s) (2 × CO_2Me), 3.28 (3 H, s, MeO), 3.28 (1 H, obscured, malonyl CH), 2.46 (1 H, dd, J_{gem} 16, $J_{2,3}$ 11 Hz, *endo*-H-2), 1.14 (3 H, d, *J* 6 Hz, Me), and 3.1 (m), 2.8—2.5, and 1.9—1.2 (9 H total, remainder); $\nu_{max.}$(CCl_4) 2 050, 1 965, and 1 745 cm^{-1}; *M* 448 (Found: C, 54.0; H, 5.4. $C_{20}H_{24}FeO_8$ requires C, 53.6; H, 5.4%).

The mixture of (8) (50%) and (9) (50%) (200 mg) gave a yellow oil, which produced a single yellow band on preparative layer chromatography (180 mg, 94%) shown to be a mixture of (16) (50%), (18) (25%), and (19) (25%) from its ^1H n.m.r. spectrum: (18) δ 5.07 (1 H, s, H-5) and 1.02 (3 H, *J* 6 Hz, Me); (19) δ 4.63 (1 H, d, $J_{3,5}$ 2 Hz, H-5), 3.92 (1 H, s, malonyl CH), 3.52 (9 H, CO_2Me and MeO), and 0.67 (3 H, d, *J* 6 Hz, Me).

Tricarbonyl{1,3—6-η-4-methoxy-7-*exo*-methylbicyclo-[4.4.0]deca-3,5-dienylium}iron hexafluorophosphate (14) (100 mg) gave a single yellow band on preparative layer chromatography (50 mg, 52%) which was approximately 95% (17). Minor contamination (≤5%) by a compound showing ^1H n.m.r. data consistent with the product of addition to the angular C-1 presumably arose by reaction of the carbanion with the minor amount (*ca.* 5%) of (15) present in the starting material. Recrystallisation from hexane at −78 °C gave pure (17) (40 mg, 42%), m.p. 72—74 °C; δ 5.2 (1 H, s, H-5), 3.64 and 3.61 (each 3 H, s, 2 × CO_2Me), 3.31 (3 H, s, MeO), 3.3 (1 H, d, obscured, malonyl CH), 1.31 (3 H, d, *J* 7 Hz, Me), and 3.2—1.4 (10 H); $\nu_{max.}$ (CCl_4) 2 030, 1 975, 1 765, and 1 745 cm^{-1}; *M* 448 (Found: C, 53.7; H, 5.5. $C_{20}H_{24}FeO_8$ requires C, 53.6; H, 5.4%).

With potassium cyanide. A 10% molar excess of potassium cyanide was stirred in acetone (5—10 ml) under nitrogen and sufficient water was added to produce a solution. The flask was opened briefly while the hexafluorophosphate (200—500 mg) was added. Stirring was continued until dissolution was complete, the mixture was poured into water (50 ml), and the product was extracted with ethyl acetate (3 × 10 ml). The extracts were washed thoroughly with water, dried ($MgSO_4$), and evaporated *in vacuo*. The products were purified by preparative layer chromatography (silica; benzene).

Compound (8) (360 mg) gave tricarbonyl{1—4-η-4-methoxy-7-methylbicyclo[4.4.0]deca-1,3,6-triene}iron (20) (140 mg crude, 57%) as an unstable yellow oil. Preparative layer chromatography in benzene–petrol (1 : 1) under nitrogen gave pure (20), δ 4.96 (1 H, d, $J_{2,4}$ 2 Hz, H-2), 3.54 (3 H, s, MeO), 3.40 (1 H, m, H-4), 2.4—1.5 (8 H), and 1.45 (3 H, s,br, Me); $\nu_{max.}$(CCl_4) 2 040, 1 970, and 1 612 cm^{-1};

M 316. The compound was insufficiently stable for microanalysis. The equimolar mixture of (8) and (9) (500 mg) gave a yellow oil which could be separated into two bands by preparative layer chromatography in benzene. The less polar band gave (20) (150 mg, 46%) and the more polar band gave a nitrile [60 mg, 32% from (9)] which could be recrystallised from light petroleum and had spectroscopic data consistent with tricarbonyl{1—4-η-6-cyano-3-methoxy-7-methylbicyclo[4.4.0]deca-1,3-diene}iron (21), m.p. 70—73 °C; δ 4.90 (1 H, d, $J_{2.4}$ 2 Hz, H-2), 3.60 (3 H, s, MeO), 3.33 (1 H, m, H-4), 2.38 (1 H, dd, J_{gem} 14, $J_{4.5}$ 3 Hz, *endo*-H-5), 2.2—1.1 (8 H), and 0.94 (3 H, d, *J* 5 Hz, Me); $\nu_{max.}(CCl_4)$ 2 225 (CN), 2 050, and 1 985 cm^{-1}; *M* 343 (Found: C, 56.5; H, 5.0; N, 4.6. $C_{16}H_{17}FeNO_4$ requires C, 56.0; H, 5.0; N, 4.1%).

Compound (14) (330 mg) gave rise to considerable decomposition, even at 0 °C. Preparative layer chromatography in benzene gave two bands. The less polar band gave tricarbonyl{1—4-η-3-methoxy-10-*exo*-methylbicyclo-[4.4.0]deca-1,3-triene}iron (22) as an unstable yellow oil (25 mg, 11%); δ 5.16 (1 H, d, $J_{2.4}$ 2 Hz, H-2), 5.0 (1 H, m, H-8), 3.62 (3 H, s, MeO), 3.40 (1 H, m, H-4), 2.4—1.3 (7 H), and 1.14 (3 H, d, *J* 6 Hz, Me); $\nu_{max.}(CCl_4)$ 2 045, 1 975, and 1 617 cm^{-1}; *M* 316. The less polar band gave a diasteroisomeric mixture of nitriles (40 mg, 16%) which could be crystallised from light petroleum at 0 °C to give a yellow crystalline solid, m.p. 77—80 °C. The ^1H n.m.r. spectrum indicated this to be a mixture of *exo*- and *endo*-tricarbonyl{1—4-η-6-*exo*-cyano-3-methoxy-10-methylbicyclo[4.4.0]deca-1,3-diene}iron (23) (67%) and (24) (33%); (23) δ 5.23 (1 H, d, $J_{2.4}$ 2 Hz, H-2), 3.68 (3 H, s, MeO), 3.3 (1 H, m, H-4), 2.48 (1 H, dd, J_{gem} 16, $J_{4.5}$ 4 Hz, *endo*-H-5), and 1.46 (3 H, d, *J* 8 Hz, Me); (24) δ 5.16 (1 H, d, $J_{2.4}$ 2 Hz, H-2), 3.66 (3 H, s, MeO), 3.3 (1 H, m, H-4), and 1.02 (3 H, d, *J* 7 Hz, Me). The mixture showed $\nu_{max.}(CCl_4)$ 2 225 (CN), 2 050, and 1 985 cm^{-1}; *M* 343 (Found: C, 56.0; H, 5.1; N, 4.0. Calc. for $C_{16}H_{17}FeNO_4$: C, 56.0; H, 5.0; N, 4.1%).

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